Research Article: Open Access

International Journal of
Experimental
Spectroscopic Techniques

Investigations by Ft-Ir Spectroscopy on Residues in Pottery Cosmetic Vases from Archaeological Sites in the Mediterranean Basin

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Abstract

The present study was aimed at investigating, by FT-IR spectroscopy, residues in some whole archaeological vases, different in form and dimensions, but all classified as containers for cosmetics. The analyses performed on the as-sampled material and after extraction with a solvent were examined and compared. The results highlighted dissimilar composition of the residues for containers different in shape and provenance. Lipids, vegetable resins, and proteinaceous compound were identified. Also some inorganic products (such as calcite or clay minerals) were found as intended ingredients of the cosmetic preparations.

The FT-IR spectroscopy provided a simple, quick and cheap analytical method, which allows obtaining reliable and sound data using a limited preparation of the samples. In addition, this technique was found very useful in case of these unbroken precious artifacts, where damage has to be avoided.

Keywords

Fourier transform infrared spectroscopy, Residue analysis, Ancient cosmetics, Archaeological pottery

Introduction

In recent years, the identification of the residues in archaeological ceramic artifacts has caught the attention of different researches due to the interest of knowing better the daily life, commercial activities, and materials of ancient societies. To this aim, chromatographic techniques are frequently employed in identifying the organic residues [1-6]. However, these methodologies are destructive, while non-destructive or micro-destructive diagnostic techniques would be preferred, and procedures for sample preparation, usually taking a long time, are required. So, Fourier Transform Infrared (FT-IR) spectroscopy has been proposed for a rapid detection of organic residues in archaeological materials [7-12], as well as for investigations of the fabrication conditions [13-17].

As widely experienced in many applications [18-23], this technique is very helpful because of its sensitivity, versatility and applicability to qualitative, but also semi-quantitative, analyses of both inorganic and organic compounds. The possibility of adapting the sampling methods and instrumental configurations makes it possible to analyse samples in different forms (solids, powders, particles, liquids or gases). In addition, accurate, reliable and reproducible analytical results are easily obtained, even where extremely reduced quantities of samples are available, thus facilitating the minimally invasive analysis of valuable artifacts.

Most of the studies applying FT-IR in the analysis of residues on archaeological potteries concern the detection of materials, usually in traces, which were in contact with vessels used for storing materials, as well as for pre-

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Received: April 07, 2017: **Accepted:** June 22, 2017: **Published:** June 24, 2017

Citation: Lettieri M, Giannotta MT (2017) Investigations by Ft-Ir Spectroscopy on Residues in Pottery Cosmetic Vases from Archaeological Sites in the Mediterranean Basin. Int J Exp Spectroscopic Tech 2:009

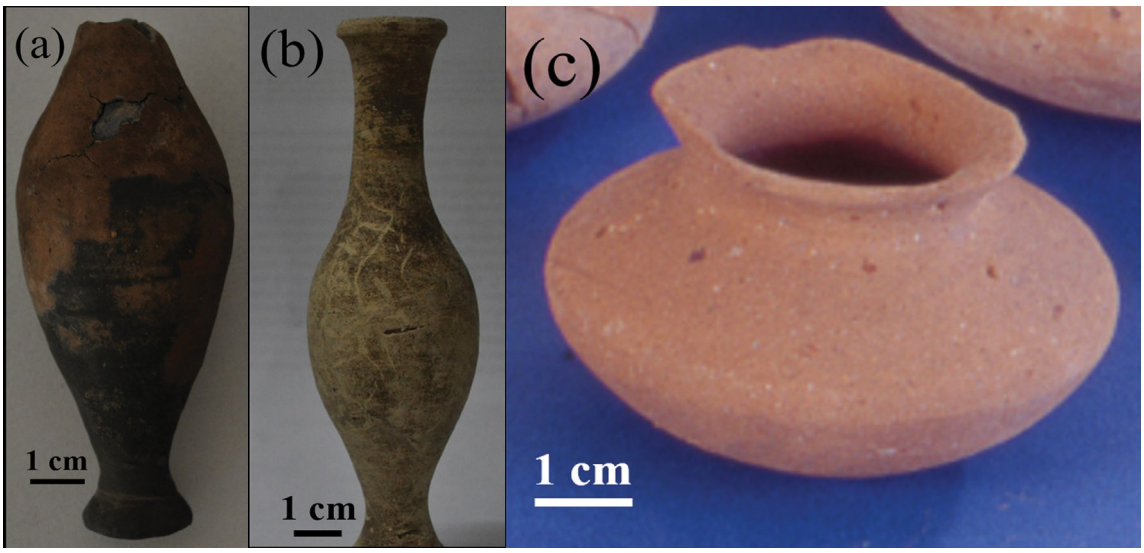

Figure 1: Photographs of the sampled vases: a) *Unguentarium* from the shipwreck in the site of Santa Sabina (Brindisi); b) *Unguentarium* from the hypogean tomb named *Ipogeo delle Gorgoni* (Taranto); c) Lenticular pixys from the sanctuary in Alaimo - Lentini (Sicily).

paring or cooking food [4,24-31]. In this field, perfumes, ointments, and cosmetics are investigated with growing interest, since some ingredients have been listed in ancient texts [32-36], but in most cases their preparation was a secret. These products were often a mixture of organic and inorganic compounds [37-40], therefore the FT-IR technique is a good choice to obtain information on both phases. In addition, a limited amount of material can be removed from the vessels, which are often precious and should be left intact or with minimal damage.

Starting from these issues, the present study was aimed at investigating residues in archaeological ceramic samples by means of FT-IR spectroscopy. This technique was chosen as a quick and cheap method to screen the samples before subjecting them to more expensive and time-consuming methodologies. Residues taken inside pottery vases, classified as containers for unguents and cosmetics, were analyzed. Both the organic and inorganic components were investigated to advance hypotheses about the function of the vases' content. The results highlighted dissimilar composition of the residues for containers different in shape and provenance.

Materials and Methods

Archaeological samples

The investigated samples were gathered in three ancient pottery vases discovered in different archaeological sites in the Mediterranean basin. The small vessels were unbroken and no residue was clearly visible inside, at least to the naked-eye.

Sample S1 was collected in an *unguentarium* (Figure 1a), which was found in a shipwreck and referred as onboard equipment. The remains of the cargo ships were discovered at the site of Santa Sabina (Brindisi, South Italy) [41,42].

The vase is in grayish ceramic fabric and was dated to 2nd century BC.

S2 was sampled in an *unguentarium* (Figure 1b) from a hypogean tomb in Taranto (South Italy), which is named *Ipogeo delle Gorgoni* [43,44]. Many *unguentaria* were found in the burial chamber. The selected vase is in pale orange ceramic fabric and was dated to the middle of the 2nd century BC.

Finally, sample S3 was collected inside a lenticular pixys (Figure 1c) unearthed in a small square votive deposit near the sanctuary in Alaimo-Lentini (southeastern Sicily, Italy) [45,46]. This vessel, due to the shape and size, was characteristic of makeup containers produced in the western Greece. The ceramic fabric is orange and the piece was dated to the second half of the 7th century BC. The use of this type of vessel is tied to ritual actions and offerings to the gods [47].

Sampling and analytical procedures

The internal surfaces of the vases were scraped with a scalpel to collect the material for the analysis.

A preliminary visual inspection of the samples was performed through a binocular stereomicroscope (Zeiss, mod. Stemi SV11) at magnifications of up to 100X. This examination was mainly aimed at trying to distinguish the residues of the content from the pottery material, inevitably taken away during the sampling.

The material gathered from the vessels was divided in two parts. The first one was finely ground with a pestle in an agate mortar, then mixed with KBr (suitable for

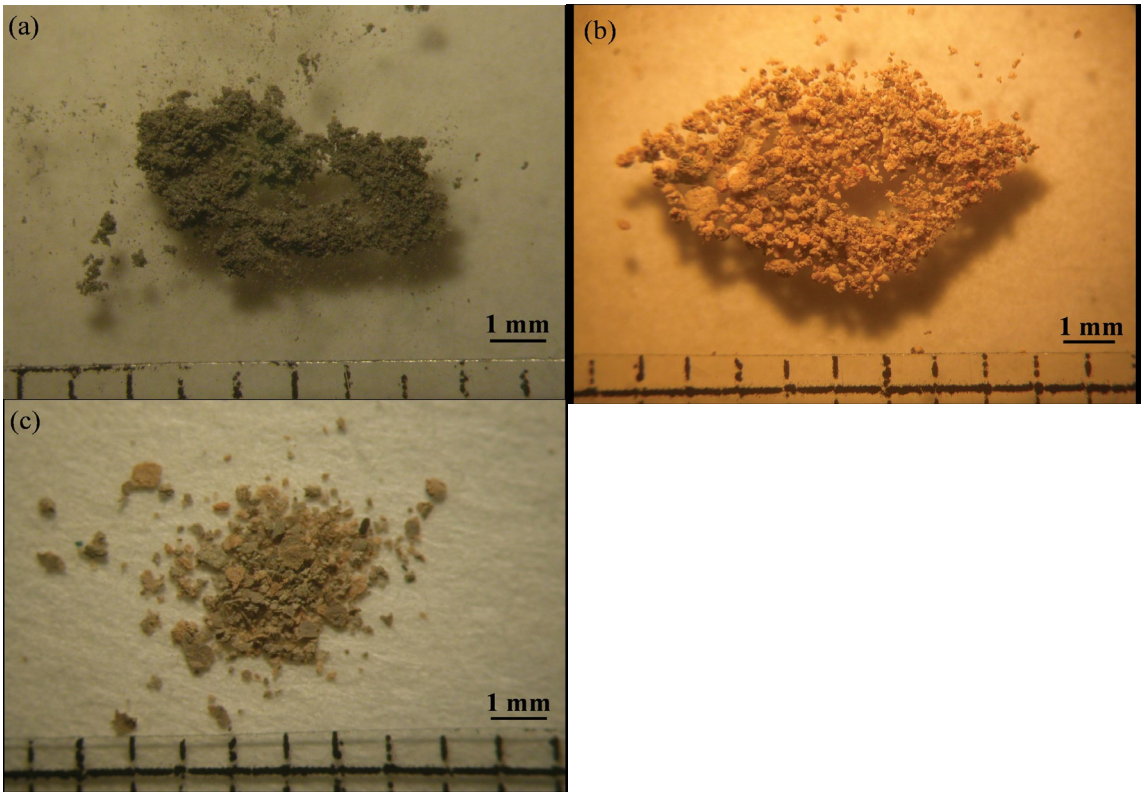

Figure 2: Images of the residues taken inside the vases: a) Sample **S1**; b) Sample **S2**; c) Sample **S3**.

Infrared analysis and provided by Mallinckrodt Baker Chemical Inc.) and compacted in a pellet 13 mm in diameter. A KBr die (Model 129, Thermo Spectra-Tech) and a hydraulic press (Mod 660, Silfradent) were employed to shape the pellets for the analyses. Following the manufacturer's suggestion, 6000 kg load was applied for approximately 1 minute. The second part of the collected material, placed in a vial, was extracted with acetone (analytical grade, provided by Carlo Erba Reagents), using 1 ml of solvent per 5 mg of sample. Sonication was carried out for 22 min in an ultrasonic bath (FALC Instruments), followed by standing for 24 hours in laboratory conditions. The extraction with a solvent was adopted to identify the organic residues without interferences from both the environment deposits and the ceramic material. Acetone was used, as suggested in other studies [4,25,48,49]. A drop of the obtained liquid fraction was placed on a KBr pellet, previously prepared, which was stored for 5 minutes at 40 °C to enhance the solvent evaporation.

All the KBr pellets were analyzed in transmission mode, immediately after the preparation. A FT-IR Thermo Nicolet Nexus spectrometer, equipped with a Deuterated Triglycine Sulfate (DTGS) detector, was used. The spectra were acquired in the range of 4000-400 cm^{-1}, with a resolution of 4 cm^{-1} and 200 scans per measurement; the background spectrum was collected on a pellet made of KBr only.

Where the analysis after the extraction was negative, μ-ATR analyses were performed on the small flakes selected under the microscope, making it possible a selective examination of minimal portions of the sample. These spectra were acquired using a Thermo Nicolet Continuum IR microscope coupled with the spectrometer. This device was equipped with a Mercury-Cadmium-Telluride (MCT) detector, which was cooled with liquid Nitrogen. A 15 × Reflachromat objective with a slide-on ATR attachment (Thermo Spectra-Tech), using a Si crystal (refractive index = 3.4; incident angle = 45°; contact area = 50 × 50 μm) was employed to collect the μ-ATR spectra. To ensure reproducibility and uniformity, the contact between the ATR crystal and the sample surface was automated and computer controlled. After each analysis, the crystal was cleaned with a soft cloth soaked in acetone. The spectra were collected in the range of 4000-650 cm^{-1}, with a resolution of 4 cm^{-1} and 200 scans for each measurement; the background spectrum was acquired in air.

The employed instrumentations were not purged with dry and CO_2-free air, therefore the contribute of absorption bands of both CO_2 (appearing in the spectrum as a doublet around 2340 cm^{-1}) and water vapor (resulting in sharp and very close peaks over 3700 cm^{-1}) are observed in the reported spectra, although a background spectrum was acquired before each analysis and automatically subtracted (by software) from the sample spectrum.

All the FT-IR data were processed with the OMNIC 8.1 software (Thermo Fisher Scientific Inc).

Discussion

The preliminary observations through the stereomicroscope evidenced that the samples were different in appearance. The sample S1 consisted in a gray powder, homogeneous in color and texture (Figure 2a). Grains of whitish material came from S2; in this sample, tiny glossy elements were observed (Figure 2b). The samples S3 was mainly made of flakes either red or gray in color (Figure 2c). Actually, the most of these latter fragments consisted of both levels, suggesting that the grayish material was a coating on the reddish ceramic fabric (Figure 3a and Figure 3b). Additionally, in this sample a very small green grain was found. A red-gray fragment and the green one were gathered to analyze them separately (Figure 3c).

The FT-IR peak wave numbers and assignments related to the compounds detected in the analyzed archaeo-

Figure 3: Images of flakes selected in the sample **S3**: a) and b) the two sides of a red-gray fragment; c) A green grain.

Table 1: Compounds detected in the analysed archaeological potteries, FT-IR peak wave numbers and assignments.

Compound	Peak wave numbers (cm^{-1})		Vibrational assignment	References
	In this study	*literature*		
$CaCO_3$	1420; 1423	1435-1404	Asymmetric CO_3^{2-} stretching of $CaCO_3$	[8,10,50,51]
	870; 873; 874;	874-879	Asymmetric CO_3^{2-} bending of $CaCO_3$	[8,10,50,51]
	712; 716	710-714	Symmetric deformation of CO_3^{2-} of $CaCO_3$	[10,50,51]
Silicates	1004; 1032; 1034; 1039	1003-1041	Si-O stretching	[52,53]
	464; 467	465-479	Si-O-Si deformation	[52]
	1634; 1644	1630-1653	OH deformation of water	[52]
	3620	3619-3625	OH stretching of structural hydroxyl groups	[52,53]
	3690	3689-3696	OH stretching of structural hydroxyl groups of kaolinites	[52]
Quartz	1080	1074-1086	Si-O stretching of quartz	[8,54]
	796; 799	798-794	Si-O stretching of quartz	[8,10]
	766; 773	776-781	Si-O stretching of quartz	[8,10,55]
Iron oxides	520	577		[55]
Kaolinites	1030	1036-1027	in-plane Si-O stretching	[52,53]
	1009	1011-1004	in-plane Si-O stretching	[52,53]
	912	912-915	OH deformation of inner hydroxyl groups	[52,53]
Lipids	1726; 1728; 1734	1751-1713	Ester C = O stretching	[56-60]
	2926; 2927	2925-2928	Aliphatic CH_2 asym. stretching	[10,61]
	2854; 2855	2854-2856	Aliphatic CH_2 sym. stretching	[10,61]
Oils	1743	1743-1747	Ester C = O stretching	[10,61]
	1457	1461-1465	Asym. bending of aliphatic CH_3 and CH_2 groups	[10,25,49,61]
	1244	1236-1244	C-O stretching	[61]
	1162	1164-1170	C-O stretching	[61]
Vegetable resins	2927	2922-2926	$-CH_2/-CH_3$ stretching	[8,25,48]
	2854	2848-2869	$-CH_2/-CH_3$ stretching	[8,25,48]
	1699	1694-1726	C=O (stretching) in carboxylic acids/ester	[25,48]
Pitch	1716	1710-1730	ketone group as part of a ring structure	[7,8,62]
Proteins	1650	1650	C=O (stretch) - Amide I band	[9,63,64]
	1543	1500-1565	out-of-phase combination of the NH in plane bending and the CN stretching vibration - Amide II band	[9,63,64]
	1458	1200-1450	in-phase combination of the NH bending and the CN stretching vibration - Amide III	[60,63]
Absorbed water (free)	3420; 3428	3420-3445	H-O-H stretching	[54,65]
	1630; 1640	1620-1642	H-O-H bending	[54,55,65]

logical potteries were listed in Table 1. In the same Table, the bands observed in the present study were compared with those already published in the literature.

The FT-IR analyses performed in transmittance mode on sample S1 (Figure 4a) evidenced the presence of a great amount of calcium carbonate (1420, 874, and 716 cm^{-1}). Also silicates (1039 and 464 cm^{-1}) and quartz (1080, 796, and 766 cm^{-1}) were very abundant. The lack of signals above 3600 cm^{-1} suggested that the silicate compounds mainly came from the pottery. In fact, peaks around 3620 and 3690 cm^{-1} are indicative of raw materials from the environment and are usually not observed in fired archaeological ceramics, where the high firing temperatures cause the de hydroxylation of the clays [66-68]. The bands centered about 3428 cm^{-1} and 1630 cm^{-1} originated from the OH stretching and H-O-H bending of the absorbed water, respectively [55]. Water molecules can have been absorbed by the pottery [65,69] during the long exposure in the underwater environment after the sinking of the ship.

A signal at 1726 cm^{-1} suggested the presence of organic compounds of lipidic nature.

The analysis performed after extraction with acetone was helpful to better identify the organic material in S1. The related result, reported in Figure 4b, matched a typical oil spectrum [60]. The -CH_2 stretching peaks were very strong and were found at 2926 and 2855 cm^{-1}. A strong and sharp carbonyl band of ester group was observed at 1743 cm^{-1}. This is a "marker" band for identification of oils [60]. Other bands typical of oils were found at 1457 cm^{-1} (aliphatic C-H) and 1162 (C-O). Also in this spectrum, the signal at 3420 cm^{-1} can be attributed to water molecules absorbed during the tests by both the sample and the KBr pellets.

These results are consistent with historical sources documenting that vegetable oils were predominantly utilized as the lipid base for scented unguents and perfumes [70-72]. Among them, non-drying oils (e.g. almond oil, olive oil) were found to be more suitable to obtain substances with the proper texture for an easy application

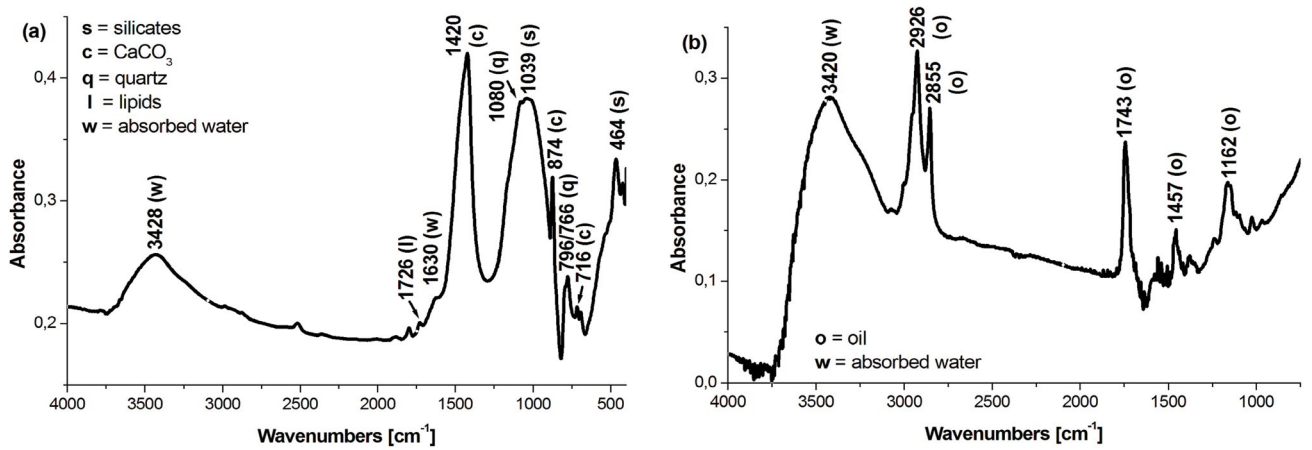

Figure 4: Spectra collected in transmission mode on the **S1** sample: a) As-sampled powder; b) Liquid obtained by extraction with acetone.

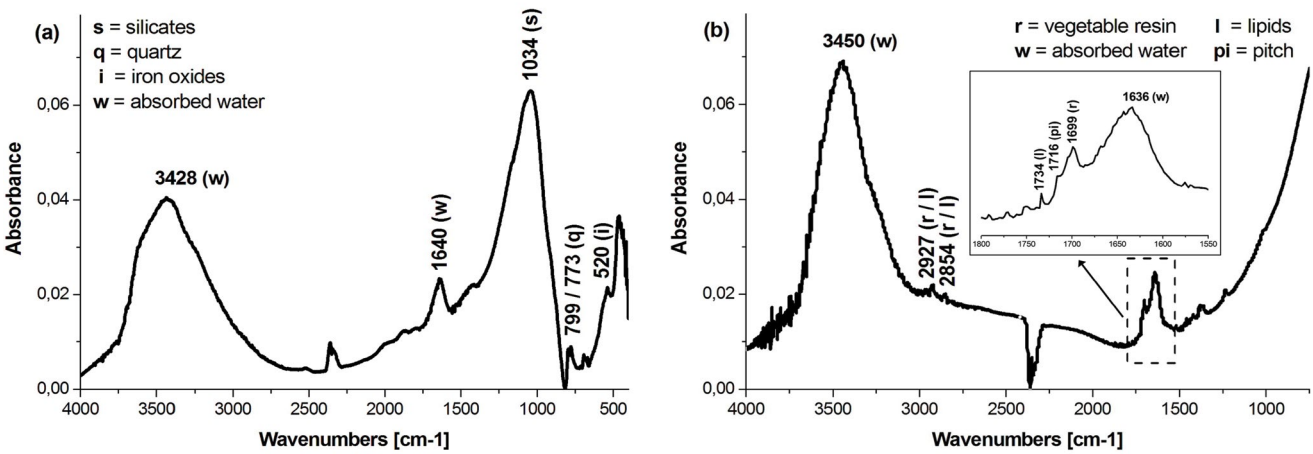

Figure 5: Spectra collected in transmission mode on the **S2** sample: a) As-sampled powder; b) Liquid obtained by extraction with acetone (the range between 1500 and 1800 cm^{-1} has been expanded in the inset box).

on the skin [30]. It is to take into account that, since in ancient times olive production was widely spread in the Mediterranean Basin, olive oil became the most common excipient in the preparation of perfumes and cosmetics. In addition, inorganic compounds were added to the unguents [73,74], therefore the high content of calcium carbonate found in S1 could arise from an intended ingredient.

In the spectrum of sample S2, acquired in transmission mode (Figure 5a), the strong absorption band at 1034 cm^{-1} allowed to recognize silicate minerals as the main constituents. The characteristic doublet at 799 and 773 cm^{-1} and the signal around 520 cm^{-1}, accounted for the presence of quartz and iron oxide minerals, respectively. The bands at 3428 and 1640 cm^{-1}, due to water, very probably originated from hydration of minerals in the ceramic body as a consequence of the exposure to water/humidity in the burial environment. Finally, no organic substance was identified.

The result of FT-IR analysis on the liquid obtained by extraction with acetone is reported in Figure 5b. In this spectrum, the strongest bands, found at 3450 and 1636 cm^{-1}, can be due to water molecules soaked up during the tests or absorbed in the clay structure [10,12,75]. The weak absorption observed at 1734 cm^{-1} suggested the presence of lipids in traces. The peaks around 2927 and 2854 cm^{-1}, due to stretching vibrations of $-CH_2$, can be ascribed to both lipids and vegetable resins [11,60,76]. The resins also gave rise to signals at 1699 and 1716 cm^{-1} as the stretching bands of carbonilic groups. In particular, the signal at 1716 cm^{-1} was indicative of ketone groups typically found in pitch [7,8,25].

According to classical sources, resins are among the main ingredients of ancient ointments and medical remedies [77,78]. Due to their antifungal, antibacterial, and aromatic properties, these products were also applied as embalming products [79,80]. Actually, the finding of this pottery in a tomb could relate its use to funerary practices. In addition, the low amounts of organic compounds inside the vessel could suggest that the vase was empty for a long time and likely the content was used just before the burial.

The as-sampled S3 powder, analyzed in transmittance mode (Figure 6), mainly contained silicates (1032, 467, and 1634 cm^{-1}) and calcium carbonate (1423, 873, and 712 cm^{-1}). No evidence of organic compounds was found. Also the analysis of the liquid extract from this sample was negative. Therefore, the small fragments (Figure 3) selected under the stereomicroscope (see section "*Sampling and analytical procedures*") were separately analyzed in μ-ATR mode.

The red-gray fragment was examined on both the surfaces. The two spectra (Figure 7) were quite similar,

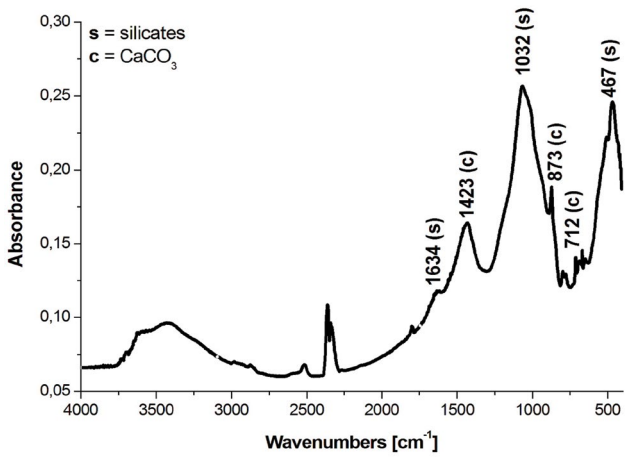

Figure 6: Spectrum collected in transmission mode on the **S3** sample.

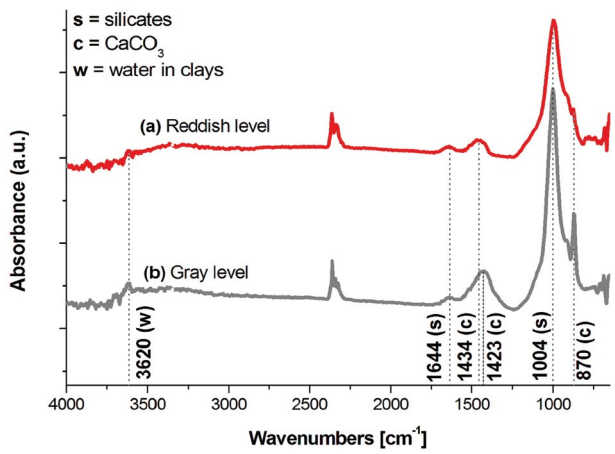

Figure 7: μ-ATR spectra collected on the two-level fragment from **S3**: a) The reddish level (see Figure 3a); b) The gray level (see Figure 3b).

showing the silicates (1004 and 1644 cm^{-1}) as the main components and a certain amount of calcium carbonate (1423 and 870 cm^{-1}). This latter was more abundant on the gray side, suggesting that this level originated from soil residues. In fact, in the same level, a peak was detected at 3620 cm^{-1}, which can be attributed to unfired clay minerals. In both cases, no signals ascribable to organic materials were found.

On the contrary, interesting results were obtained from the FT-IR analysis carried out in μ-ATR mode on the green fragment (Figure 8). In this spectrum, peaks at 1728 and 1244 cm^{-1} can be ascribed to a lipid. In addition, bands at 1650, 1543, and 1458 cm^{-1} were recognized. These three signals are referred to as amide I, amide II, and amide III, respectively, and form the typical pattern of proteinaceous materials [60]. This was an unexpected result since proteins easily suffer denaturation and have been rarely detected in archeological pottery. However, in the literature some studies discuss about

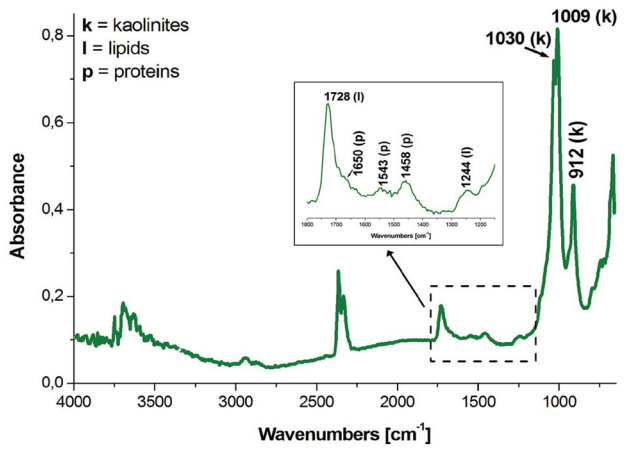

Figure 8: μ-ATR spectrum collected on the green grain from **S3** (see Figure 3c); the range between 1150 and 1800 cm^{-1} has been expanded in the inset box.

proteinaceous compounds which survive to decay because of protective coatings [81], as collagen from boiled meat [82], or in stick for make-up purposes [83]. In the spectrum of the green fragment, the strongest peaks were found at 1030, 1009 e 912 cm^{-1}, which are due to inorganic clay minerals belonging to the kaolinite group [84]. From the ancient times until nowadays, these kind of materials have been frequently used in cosmetics, as well as in pharmaceutical applications [85,86]. The clay mineral probably protected the proteinaceous material against the degradation processes. The absence organic compounds in the whole sample suggested that the pyxis did not contain liquid substances. The obtained results let us suppose that the green fragment was the residue of a solid material used as a cosmetic make-up.

Conclusions

In this study some whole pottery vases, different in form and dimensions, but all classified as containers for cosmetics, were analyzed by FT-IR spectroscopy. The results obtained from investigations on the as-sampled material and after extraction with a solvent were examined and compared.

The knowledge achieved about the sampled artifacts and their contents depended on the analyzed sample, on its collection and preparation, as well as on the applied test methodology. The analyses in transmission mode on samples scraped as a powder provided information mainly about inorganic materials. In particular, the constituent materials of the pottery and the residues from the soil and/or the environment were easily detected. The presence of inorganic materials limited the detection of organic compounds, usually found in traces. However, the extraction with a solvent helped to identify the organic substances, even if just a partial characterization was performed, due to the intrinsic limits of the FT-IR technique. The analyses in μ-ATR mode allowed a selective and useful examination of minimal portions of the sample.

The use of the sampled artifacts as cosmetic vases was confirmed. The obtained data allowed tracing a rough composition of the content, which, in accordance with the ancient texts, resulted essentially based on organic materials (lipids, vegetable resins, and proteinaceous compounds). Also inorganic compounds were found as intended ingredients of the preparation, probably added as pigments or to tune the texture of the cosmetic.

The detection of the organic compounds together with the ceramic material let suppose the storage, inside the containers, of a liquid substance (to some extent viscous) which penetrated into the porous fabric of the pottery. In this case, a selective sampling of the residues was not possible. In fact, where the organic compounds and the pottery were not identified in the same sample, well distinguishable residues due to the content were observed, suggesting the presence of a cosmetic in solid form.

The obtained results confirmed that the FT-IR spectroscopy provides a simple, fast and economical analytical method, which allows obtaining reliable and sound data using a limited or no preparation of the samples. In addition, this technique was found very useful in case of unbroken artifacts, when the archaeological objects cannot be moved into the laboratory, and where an extensive sampling - and the damage thereof - has to be avoided.

Acknowledgements

Thanks go to Prof. Rita Auriemma (Università del Salento - Dipartimento Beni Culturali) for providing the *unguentarium* from the shipwreck in Santa Sabina. The authors are grateful to Soprintendenza Archeologica di Taranto for the opportunity to analyze the artifacts from the *Ipogeo delle Gorgoni* and for providing the archaeological samples. Thanks are also due to Soprintendenza per i Beni Culturali e Ambientali di Siracusa for granting access to the Museo Archeologico di Lentini in order to perform the sampling.

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