

Study of the organic residue from a 2600-year old Etruscan plumpekanne

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Received 5 July 2006; received in revised form 20 November 2006; accepted 1 December 2006

Abstract

Excavation of the Etruscan Necropolis dell'Osteria near Vulci (VI Century B.C.) brought to light in Tomb 2 a bronze plumpekanne. According to preliminary X-ray observation, an unusually thick deposit of organic nature lay at its bottom. Numerous samples of the residue were investigated using microFTIR and diffuse reflectance FTIR spectroscopy. For comparative purposes similar analyses were performed on samples of resins mentioned in classical sources. Spectroscopic results identify the residue as mastic or incense, both triterpenic resins. The former seems to be preferred since, according to classical sources, it was used as must additive.

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Keywords: Fourier transform infrared spectra; Diffuse reflectance; X-ray diffraction; Resins; Etruscan oinokoai

1. Introduction

During the spring 1998 excavation of the Necropolis dell'Osteria near Vulci, a significant Etruscan site in Tuscia, a sepulchre was discovered dating to the end of the VI Century B.C. A man and a woman were buried in it in two inviolate chambers (Tomb 2). The woman's dowry appeared very rich consisting in a complete banquet set. A very deteriorated and fragile bronze plumpekanne was among the numerous objects found (inv. 131326).

Inspection and cleaning, of the find before restoration, revealed the presence of an unusually copious residue adhering to its bottom, forming a compact layer nearly 2 cm thick. The amorphous material had an opaque-dark resinous appearance and was still scented.

Plumpekanen, like other differently shaped oinokoai, were used to contain and pour wine [1–3]. It seemed reasonable to infer the existence of an internal coating or of an additive to flavor wine. The presence of the deposit only at the bottom of the find and its abundance seemed to support the latter hypothesis.

In recent years, the identification of resinous materials of archaeological interest has received growing attention considering that plant extracts have been used for thousands of years, by

many cultures, for a number of purposes. Among these are as decorative finish, coloring agents, pottery repair or medicine.

The principal technique applied to the determination of the biological source of resins and for their identification is chromatography–mass spectrometry (GC–MS) which can even monitor the extent of degradation due, for example, to oxidation processes or hydrolysis [4–6]. Such a technique, however, requires the destruction of a small amount of the material and cannot be carried out *in situ*.

In contrast, Raman and infrared spectroscopy have potential as nondestructive and noninvasive means of determining the nature of the resin and possibly of identifying it.

A number of successful identifications of archaeological resin samples obtained with the former technique can be found in literature [7–11], while infrared data are rare.

In this instance, we wanted to check the usefulness of infrared spectroscopy as a tool for identifying the archaeological deposit. Preliminary microFTIR analyses of the remains were carried out *in situ*. During the restoration of the plumpekanne, however, part of the residue was necessarily removed. Some microsamples were therefore analysed in X-ray diffraction (XRD) to ascertain their degree of crystallinity, and infrared spectra were also taken in diffuse reflectance to compare results obtained with both methods.

As infrared spectroscopy is a fingerprint technique and the vibrational spectra of unknown materials require comparison with standards, a number of resins mentioned in classical sources, such as *Naturalis Historia* [12] and *Enquiry into*

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Plants [13] have been spectroscopically characterized in the same experimental conditions, with particular attention to those involved in wine production or storage. When possible, both modern and aged specimens of the same material were investigated.

2. Experimental

2.1. Methodology

Before restoration the plumpekanne was lifted as a whole, with detailed photographic documentation and an accurate sampling of the material carried out to characterise the alloy [14–16].

At this stage, the presence of the residue mainly at the bottom and to a lesser extent on the walls was evidenced. Before restoration, a preliminary spectroscopic inspection was carried out *in situ* using a Fourier transform infrared spectroscopy (FTIR) microscope (IRscopeII, Bruker) in the 4000–600 cm^{-1} range, with a resolution of 1 cm^{-1} , cumulating at least 200 scans.

The item was therefore moulded in the original shape to give it the stability and the aesthetic readability for exhibition.

Numerous microsamples of the residue, removed during the cleaning of the artefact, were analysed by X-ray diffraction (Seifert MZ IV) using a Cu $K\alpha$ radiation and curved graphite monochromator attachment operating at 40 kV accelerating voltage and a 20 mA beam current in the range 2θ 0–70° with a step 0.02. To complete the spectroscopic investigation, several microsamples (about 0.001 mg) were powdered and dispersed in KBr excess and studied in diffuse reflectance (DR) using an Equinox 55 (Bruker) in the 4000–400 cm^{-1} range with 1 cm^{-1} of resolution cumulating 200 scans or more. Samples of the soil in which the plumpekanne was buried were also analysed with both aforementioned techniques.

For comparison the standards were analysed in the same experimental conditions as the residue. Infrared patterns of solid and powdered specimens were identical, with the exception of an overall smoothing in the former case causing a less precise definition of the peaks frequency. For this reason, the following discussion is based on DR spectra.

2.2. Reference samples

From a chemical point of view, it is known that vegetal resins are mixtures of mono-, sesqui-, di- and tri-terpenes, characterized by 10, 15, 20 and 30 carbon atoms per molecule, with alcoholic, carboxylic and carbonyl functional groups. Mono- and sesqui-terpenes are normally found together in the same compound but, due to their high volatility, are seldom found in old specimens. In contrast, di- and tri-terpenes are only separately present in the same material and this allows a classification of resins in two wide classes [4,10].

Di-terpenoids are present in resins from *Pinacea* (genera *Abies*, *Pinus* and *Larix*), *Cupressacea* and *Hamamelacea* families while tri-terpenoids are found in resins from *Pistacia*, *Commiphora*, *Canarium* and *Boswellia* genera [4].

In this work, therefore, reference resins have been collected following two criteria: they must be representative of the genera

Table 1
Analysed samples

Sample	Provenance
Tolu balsam ^a	Prodotti Chimici Puri e Industriali Giusto Faravelli (Milano) Chem. Dept. Museum
Sandarac ^a	Prodotti Chimici Puri e Industriali Giusto Faravelli (Milano) Chem. Dept. Museum
Colophony ^a	Plant Biology Dept. collection
Elemi gum ^b	Plant Biology Dept. collection
Styrax ^b	Recent specimen (herbalist collection and Plant Biology Dept. collection); aged specimen (Stabilimenti Chimici Farmaceutici Riuniti, Schiapparelli (Torino) Chem Dept. Museum
Frankincense ^b	See styrax
Mastic ^b	Aldrich and Plant Biology Dept. collection
Myrrh ^b	Plant Biology Dept. collection and Chem. Dept. Museum (Organic Chem. Inst. Collection no. 18)

^a Diterpenic resins.

^b Triterpenic resins.

mentioned in both classes and they must come from Mediterranean area trees to reproduce, as closely as possible, materials known and used in the past with particular attention to those employed for flavoring wine.

Those chosen were based on references found in two classical sources: Theophrastus “Enquiry into Plants” [13] and Books XII–XVI of Pliny’s “Natural History” [12].

Several samples of Colophon (*Pinacea* family, Asia) and sandarac (*Cupressacea* family, genus *Tetraclinis articulata*, Spain and North Africa) were studied to characterise the spectral features of di-terpenoid resins. Among triterpenoids: frankincense (*Boswellia* genus, North Africa), mastic (*Pistacia* genus, South Mediterranean), myrrh (*Commiphora* genus, Northeast Africa) and styrax (*Hamamelacea* family, from *Liquidambar orientalis*, Asia) were chosen. Tolù balsam gum (*Myrospermum toluiferum*) and Elemi oil (genus *Canarium* and *Bursera*) were also considered as representative of di-terpenoid and triterpenoid compounds, respectively, even if not originating from the Mediterranean area.

With the exception of mastic (furnished by Aldrich), recent reference samples in this study, were obtained from herbalist and/or Plant Biology Department (University “La Sapienza”, Rome) collections. They were compared to ancient samples saved in the Chemistry Department’s Museum (University “La Sapienza”, Rome). Table 1 lists the reference samples selected, together with their provenance and supplier.

Archaeological considerations exclude that oinokoai could have contained honey or beeswax [1–3]. Nevertheless, the residue spectra were compared both to those of beeswax microsamples and to honey spectra reported in literature [17]. Archaeological specimen spectra were also compared to those of samples reported in IRUG database [18], when available.

3. Results and discussion

The portion of the residue adhering to the bottom of the plumpekanne appeared dark brown turning gradually to light brown towards the opening of the vessel.

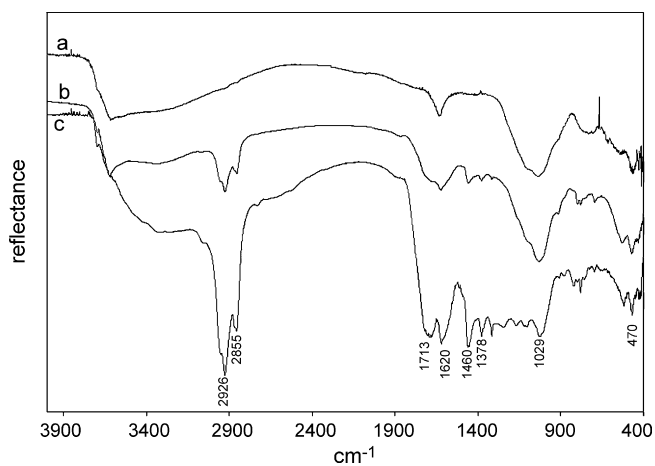


Fig. 1. Absorption bands (cm^{-1}) of pure soil (a), light (b) and dark brown (c) samples.

Preliminary X-ray analysis revealed that the composition of the light brown portions was largely due to the soil in which the plumpekanne was embedded. Analcyme ($\text{NaAlSi}_2\text{O}_6n\text{H}_2\text{O}$), K-feldspar (KAlSi_3O_8), plagioclase ($\text{NaAlSi}_3\text{O}_8$), muscovite and quartz (SiO_2) were individuated as predominant components. A very weak broad absorption suggested the presence of a minor noncrystalline component. The situation was reversed in samples taken from the darker part of the residue, where the broad band of the amorphous portion gained intensity, overlapping the crystalline components' extremely weak signals. Because of its position (around $15\ 2\theta$), an organic nature could be tentatively proposed for the amorphous component.

Infrared investigation confirmed that the light brown and dark brown samples, while reproducible among them, were different. The spectra of the clearest portions were identical to those of pure soil mainly constituted of silicates. The broad absorption at 3500 and the peak at $1620\ \text{cm}^{-1}$ are therefore, attributed to the stretching and bending motions of O–H groups, respectively, and peaks at 1029 and $470\ \text{cm}^{-1}$ are assigned to the Si–O stretching and O–Si–O bending modes, respectively (Fig. 1a and Table 2).

Additional bands started to appear in darker specimens around $2900\ \text{cm}^{-1}$ and in the 1400 – $1000\ \text{cm}^{-1}$ range and gained intensity in samples coming from residue layers adhering to the bottom of the vessel (Fig. 1b and c, respectively).

The presence of an organic component, suggested by X-ray diffraction patterns, seems strongly supported by the appearance of bands not attributable to soil constituents. Bands at 2945 , 2926 and 2854 fall in the region where C–H stretching of methyl or methylene groups is expected. The strong absorption peak at $1713\ \text{cm}^{-1}$ suggests the existence of a C=O bond and features at 1460 , 1378 and $1316\ \text{cm}^{-1}$ can be confidently attributed to $\delta(\text{CH}_2)$ “scissors” and $\delta(\text{CH}_3)$ deformation modes. Less intense features at 1244 , 1179 and $836\ \text{cm}^{-1}$ are assigned to C–O–H, C–C stretching and CH_2 rocking modes, respectively.

The gain in intensity of the mentioned peaks in the dark brown samples where the organic material should predominate according to X-ray suggestions, is also significant.

Table 2

Wavenumbers (cm^{-1}) and proposed vibrational assignment for specimens of the soil embedding the plumpekanne and of the light and dark brown portions of the inner residue

Soil, ν (cm^{-1})	Pale brown residue, ν (cm^{-1})	Dark brown residue, ν (cm^{-1})	Approximate assignment
~ 3609	~ 3617	~ 3611	$\nu(\text{OH})$
	2945 m, sh	2945 m, sh	
	2926 ms	2926 ms	$\nu(\text{CH})$
	2858 m, sh	2858 m, sh	
	2855 m	2855 m	
		1713 ms, br	
1620 m, br	1620 m, br	1620 s, br	$\delta(\text{OH})$
	1460 mw	1460 ms	$\delta(\text{CH}_2)$ scissor and/or
	1378 w	1378 m	(CH_3) deformation
	1316 vw	1316 mw	
	1244 vvw	1244 mw	$\nu(\text{COH})$
		1179 mw, br	$\nu(\text{CC})$
		1114 w, br	
1029 s, br	1029 s, br	1029 w, br	$\nu(\text{SiO})$
	780 mw	836 w, br	$\rho(\text{CH}_2)$
520 mw, br	520 mw, br	519 mw	$\delta(\text{CCO})$
470 m	470 m	470 m	(OSiO) bending
425 w, br	425 w, br		

The chemical composition of the standard materials basically consists of saturated aliphatic waxi alkanes with esters and unsaturated or aromatic components.

The spectroscopic range where O–H and C–H stretching modes are observed (4000 – $2000\ \text{cm}^{-1}$) seems not illustrative for compositional differences. In contrast, the 1750 – $1000\ \text{cm}^{-1}$ interval is crucial for the classification of resins and the identification of unknown materials. The FTIR spectra of di- and tri-terpenoid standards limited to the 2000 – $400\ \text{cm}^{-1}$ range are reported in Figs. 2 and 3, respectively.

An attempt is made to assess which IR active bands or group of bands could be used to distinguish the spectra of any di-terpenoid from those of any tri-terpenoid compound (Table 3).

In the C=O stretching region, an intense double band is observed whose maximum lies around $1690\ \text{cm}^{-1}$ in the

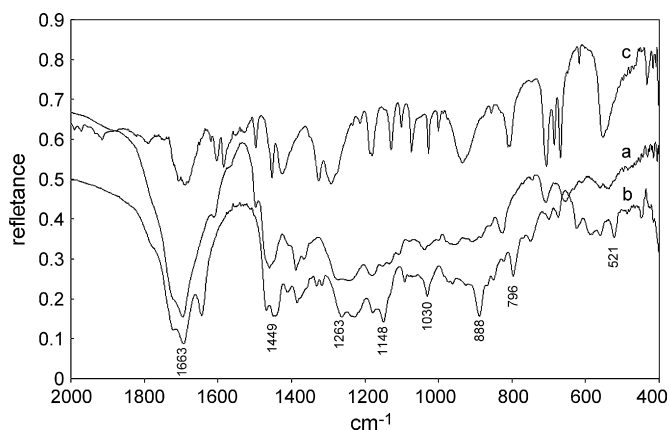


Fig. 2. FTIR spectra of diterpenic standards in the 2000 – $400\ \text{cm}^{-1}$ range: colophon (a), sandarac (b) and Tolu balsam gum (c).

Table 3
Wavenumbers/cm⁻¹ and proposed assignment for reference resins studied in this work

Tolu balsam, ν (cm ⁻¹)	Colophony, ν (cm ⁻¹)	Sandarac, ν (cm ⁻¹)	Elemi balsam, ν (cm ⁻¹)	Incense, ν (cm ⁻¹)	Mastic, ν (cm ⁻¹)	Myrrh, ν (cm ⁻¹)	Styrax, ν (cm ⁻¹)	Approximate assignment
?			3291 s, br	3343 m, br	3441 m, br	3383 m, br		ν (OH) sym
3071 ms		3078.m						ν (OH) asym
2883 ms, br	2937 s, br	2940 s.br	2945 s, br	2917 ms	2949 ms, br	2969 s, br		ν (CH ₃) asym
2837 ms	2868 ms	2846 s		2849 ms	2869 m, br	2932 s, br	2871 m, br	
						2866 sh		ν (CH ₂) asym
2677 ms		2730 m						Backbone
2606 ms	2647 m, br	2675 m						
2089 m								
1989 m								
1971 m								
1933 w, sh								
1915 m						1765 s		
1787 m						1733 sh		
				1736 m			1746 sh	ν (CO)
1707 ms	1725 sh	1722 sh	1704 s, br	1712 sh	1706 s	1681 sh	1719 ms	
1687 s	1694 s	1693 ms						ν (C=C)
		1644 m					1637 w	
					1640 sh		1691 w	
1602 s	1609 m							
1584 m	1565 w		1587 m					δ (CH ₂)
			1504 m				1514 w	δ (CH ₂)
1496 m	1497 w					1441 ms	1497 sh	δ (CH ₂)
1453 ms	1459 ms	1468 m	1462 s	1454 m	1455 ms		1451 mw	δ (CH ₂)
1425 m, br		1449 m	1417 ms					
		1410 w						
	1387 ms	1384 m	1378 ms	1377 m	1377 ms	1380 ms		
	1364 w					1336 w, br	1378 mw	
1325 m		1330 w	1331 m					δ (CH ₂)
		1316 w					1329 w	δ (COH)
		1263 m					1311 w	
	1243 mw	1227 m	1234 m	1241 m	1246 m	1243 m	1273	δ (COH)
1186 m					1245 w, br		1203 vw	
1180 m	1181 mw	1179 w	1173 w	1169 w, br			1170 w	
						1140 m		
1126 m		1148 m						ν (CO)
1073 m		1091 w	1129 mw		1113 w		1111 vw	
					1077 w	1085 m	1071 mw	ν (CO)
1027 m								ν (CO)
1000 w	1037 w	1030 mw	1036 mw		1029 w, br	987 m	1026 mw	ν (CO)
943 m, br			995 mw	1028 m, br		960 m, br		
	955 w, br	961 w, br				916 vw		
	904 w, br				928 w			ρ (CH ₂)
		888 m			884 w	853 w.br	878 w.br	ρ (CH ₃)
		866 w		888 w, br				ρ (CH ₂)
		849 w			836 w, br			
811 m		821 w	827 mw					
805 m	824 mw		664 mw					ν (CC)
						733 m	770 w	
706 s		796 m						δ (CH ₂)
684 m	707 mw	749 w					713 w	ν (CC)
		698 w		719 vw				
	653 w	674 w				597 w		ν (CC) ring
		624 w						ν (COC)
552 s, br		586 w, br						
		558 w, br						
		521 w					527 m, br	ν (COC)

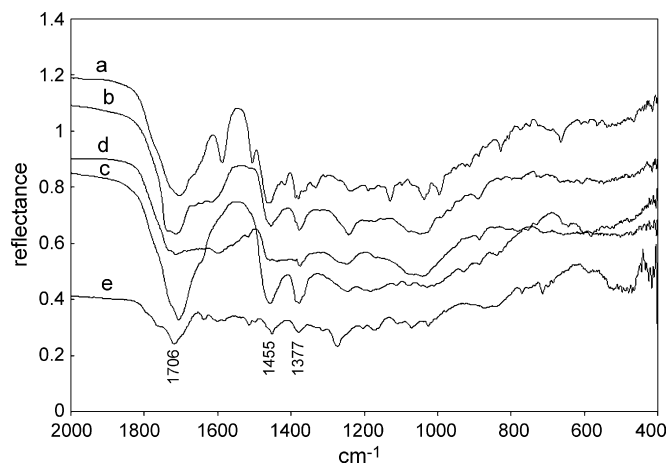


Fig. 3. FTIR spectra of triterpenic standards in the 2000–400 cm^{-1} range: Elemi (a), incense (b), mastic (c), myrrh (d) and styrax (e).

case of di-terpenoids and 1710 cm^{-1} in the case of tri-terpenoids. The residue's major band (1713 cm^{-1}) fits the latter value.

Both colophon and sandarac present well defined and almost intense bands in the $1250\text{--}1150\text{ cm}^{-1}$ interval where δ (COH), δ (CH) and ν (C–C) are expected which are normally absent in spectra of tri-terpenoids with the exception of styrax showing two weak bands at 1203 and 1170 cm^{-1} . No intense bands in the same range are detected in the residue spectrum.

Tolu balsam gum spectrum is easily distinguished from those of other di-terpenoid specimens both for the number of active bands detected and their spectral position.

Spectra of tri-terpenoid resins, with the exception of Elemi oil, show strong similarities, mainly consisting of the aforementioned fundamental around 1720 cm^{-1} , with a shoulder at the higher frequency side and two broad medium intensity bands at 1454 and 1377 cm^{-1} . An additional band at 1273 cm^{-1} is observed only in styrax samples.

The spectral features of the archaeological sample show strong similarity with those of frankincense, mastic and myrrh and suggest its tri-terpenoid rich composition. It is worth observing, however, that aged myrrh specimens show a clear smoothing of the absorption peak at 1454 cm^{-1} , which is intense in contemporary samples, and the parallel growth of a broad band centered about 1050 cm^{-1} . Both features are absent in the archaeological remains. On grounds of spectroscopic data, it is not possible to define whether mastic or incense is the unique or main component of the remains. The former seems to be preferred considering that in early times it was a common additive of must [12]. Its alternative use as a sealant can be ruled out considering that the remains were present only at the bottom of the vessel and no traces have been detected at its opening. In addition, sealant materials have been found up to now, only in archaeological pottery and never in metallic containers [8,11,19] (Table 3).

4. Conclusions

X-ray, microFTIR and FTIR spectroscopy have been employed to identify the nature of a residue found in an Etruscan plumpekanne.

The results are consistent with an organic origin of the material and suggest unambiguously the presence of a triterpenic resin, which is mastic or incense. The former seems to be preferred, as according to classical sources, it was a common must additive. Alternative use as a sealant can be confidently excluded on grounds of the archaeological context.

The research drew on spectroscopic data collected on a set of reference resins chosen among those commonly used in earlier times and representative of the chemical types, *i.e.* those containing di- or tri-terpenoid constituents, into which they can be broadly divided from a chemical point of view.

Acknowledgments

Thanks are due to Dr. A.M. Moretti Sgubini, Dr. F. Boitani, Dr. L. Ricciardi, Mrs. A. Carraro, Mr. R. Mazzocchi and Dr. J. Ehrman for helpful discussion. Thanks are due to S. Stellino for X-ray diffraction analyses, Dr. M.G. Spalluto and Dr. E. Zeuli for providing natural and Museum samples.

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