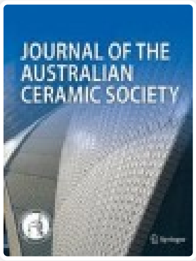

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RESEARCH

A comprehensive archaeometric analysis of a novel special organic finding in a glass unguentarium: NMR, FT-IR, SEM/EDX

Erdener Pehlivan[1] · Ebru Yabaş[2] · Ali Özer[2,3,4]

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Abstract
In this study, systematical analyses were employed to determine that which period the historical artifact belonged, and evaluations were based on the glass-making technology of the period. In addition, since organic substances were carried in these glass bottles, they are likely to be the medicine or ornaments at that time; by using recently developed techniques as NMR-SEM–EDX and interpret them in the correct way, it was possible to predict what the yellow oily looking organic substance might be in. As the mouth of the glass bottle is completely closed with clay, the characterization of this organic material was made on the clay sample taken from the underneath of the environment without damaging the historical artifact. The trace organic matter residues on the clay were isolated and characterized by NMR spectrometry; this sample was characterized with FT-IR. Finally, the surface morphology of the clay–oil mixture was examined morphologically with SEM, and with EDX, elemental analysis was performed. In the results obtained, it was concluded that the organic material in the historical artifact could be olive oil with a high content of palmitic acid. With this study, the content of the artifact could be clarified by making a structural examination of the remains without damaging the historical artifact.

Keywords Palmitic acid · NMR · FT-IR · SEM · Olive oil · Glass unguentarium

Introduction

Natural glass forms, such as obsidian and rock crystal, were employed before man developed the technological infrastructure to use manufactured glass [1–9]. Obsidian may be characterized as the quick cooling of silicon-rich lava in terms of the formation process. Obsidian comes in a variety of colors, most commonly in translucent and black, and also as green and red [10, 11]. Rock crystal is another glass-like substance that has been utilized since ancient times. The structure of this substance, which was widely utilized throughout the Roman period, is translucent and colorless [2, 5, 12].

According to Plinius, the invention of glass was based on a coincidence. According to Plinius, the events that led to the development of glass were as follows: Phoenician sailors utilized hard soda flakes to restrict their fire, which then formed into a translucent mass (Plinius, Nat. Hist. V, cap. 17).

In the light of archeological findings, the earliest artificial glass production was found to be carried out in Mesopotamia in the second half of the fourth millennium BC by coating beads of different materials with glaze [1, 2, 13–17]. Beads made of pure glass began to appear from the second half of the third millennium BC. Monochrome glasses produced in this process have become an easily accessible alternative to precious stones [18], [1, 19, 20], [3, 21, 22]. When evaluated in terms of Anatolia, the earliest glass finds were excavated in Boğazköy Büyükkale, and these finds were dated to the Assyrian Trade Colonies Age, 1700 BC [22], [1, 3]. Likewise, the glass beads found in the Yanarlar Hittite Cemetery were also dated to this period [1, 20, 22, 23]. Glass has been widely used since the end of the first half of the second

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millennium BC. Glass known in the Near East in the late second millennium BC was not yet produced in the Greek world [12]. Glass production started in the seventh century BC and later, as a result of the Greek world's relations with the east. Oriental styles may be recognized in Greek art during this time period. Glass was a commodity made in the east and exported to the west until this time, which might be named as the orientalizing period. Glass product manufacturing, started to diminish at the beginning of the first millennium BC, started again towards the end of the first quarter of the first millennium BC, with Syrian-Palestinian origins [20, 24–26]. During this time, an enormous number of works fabricated using the inner mold technique has increased. The inner mold method that was abandoned in Egypt in the eleventh century BC became widespread in Mesopotamia in the eighth century BC and was later introduced to Rhodes and Italy. Until the first century AD, the inner mold method was utilized.

There are mainly six techniques, named as the inner mold technique, cold cutting technique, molding techniques (mold casting technique, lost wax technique, massive casting technique, mold printing technique), mosaic glass technique, (millefiori technique, reticelli technique, banded glass technique, gold banded glass technique), crushing technique, and blowing technique (free blowing, mold blowing), and as a total, 13 different techniques of glass production with different sub-variations of these six techniques occur [27], [1], [7, 28], [3, 5, 14, 19, 21, 22, 29–34], [4, 24, 35, 36].

On the other hand, in recent years, it has been observed that archeology has become into a versatile field that seeks information in fields such as chemistry, physics, geology, mathematics, and computer science. Particularly when examining the structure and nature of materials, the field of chemistry can be significantly used. Characterization of archeological materials is important for understanding and exploring past societies and reconstructing their accurate chronology. As mentioned, although these techniques provide a great deal of information, their importance has been recognized in the recent years.

Especially, nuclear magnetic resonance spectrometer (NMR), Fourier transform infrared spectrophotometer (FT-IR), and scanning electron microscope (SEM) are used in the literature widespread in characterization processes [37], [38, 39]. These techniques help us to identify the raw material sources, verify the originality of the artifact, identify the old technologies, and examine the structural and dynamic properties of materials.

The chemical structure of archeological artifacts can be studied using liquid- and solid-state NMR for both organic and inorganic materials. NMR technique, which is also a method of classifying atoms in the molecule according to different chemical environment, reveals the general structure of an organic molecule. Unless there is a structurally specific situation, ^{1}H-NMR and ^{13}C-NMR analyzes are generally preferred in archeological studies. While the ^{1}H-NMR spectrum provides information about the hydrogen content, the ^{13}C-NMR spectrum provides information about the carbon content in the structure. NMR spectra provide a series of peaks or resonances of the studied atomic nuclei. The position of the resonance relative to a standard is known as the chemical shift and differs with the chemical environment of the atom. Using this difference, one can predict the chemical structure of molecules [37], [40–42].

With FT-IR, it can be said that it will be especially useful in determining the functional groups in the chemical structures of materials. FT-IR is not a primary characterization method that can be used alone; it is more used to provide results that support other analysis methods. It uses the molecular vibrations such as in-plane, out-plane, bending, or stretching. This characterization is of interest to chemists especially mixing organic materials or polymers to produce new ones or used for particular vibrations of embedded components into a system.

Microscopic techniques have been a very important part of understanding the physical appearance and morphology of archeological findings. This is a must to understand the pore size, structure, grain size of sintered/fired product to study the possible firing temperature, finding a glassy phase among the phases, identifying different elements to estimate a provenance and many more things are of interest to researcher for the last few decades [38].

SEM deals with the energetic electrons scattered from sample surface down to a few microns depending on the accelerating voltage, counted by a detector and digitally visualized. SEM became a very first technique to visualize materials after special electronic devices taken place and by computer industry developed. By the aid of SEM, a researcher can quantify the elements by energy dispersive x-ray spectroscopy (EDX or EDS) and also can identify the possible phases [39, 43].

Experimental

Permission documentation for unguentarium analysis and extraction of samples

Permission of the unguentarium and extracting out the material in it have been obtained by the documentation of the Sivas Governorship, Provincial Directorate of Culture and Tourism, Sivas Museum Directorate, on 24.05.2021 with the number E-19007571–150[150]-1402514. Within this permission, the glass was taken to the museum laboratory for hands on extraction of about 0.20-g clay from the neck of the unguentarium. By wearing sterile gloves, a plastic lab spatula was used for taking out the samples, after taking out the clay and oil mixture from the glass and was sealed again in the same way as earlier to keep the oil sample inside. There was no touch or any treatment to the bottom of the unguentarium to reach or damage oil, anyway. The extraction of clay + oil mixture was also witnessed by the museum management not to harm anything particular.

SEM and EDX analysis

SEM was evaluated by a field emission gun–equipped microscope to decrease the charging effect of powder samples and to gain an electron depth analysis possibility. The surface morphology of powder form of sample was examined with a TESCAN® MIRA3 XMU (Czechia) scanning electron microscope, and quantification of elements of interest was conducted by EDX (Inca x-act, Oxford Inst., UK) mounted to SEM. Samples were separated by a 100-mesh filter using ethanol as solvent to dissolve the organic content to pass through and then, both powders and organic product was left in a drying oven at 60 °C for 12 h to ensure drying. The temperature was not held as high as 120 °C not to degrade the interested organic product. After completely drying, the both samples were taken onto a carbon tape on aluminum stubs to conduct microscopic investigation. The filtered ceramic powder was sticky due to possible residual organic while organic product remains as solid gel-like structure spread on the carbon tape. In order to prevent charging of nonconducting samples, the working voltage was adjusted wisely to 8 kV to obtain better images of materials.

NMR analysis

NMR analyzes were performed with liquid NMR spectrometry. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a JEOL JNM-ECZ400S 400 MHz NMR spectrometer (Japan). For this, the sample with clay was firstly mixed with chloroform, and the insoluble clay phase in chloroform was separated by filtration. The solvent part dissolved in chloroform was removed, and the residue was dried in vacuum. NMR solution of the obtained sample was prepared under argon gas using deuterated chloroform ($CDCl_3$). ^{1}H-NMR and ^{13}C-NMR spectra were scanned in the range of 0–20 ppm and 0–250 ppm, respectively. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): $d = 2.33$ (t, 2H, $-CH_2$); 1.60 (t, 2H, $-CH_2$); 1.24 (s, 12H, $-CH_2$); 0.85 (t, 3H, $-CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 33.8$; 31.8; 29.8; 29.6; 29.5; 29.4; 29.3; 29.2; 24.8; 23.8; 14.2.

FT-IR analysis

FT-IR spectra were measured on a Bruker Tensor II spectrometer (Germany). The FT-IR spectrum of the sample with clay was taken with the ATR technique, IR (ATR) υ (cm^{-1}): 2918; 2850; 1706.

Results and discussions

Characterization with SEM–EDX

As seen from SEM image of clay at Fig. 1a, after rough filtering with 100 meshes and drying for 12 h, there are still organic residues on and around clay particles as seen by white arrows. As the organic material behaves like a binder for clay, they are agglomerated to produce coarse soft agglomerates about 300 micron while there are some 10 to 50 micron sized particles in present.

By EDX elemental analysis, taken from the whiter spot of SEM images, it is seen that the clay sample was consist of mainly Si, Fe, Mg, Al, Na, and Ca combined with oxygen mostly, and this material is very well known as smectite family that got hardened after drying to obtain good sealing for something underneath. The clay may be possibly formed as a mixture of different phases such as olivine, Na montmorillonite, and iron oxide and by using water to make it plastic; afterwards, when the water is evaporated, it stuck inside the neck of unguentarium as a porous seal. Those pores are tend to be filled with organic product's vapors after years, and it is good to practice having some clay sample to analyze organic product as well.

As EDX measures the surrounding area of about 5 micron, some carbonaceous material like organic material can also be detected along with clay ingredients.

Figure 1c represents the solid gel-like organic sample on carbon tape with some fine particle residues from clay mineral, as illustrated by spectrum of EDX analysis in Fig. 1d to be other than C and O. The organic product seems to be delaminated by electron beam damage but no charging occurs due to tiny amount of organic and the backscattered electron detector (BSE) is used for identifying different atomic density materials, as clay (higher density is seem lighter) vs. organics (lower density is seem darker). BSE detector is very helpful for those cultural heritage materials not to be able to coat with gold to be in showcase afterwards. As seen by white arrows in Fig. 1c, tiny clay residues with lighter scattering by BSE detector, is known as higher atomic density materials.

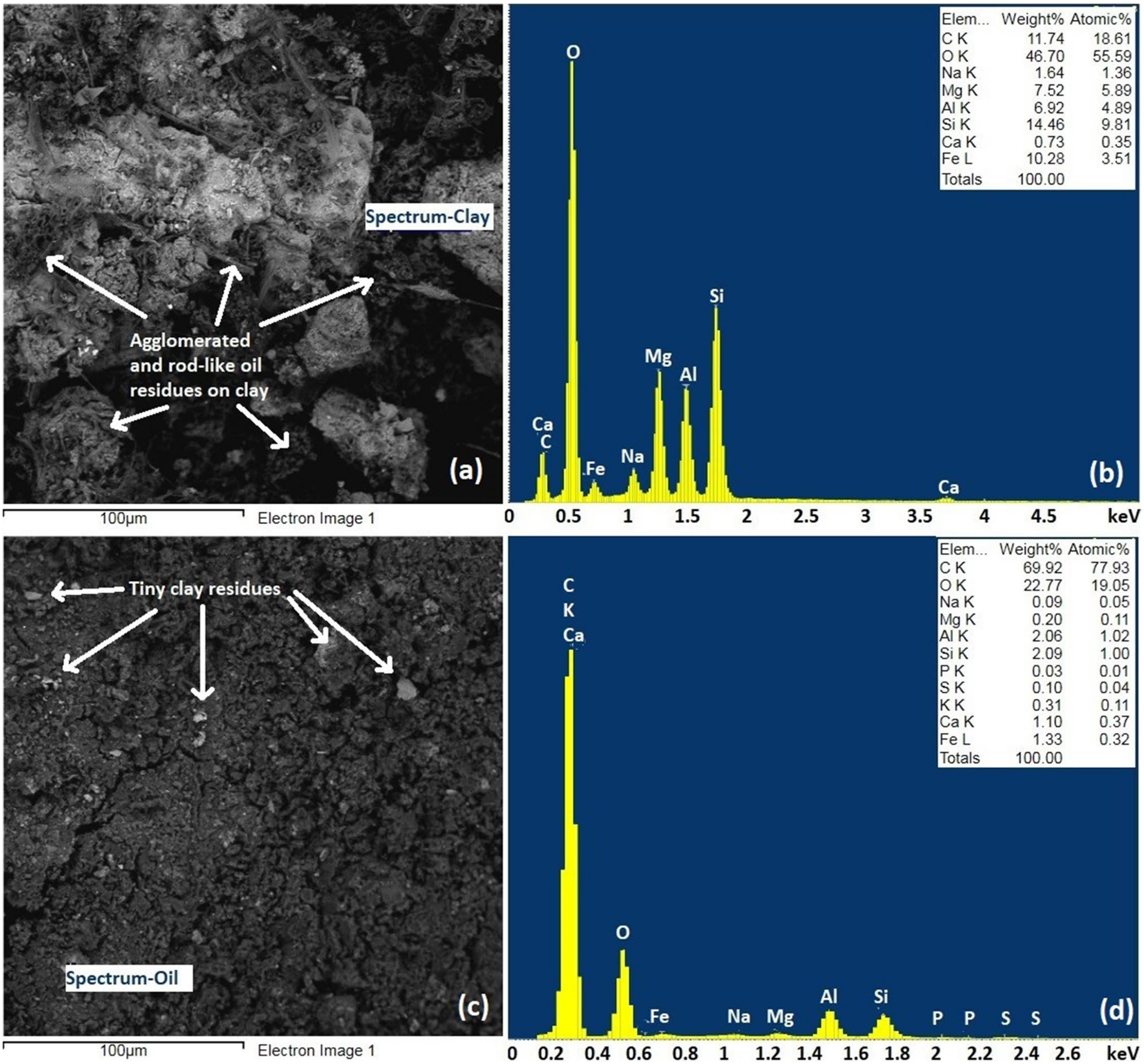

Fig. 1 SEM images of clay (**a**) and organic product (**c**) and corresponding elemental compositions at (**b**) and (**d**), respectively

Characterization with NMR

NMR, as a useful analytical tool in the examination of archeological artifacts, may identify raw material sources, verify the originality of the artifact, and describe ancient technology. In this study, NMR spectrometry was used to determine the chemical structure of the possible organic compound. In the 1H-NMR spectrum of the sample, the cleavages in the peaks are observed quite clearly and would give information about the chemical environment of the hydrogens in the chemical structure. In the NMR spectrum, the number of signals indicates how many different kinds of protons exist, while the position of the signals indicates how much the proton is shielded. On the other hand, the intensity of the signals indicates how many protons there are, while the splitting of the signals indicates how many protons are on the neighboring atoms. While no peak was observed in the aromatic region in the ^{1}H-NMR spectrum of the sample measured in $CDCl_3$, peaks were observed in the aliphatic region. The singlet peak observed around 7.3 ppm is the characteristic peak of the NMR solvent $CDCl_3$ (Fig. 2). This shows us that there are basically aliphatic -C-H bonds in the chemical structure of the sample. As seen in the chemical structure of palmitic acid in Fig. 3, the peaks of the protons at the "**a**" position at 2.33 ppm, at the "**b**" position at 1.60 ppm, at the "**c**" positions at

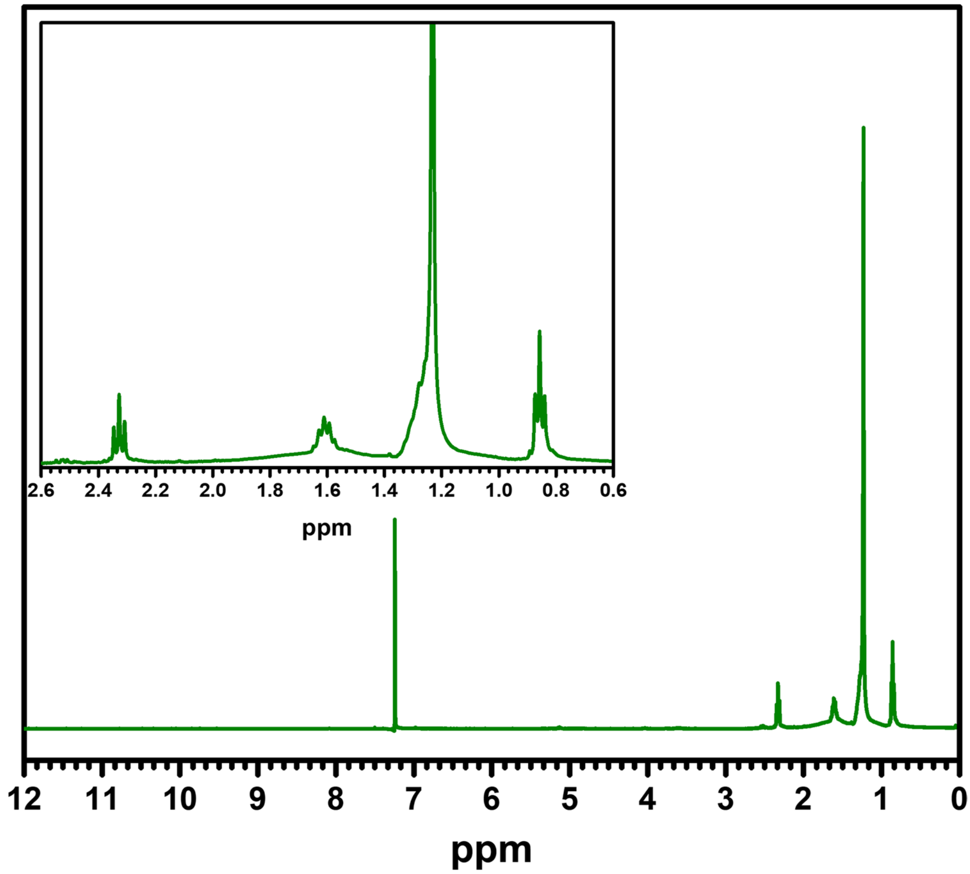

Fig. 2 ^{1}H-NMR spectrum of the sample dissolved in chloroform

1.24 ppm, and at the "**d**" position at 0.85 ppm in ^{1}H-NMR spectrum (Fig. 2) were observed. The integral ratios of these peaks are in agreement with the proton numbers. In the NMR spectrum, hydrogen peaks belonging to the carboxylic acid groups in palmitic acid could not be observed. It can be thought that this is due to the intermolecular interaction of the sample due to the storage of the sample for many years. It is also known that carboxyl groups can form dimers in non-polar solvents. Similar effects are also found in the literature [44–46]. It is also interesting that the sample isolated from the clay sample is quite pure and has been preserved purely from the past to the present. The results of the NMR analysis supported that the sample examined could be "palmitic acid".

While we were preparing this NMR sample, the material was separated from the clay by dissolving it in chloroform. Chloroform is a low polarity organic solvent. It was also thought that there might be another organic material on clay that is insoluble in chloroform. In order to understand this, the clay sample, which is insoluble in chloroform, was also treated with dimethyl sulfoxide, which has a high polarity. This process was performed with deuterated dimethyl sulfoxide (DMSO-d_6) in order to make direct NMR analysis. The precipitated clay was filtered off under argon gas, and ^{1}H-NMR analysis of the organic phase was performed. As seen in Fig. 4, no peaks were observed except for the NMR solvent peaks. According to this result, it can be concluded that the only material on the clay was pure palmitic acid.

The ^{13}C-NMR spectrum of the sample was also examined which was thought to be palmitic acid. In the obtained spectrum, the carbon peaks are in harmony with the structure of palmitic acid (Fig. 5), and the ^{13}C-NMR spectrum of the sample is compatible with the spectrum of palmitic acid given in the literature. The peaks of all carbon atoms appeared in the range of 10–40 ppm. This confirms that the compound has aliphatic groups.

Characterization with FT-IR

We also performed FT-IR analysis of the sample, which is mixed with clay, in order to determine the chemical structure of the material. We also took the FT-IR spectrum of pure clay for comparison. As seen in Fig. 6, when the FT-IR spectra of pure clay and sample with clay were compared, sharp peaks were observed in the range of 2918–2850 cm^{-1}. These are the peaks belonging to the characteristic aliphatic C-H groups. In addition, the peak occurring at 1706 cm^{-1} is thought to belong to the characteristic C=O [44, 47, 48]. As

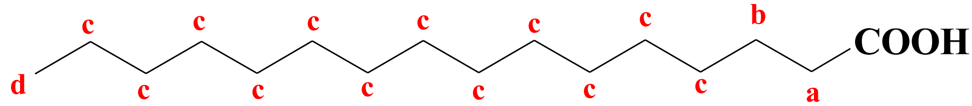

Fig. 3 Chemical structure of palmitic acid

a result, the FT-IR spectrum also supports that the chemical structure of the substance is palmitic acid.

As additional information, the region in between 1500 and 400 cm^{-1} in the FT-IR spectra is called the fingerprint region. Since the vibrational frequencies of the whole molecule come in this range, the peak changes in this region may mislead us. Therefore, we examined the changes in the FT-IR spectrum in the range of 4000–1500 cm^{-1}.

Archaeological backgrounds of the artifact and proposed organic product

The artifact, which is the topic of the research (Fig. 7), was confiscated from Kurtlapa hamlet, 50 km north of Sivas province's central district, and delivered to the Sivas Museum on September 25, 1997. The work has been exhibited in the Sivas Museum Glass Works showcase with inventory number 97/3 since this date. As a result of detailed measurements, it was determined that the artifact had a height of 8.5 cm and a rim diameter of 1.6 cm. The color code of the work in the Munsell color catalog is G1 8/10GY. The work is made in the free blowing technique and is transparent. When the vessel in question is examined in detail, it is seen that it has a straight neck and a narrowing structure at the transition from neck to body. After the narrowing of the neck passage, it is seen that the body of the vessel reaches a width of 9.6 cm. In the bottom part, it is seen that it narrowed again and reached a bottom diameter of 4.6 cm. Similar vessels are found in the Eastern Mediterranean region. Analogically similar vessels are examined; it can be argued that the vessel subject to the article belongs to the third–fourth century AD, the Late Roman Imperial Period [2, 49], Lightfoot–Aslan 1992).

The free blowing, that container is also produced, is a technique in which production is carried out without mold. The tip of the metal blowing rod, called as a pipe, is heated up to "experimentally known" softening point of glass around 600–800 °C. Then, the pipe is immersed in the glass crucible, and the glass is wrapped at a certain amount by the blowing expert. At this stage, the pipe is constantly rotated to ensure the winding process and to prevent the glass from extending downwards by sagging. To blow the shape of the glass, the glass pellet is subjected to repeated heating steps [7, 9, 13, 30, 33, 50]. Afterwards, when blown from the tip of the pipe, the glass inflates like a balloon and takes the shape of a smooth sphere [33, 50]. The glass, is given the desired form after the blowing process, is separated from the pipe after the bottom begins to solidify and shrunk. The mouth is formed after this period [13, 30], Geyik Karpuz 2014, [7, 9]. Finally, the container is separated from the noble. Sometimes, there is a trace of noble on the bottom of the container. With the use of a wheel, the container is polished to remove this trace [7, 13]. When the early period vessels are inspected, it is considered that they were created in a technique that can be called tube blowing. For this reason, the form of the containers is in the form of an elongated bulb [7].

Olive oil, wine, cosmetics, ointments, medications, and scents are known to be among the organic components created during the period the container belongs to. Pliny the Elder states that an ointment called "Pardalium" was produced in Tarsus, rose perfume was produced in Phaselis, and saffron oil was produced in Soli, regarding scent production centers and scents produced (Pliny, Nat. Hist. XVIII, Cap. 2).

Olive oil, which is also known for its palmitic acid content, is, without a doubt, the most extensively produced and consumed of these organic compounds. Hence, it is possible to have information about the production process of olive oil. It is feasible to describe the olive oil manufacturing process in the era when the glass, was made using both ancient sources and archeological evidence.

Olive trees come in 20 distinct kinds and are green in all four seasons. *Olea europea* and *olea europea sylvestris* are two of these species that are grown in Anatolian geography. The species called *Olea europaea* is the cultivated olive. *Olea europaea sylvestris* is a wild olive species locally called "deli" or "delice" [51]. In Turkey, various kinds of the cultivated olive, known as *Olea europea*, are grown. [These varieties are named as Ayvalık, Çakır, Çelebi, Gemlik Memecik. [52]: 155)]. Cultivated olives have leaves that are over 4 cm long and a fruit that is roughly 35 mm in diameter. When "delice" olives are examined, it is seen that the leaves are shorter than 4 cm and the fruit is around 15 mm.

It has been discovered via geological studies that olive is a plant that is almost as old as human history. Although several hypotheses concerning its origins have been proposed, the prevailing consensus is south-eastern Anatolia and Syria. Thanks to the Phoenicians, one of the merchant peoples in the south of this region, it spread primarily to the Aegean islands and then to the world [53]. Based on this information, it is reasonable to conclude that olive cultivation was practiced throughout almost entire Mediterranean basin in the period when the glass vessel, was created [for detailed information on the subject, see [54, 55].

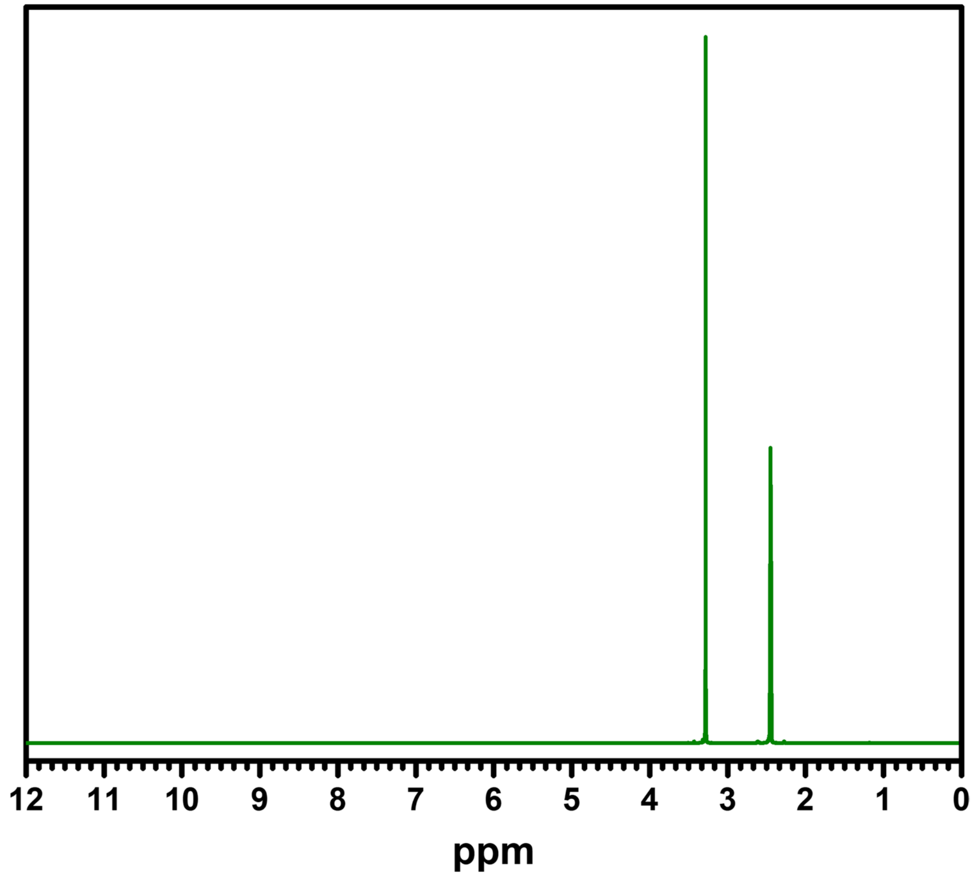

Fig. 4 ^{1}H-NMR spectrum measured in DMSO-d_6

The moment when the olive fruit begins to turn from green into black, according to Plinius, is the most perfect time for harvesting olive fruit (Pliny, Nat. Hist. XV, Cap. 2). Since the contemporary world expresses the natural calendar in months, it is feasible to claim that it corresponds to a date like December [56], XII,52,1, [55]. These fruits, which were harvested in December, are immediately included into the manufacturing process. (The time spent waiting for the olives to be processed after gathering has a detrimental impact on the olive oil's acidity and, as a result, its flavor).

The first step in the production process is the squeezing of the olives. At this stage, as primitive hand or foot crushing method can be used, it is also possible to subject it to the pressing process. After this step, the crushed olives, called pulp, are separated from the oil. Finally, the solid elements in the obtained liquid and other liquids from the fruit are separated from the olive. The resulting liquid is then ready for consumption.

It is seen on an amphora with a neck in the black figure technique attributed to Antimenes and dated to 520 BC, in which long poles were used during the collection of olives. On the vase, four individuals are pictured gathered around an olive tree. On top of the tree, one of the figures is shaking the tree from branches. To the right and left of the tree, two people shake (hit) it with long poles. The fourth person is shown picking up olives that have fallen to the ground. The vase in question is an important archeological data regarding the olive harvest [57].

As a primitive method, hand squeezing can be done in a bowl after the olives are harvested. This technique can also be called the mortar method. With the development of this process, the foot crushing method can be applied, which can produce more oil as more pressure will be applied with this method. In this method, olives were usually placed in a sack and then crushed. Hot water is usually used to separate the pulp and oil. In response to the growing population and demand, techniques that allow for the processing of more olives per unit of time have been implemented. Press stones have an important place among these techniques.

When the crushing stones in olive press systems are studied, it is discovered that they revolve both around themselves and around an axis. With the advancement of ancient technology, it is seen that from the second half of the fourth century BC, systems called *mola olearia* began to be used. Depending on the size of the stones, human power and the powers of animals such as donkeys, mules, horses, oxen, and camels were used to move these systems [58]. Apart from the *Mola olearia* system, it is known that a system called *trapetum* is also used yet, *trapetums* are insufficient for grinding olives [51]. Due to this inadequacy, the *mola olearia* system was found to be more useful and became widespread (Lolos 2011, URL-1), [59].

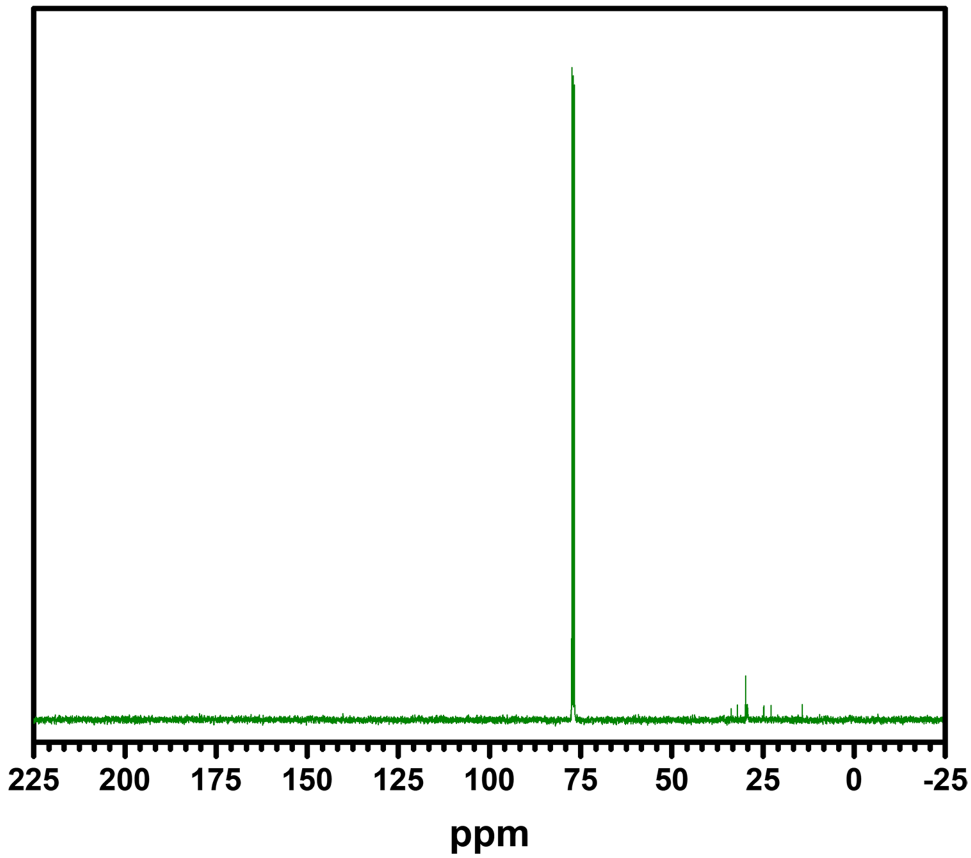

Fig. 5 ^{13}C-NMR spectrum of the sample dissolved in chloroform

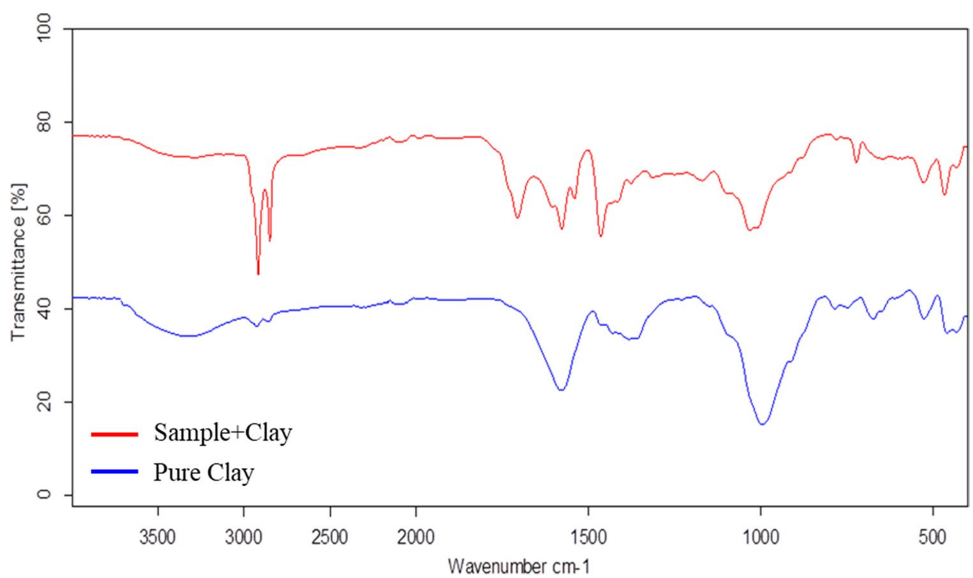

Fig. 6 FT-IR spectra of the sample, organic side mixed with clay (—) and of pure clay (—)

The next step of the olive, which is made into pulp with the help of tools called *trapetum* or *mola olearia*, is the pressing process. Types of presses used in the pressing process are wedge presses, pole presses (single counterweight), fixed crane, crane/screw press on counterweight, and direct screw presses [60]. Direct screw presses can have single or twin screw [for detailed information about press mechanisms and types, see [60].

The liquids extracted from the olive are put into a stone jar during the pressing process. While this liquid is resting in the vessel, the residues from olives and other liquids other than oil submerge. In this process, the olive oil remaining on

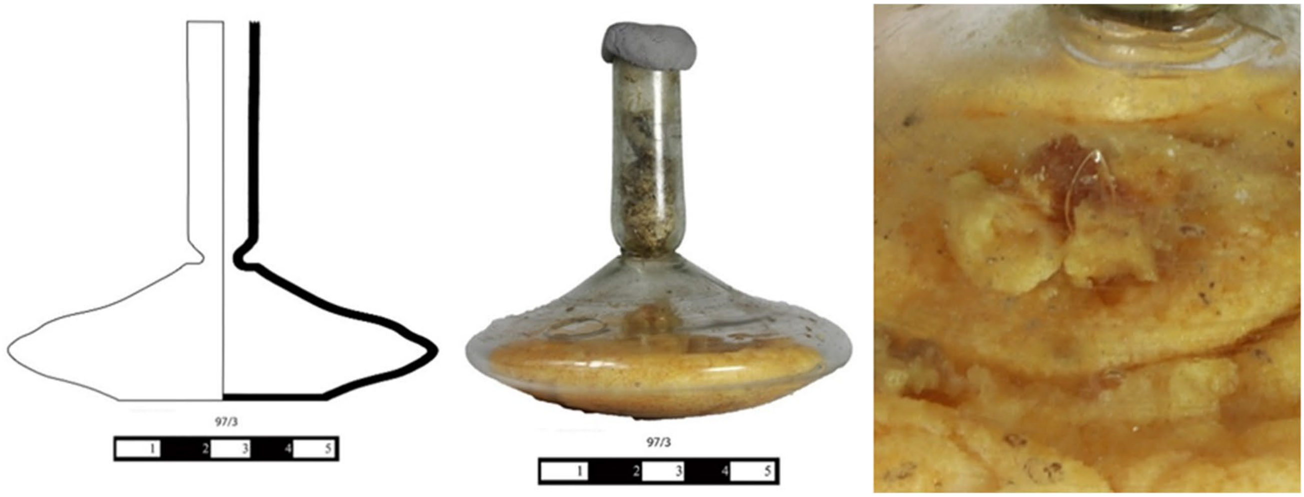

Fig. 7 Picture of the artifact that is the topic of the research

the top is collected from there with the assistance of various containers and transferred to another container with a hole at the bottom and with a strainer feature. Hot water is added to the olive oil during the resting process in the container. After this resting period is completed, the hole at the bottom of this container with a filter feature is opened, and the pulp, hot water, and other liquids that have settled to the bottom are poured until pure olive oil comes [58]. Olive oil, which is then filled into *amphorae* or *unguentarium*, meets with the buyer in the markets.

Conclusions

The glass unguentariums are specifically important for the time period they have been used, by means of glass-making technology and also for carrying scent and other organics to be used as medication or ornaments. Collecting samples from those organic materials is very time consuming and special permissions from the museum managements and the municipal directors of cultural and social studies.

Following conclusions can be derived from the results of this work as below;

– It is very important not to harm the organic product in the carriers, it is the best to obtain organic products from their evaporated and condensed parts like from the necks and from clay mixtures used for sealing them. The archaeometric analyses of those materials are very difficult to interpret as they are hard to handle and hard to collect, even very small amounts of materials can be achieved and filtered for investigations. Another difficult thing for interpretation is if there was a scent in that oil, it should have been gone, so there is no possibility of finding out which specific scent is as the time spent were much after putting them in, unless they were sealed to airtight.
– NMR, FTIR, and SEM (EDX) techniques were employed to analyze that material to a high extent by using different solvents to interpret data more understandable.
– For SEM (EDX), only ethanol is enough due to rough separation should be fine because of powders need only to be visible under SEM. On the other hand, liquid state ^{1}H-NMR and ^{13}C-NMR analyses were performed in $CDCl_3$ to analyze the hydrogen and carbon elements in organic materials. As a result of the obtained NMR analysis, it was observed that the structure of the organic matter was similar to that of palmitic acid as described in other consistent literature. Palmitic acid is an organic compound known to be high in olive oil. Based on this data, it is thought that the archeological artifact found would strongly be olive oil as of NMR, FT-IR and SEM–EDX analysis.
– By the time passed, the olive oil could be crosslinked by OH^- ions related to humidity and this may colorize the outermost surface of oil and makes it more solid. The freeze–thaw cycles by more than 500 years are also another reason for getting more solid textured and more yellowish in color which is another type of crosslinking possibility.
– By the aid of these analytical techniques, an important attempt was done to identify the specific and novel finding in that unguentarium that was not determined for over 50 years in Sivas Archaeology Museum through microscopy and spectroscopy by SEM–EDX and FTIR, NMR, respectively. This was the first ever organic product, found non-degraded, to the best of our knowledge in Turkey.

– Regional importance of olive oil also needs to be considered to be transported in these kinds of special vessel structures made of glass. Even nowadays, the glass still protects its extraordinary character for holding and transporting chemicals and other liquid-like materials without being affecting from environment by sealing.

Highlights

– A glass unguentarium was evaluated for a novel organic finding inside by means of NMR, FTIR and SEM–EDX analysis techniques.
– NMR technique makes it possible to determine the exact organic structure along with other impurities by H and C coordinations and peak splitting. The suggested structure was palmitic acid that mostly abundant in olive oil.
– SEM–EDX analysis evaluates the C, O and H related material for organic part while clay type inorganic mineral part was specified from the seal material as soil.
– FTIR helps to determine organic findings within NMR as investigating the vibrational molecules to be C-H–O related asymmetric and symmetric stretching and bending modes.
– Along with the comprehensive archaeological background investigations, the novel finding was evaluated as being very pure olive oil from palmitic acid content.
– This finding was also approved by periodic range and belongings as well as the unguentarium production.

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Data Availability Confidental data was kept in Sivas Archaeology Museum as report. Data is available upon the Manager's approval.

Declarations

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Conflict of interest The authors declare no competing interests.

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