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The study of pitch via gas chromatography–mass spectrometry and Fourier-transformed infrared spectroscopy: the case of the Roman amphoras from Monte Poro, Calabria (Italy)

Francesca Caterina Izzo*, Elisabetta Zendri¹, Angela Bernardi¹, Eleonora Balliana¹, Manuela Sgobbi¹

Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155/b, 30174 Mestre, Venezia, Italy

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ABSTRACT

The analysis of the composition of organic residues present in ancient pottery are an important source of information for archaeologists. The chemical characterisation of these materials gives information on diets, habits, technologies and original use of the vessels.

In this paper the resinous materials from the interior surfaces of Roman amphoras and the contents of two particular vessels (called *Kadoi*) coming from Monte Poro, in Calabria (Italy) were studied. The organic materials were identified by Fourier-transformed infrared spectroscopy (FT-IR) and gas chromatography coupled with mass spectrometry (GC–MS). The presence of monocarboxylic acids and terpenic species shows that the organic residues were of vegetable origin or mainly consist of vegetable-based resins. Moreover, the presence of characteristic diterpenic biomarkers permits to recognize the use of pine resin and pine pitch, while the presence of methyl dehydro-abietic acid is likely linked to the use of wood tar and not only to the pine pitch. It was not possible to identify with accuracy the species of Pine used to prepare the pitch since the profile of diterpenoid acids of an aged and thermal treated resin is very different from the one of fresh resin. Nevertheless, the hypothesis about the use of *Pinus Laricius* and *Pinus Negrus* to prepare the pitch is plausible as these two species were and are both very abundant in Monte Poro's area.

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1. Introduction

From very ancient times humanity has been needed to transport food and drink from the centres of production to the places of consumption (Font et al., 2007; Romanus et al., 2009; Barone et al., 2012). For this purpose ceramic vessels were frequently used and moreover they were used for cooking and preserving substances even not directly connected to alimentary use (for example medicines, perfumes, colouring matters etc.) (Colombini et al., 2004; Colombini et al., 2003). Often, if the contents was liquid like wine or oil, it was necessary a waterproofing treatment of the interior surfaces to reduce the porosity of ceramic materials and to use them for the transportation and the preservation also in long trips.

Organic residues of these waterproofing treatments in pottery can derive from a large range of natural organic substances which were picked up, transformed and selected based on their properties. These substances are, therefore, an important evidence of the specific use of pottery within the archaeological context (Quercia, 2008; Colombini et al., 2004; Michelaki et al., 2012).

In Roman time, for amphoras which were designed for preserving and transporting wine, waterproofing treatments were realized using a substance that Plinius and Columella called *pix* (pitch) (Plinius, 1984).

Pitch is an organic substance obtained by combustion of resin exudates or resinous wood, insoluble in water but soluble in organic solvent; it has a variable colour from light ochre to black. This substance was probably preferred to other organic compounds for its capacity to impart a particular aromatic strength to the wine (Forster and Heffner, 1958).

The complexity of studying the organic residues from ancient pottery is due to their chemical and physical properties and, moreover, to the unavoidable changes occurring during the preparation and the degradation processes.

* Corresponding author. Tel.: +39 041 234 6730; fax: +39 041 234 6729.

E-mail addresses: fra.izzo@unive.it (F.C. Izzo), elizen@unive.it (E. Zendri), angela.bernardi@libero.it (A. Bernardi), eleonora.balliana@unive.it (E. Balliana), manuela@unive.it (M. Sgobbi).

¹ Tel.: +39 041 234 6730; fax: +39 041 234 6729.

2. Materials and methods

2.1. Analysed samples

A set of samples was collected from Roman amphoras discovered in the neighbourhood of Monte Poro in Calabria, Italy.

The resinous materials found within some of them were studied and here presented into two categories:

- Waterproofing treatment of the internal surfaces of amphoras which were used for preserving and transporting wine (Panella, 1998) respectively: a *Keay 52* from Trainiti and a *Dressel 1* from Briatico Punta Safò. In the studied cases waterproofing organic treatments are present as blackish residues, with a quite good adhesion to the interior surface pottery but easily removable by a scalpel (see Fig. 1a);
- Content of *Kadoi* from Monasterace Punta Stilo where organic residuals have preserved in great quantity inside the container (see Fig. 1b): these residuals are probably the real contents of the vessels more than remains of waterproofing treatments.

Although the localities of provenance are different in all cases, the pottery come from subaqueous contexts which have permitted the conservation of organic residues studied in this paper (Serpico and White, 2000).

The samples were ground in an agate mortar and the obtained powder was separated into two parts for analysis by FT-IR and GC–MS.

2.2. Reagents

The organic residues from the samples were extracted using acetone from Sigma–Aldrich (Milan, Italy).

The following standards were used for the optimisation the GC–MS method and for the peaks assignation: lauric acid, myristic acid, palmitic acid, stearic acid, azelaic acid, sebacic acid, pimic acid, abietic acid from Sigma Aldrich with purity >99%.

Different types of natural oils (linseed oil, walnut oil, poppy seed oil, safflower oil, sunflower oil) and resins (colophony, mastic, dammar, sandarac) were also analysed as standard materials.

The samples were prepared for GC–MS analysis with Meth-Prep II™ from Alltech Associates Inc.

2.3. Analytical procedures

To identify the nature of organic residues Fourier-transformed infrared spectroscopy (FT-IR) and gas chromatography–mass

spectrometry (GC–MS) were used. The first analytical technique allows the identification of the class of substance analysed based on the transitional vibrations of the functional groups (Silvesterin et al., 1991; Derrick et al., 1999), GC–MS permits a more specific identification of organic compounds present in the samples (Colombini et al., 2004; Colombini et al., 2003; Colombini and Modugno, 2009; Koirala and Rosentreter, 2009; Shackley, 1982).

2.3.1. Fourier transformed infrared spectroscopy (FT-IR)

Resinous fractions present in 2–5 mg of samples were extracted using 5 mL of acetone. After drying, the extracts were mixed with KBr, compressed as micropellets (10 Tons pressure) and then analysed using a double beam Thermo Nicolet Nexus 670 FT-IR spectrometer, associated to Omnic E.S.P. 10 software to elaborate IR spectra.

Spectra were collected in the range of 4000–400 cm^{-1} with 4 cm^{-1} resolution.

2.3.2. Gas chromatography–mass spectrometry (GC–MS)

The extracts were transesterified by a one-step process using 30 μL quaternary ammonium salt, namely *m*(trifluoromethylphenyl) trimethylammonium hydroxide. 1 μL of derivatised sample was injected in the chromatographic column's head using azote like mobile phase. Chromatographic separation was performed on a chemically bonded fused silica capillary column HP5, 60 m length, 0.25 mm internal diameter, 0.25 μm film thickness of stationary phase. The instrument used was a Hewlett Packard HP6890 equipped with a mass spectrometric detector HP5973 with a quadrupole analyser. The inlet temperature was 300 °C, the MS interface was at 270 °C. The temperature program was set from 120 °C to 300 °C with a ramp of 10 °C/min, 3 min. The MS was run in Full Scan mode (*m/z* 40–600), 1.9 scans/sec. Solvent delay was set at 4.5 min. The transfer line was at 240 °C and the source temperature was 220 °C. Electron ionisation energy was 70 eV.

Compounds were identified by use of the NIST and MS Search 1.7 library of Mass Spectra and a library created by the authors for resinous materials.

3. Results and discussion

The analyses performed on the organic residues from the waterproofing treatments and from the content of *Kadoi* show different results, probably due to different conditions of use and conservation of the ceramic materials. Some of the obtained results are here reported as representative of the two above mentioned typologies of organic residues.

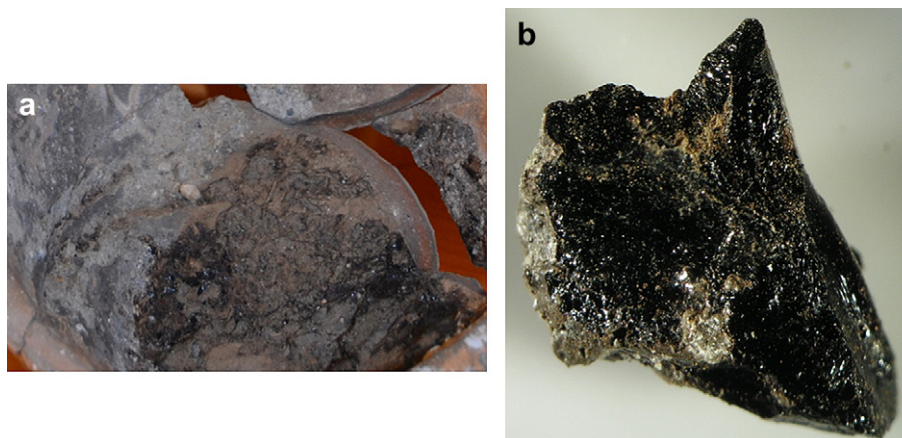


Fig. 1. a. Interior surface of Dressel 1: detail of the waterproofing treatment where sample A was taken (8 \times). b. Sample 8h of the organic residue contained in a *Kados* (20 \times).

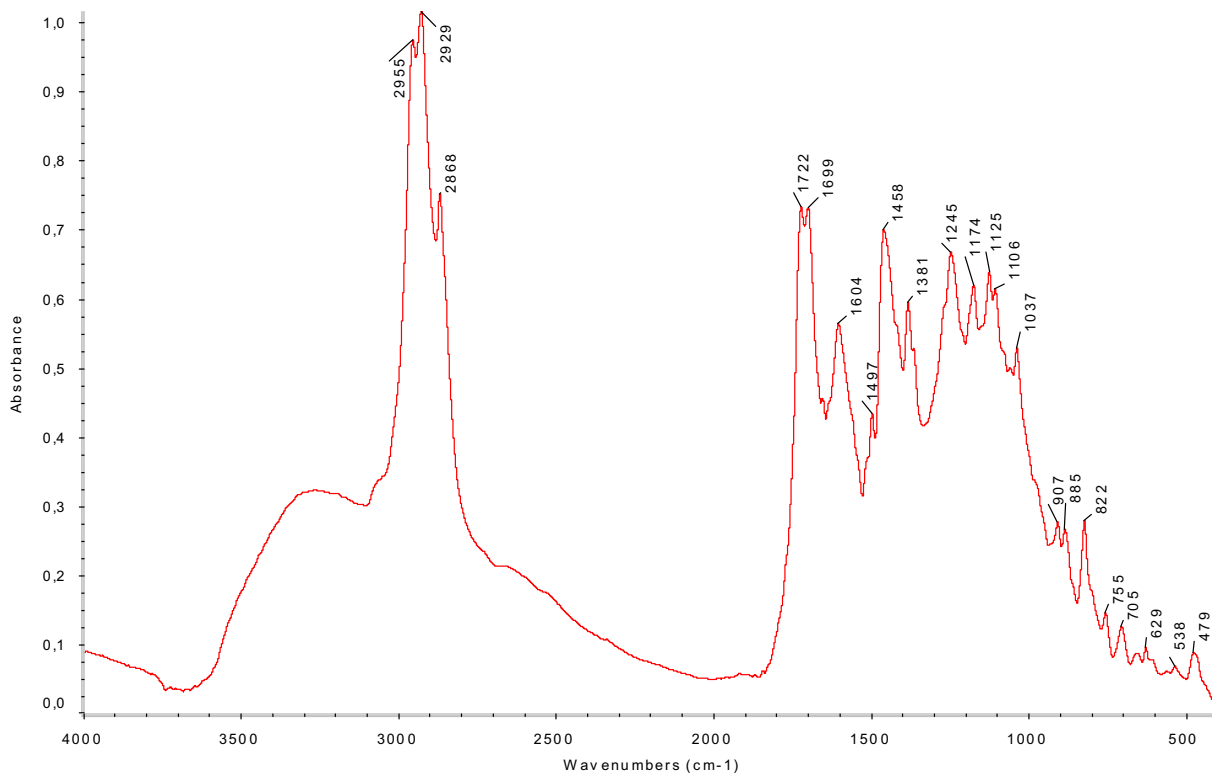


Fig. 2. FT-IR spectrum of a waterproofing treatment sample (sample C) after extraction of the resinous material.

The FT-IR spectrum of sample from of the waterproofing treatment of the interior surfaces of an amphora shows the typical transmittance profile of a diterpenoid resin such as that of the Pinaceae family (Fig. 2). It is possible to observe the stretching

vibrations due to $-CH_2$ and $-CH_3$ groups at 2955, 2929 and 2868 cm^{-1} awardable to the hydrocarbon skeleton of the resin. The stretching band of carbonilic group at 1722 and 1699 cm^{-1} and the stretching vibrations due to aromatic ring at 1604 and 1497 cm^{-1}

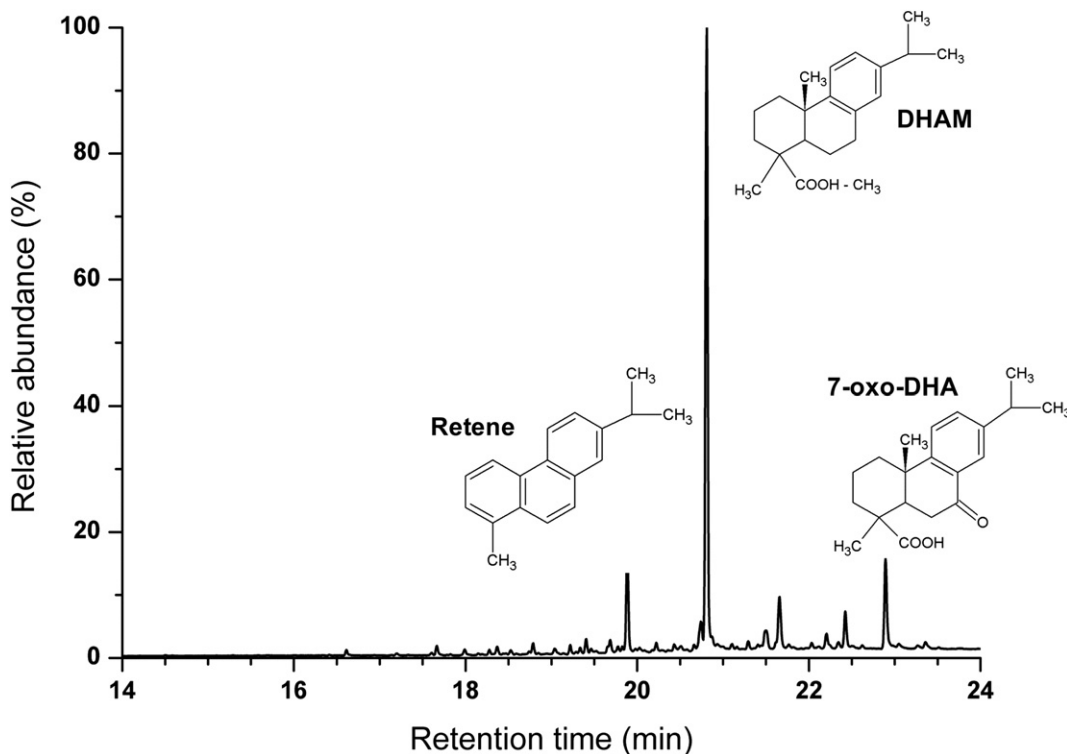


Fig. 3. Total ion chromatogram of a waterproofing treatment sample (sample C) after extraction, transesterification and GC–MS analysis.

Table 1
Identified methylated compounds in waterproofing treatments of internal surfaces after extraction, transesterification and GC–MS analysis.

Retention time (min.)	Molecular ion (<i>m/z</i>)	Compounds
14.50	242	Myristic acid methyl ester
16.62	270	Palmitic acid methyl ester
17.99	284	Phenanthrene
18.53	298	Stearic acid methyl ester
18.80	272	Diisopropilabietic acid methyl ester
19.04	316	Dehydroabietic acid methyl ester
19.22	316	Dehydroabietic acid methyl ester
19.69	271	Succinic acid methyl ester
19.89	234	Retene
20.82	314	Dehydroabietic acid methyl ester
21.53	330	3-hydroxy-dehydroabietic
21.65	342	7-oxo-abietic acid methyl ester
22.03	344	Pinaceae essence
22.20	329	15-methoxy-dehydroabietic methyl ester
22.43	330	15-hydroxy-dehydroabietic methyl ester
22.90	328	7-oxo-dehydroabietic acid methyl ester

Table 2
Identified methylated compounds in the content of a *Kados* after extraction, transesterification and GC–MS analysis.

Retention time (min.)	Molecular ion (<i>m/z</i>)	Compounds
16.62	270	Palmitic acid methyl ester
17.62	314	Dehydroabietic acid methyl ester
17.65	284	Phenanthrene
17.99	284	Phenanthrene
18.80	272	Diisopropilabietic acid methyl ester
18.96	316	Dehydroabietic acid methyl ester
19.88	234	Retene
20.03	316	Pimaric acid methyl ester
20.53	316	Abietic acid methyl ester
20.58	316	Isoimaric acid methyl ester
20.73	312	6-dehydroabietic acid methyl ester
20.82	314	Dehydroabietic acid methyl ester
21.29	316	Abietic acid methyl ester

are also present. Other bands are those at 1458 e 1381 cm^{-1} due to the $-\text{CH}_2$ and $-\text{CH}_3$ bending and at 1245 cm^{-1} due to the OH bending. The finger print region shows a great correspondence with standard FT-IR spectrum of rosin as reported also in (Silvesterin et al., 1991) and (Derrick et al., 1999).

The correspondent GC–MS chromatogram, in Fig. 3, shows the presence of methyl esters of saturated fatty acids with a number of carbon atoms which ranges from 8 to 24, such as stearic acid, palmitic acid and miristic acid. Moreover it is possible to detect the presence of the methyl esters of tricyclic diterpenoids, such as 7-oxo-dehydroabietic acid (7-oxoDHA), 7-oxo-abietic acid (7OA), 15-hydroxy-dehydroabietic acid (15HyDA) and 15-methoxy-dehydroabietic acid (15MeDA) (see Table 1 for the complete list of

detected compounds). These compounds are some of the typical oxidation products of a resin from the Pinaceae family (Colombini and Modugno, 2009). The methyl esters of diisopropilabietic acid, which is distinctive of Pinaceae family, and dehydroabietic and 3-hydroxy-dehydroabietic acids are present as well. These last two compounds are indicators that the used pitch was obtained from a destructive distillation of resinous wood. During wood distillation, in fact, gaseous methanol is produced and reacts easily with diterpenic acids to produce methyl-dehydroabietate. This compound is usually absent when pitch is produced by pyrolysis of the resin alone; this conclusion agrees also with the presence of band at 1722 cm^{-1} in the FT-IR spectrum of Fig. 2.

The GC–MS chromatogram shows also the presence of retene which is considered a marker for pine pitch since it appears when the resin is heated to high temperatures. The presence of essences of tree species like *Pinus Laricius* and *Pinus Negrus*, both very

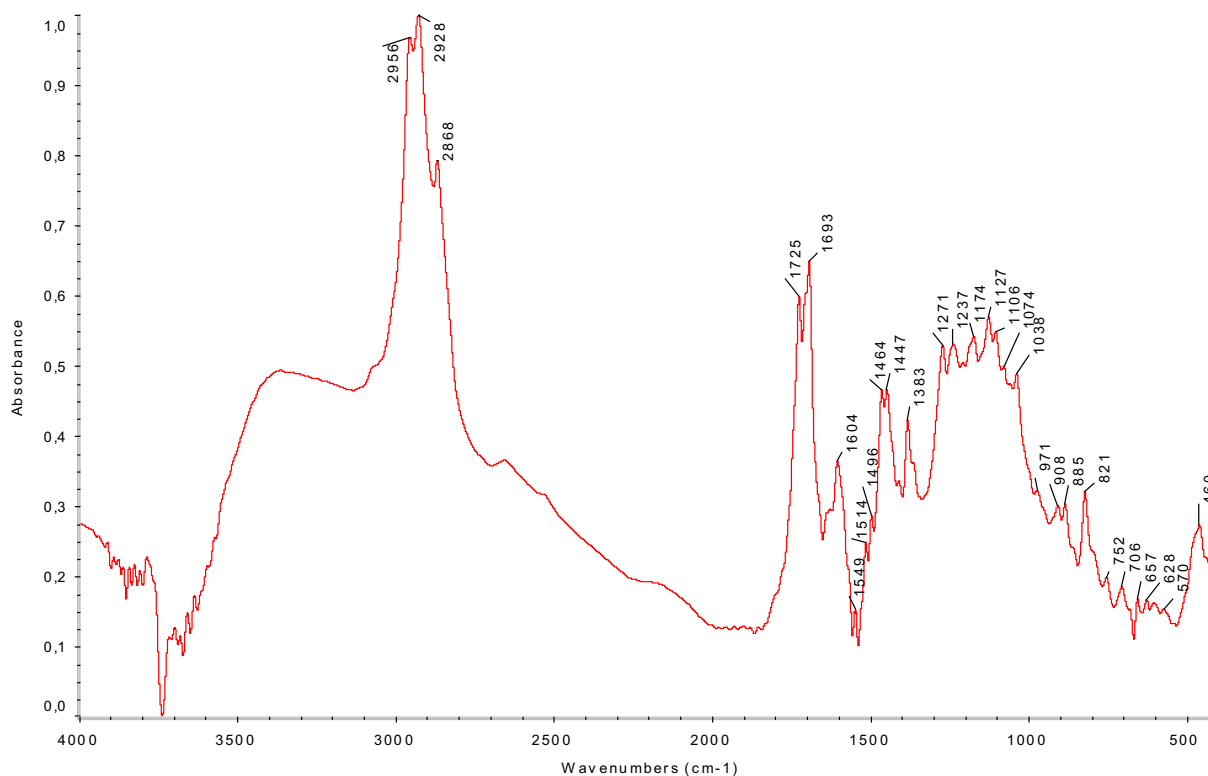


Fig. 4. FT-IR spectrum of the resinous material contained in a *Kados* (sample 101) after extraction of the resinous material.

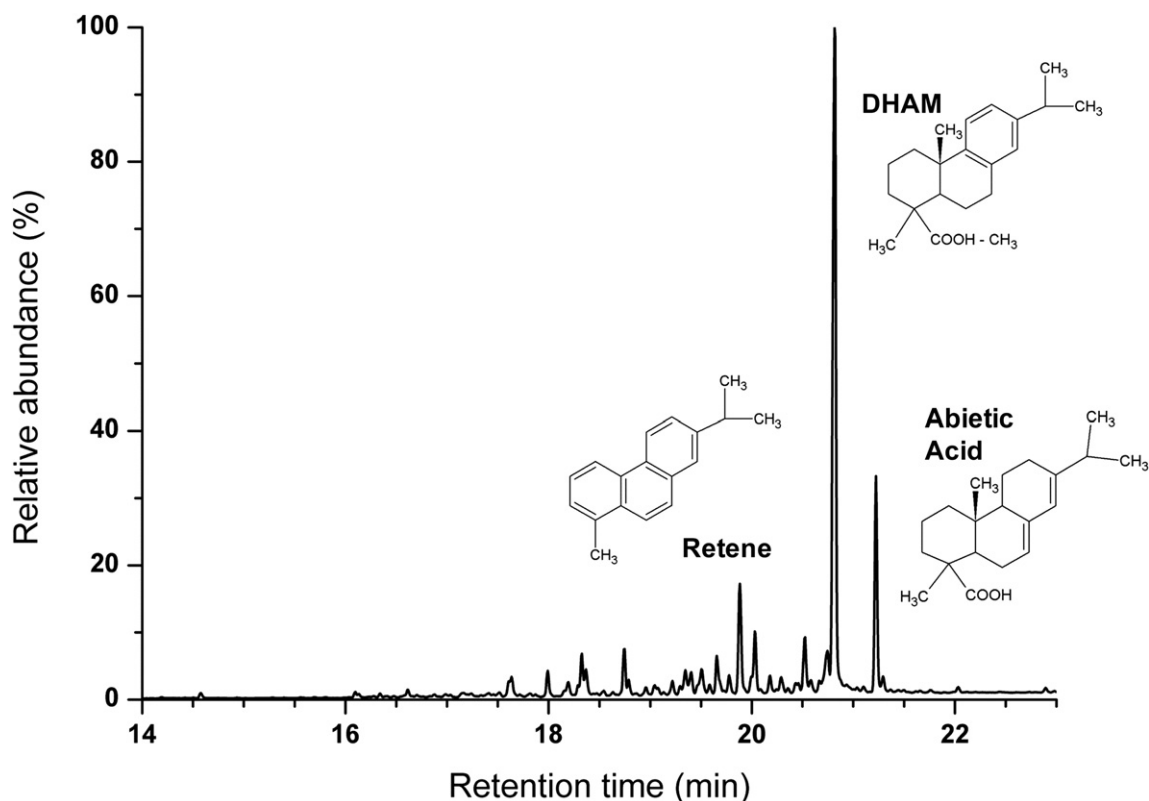


Fig. 5. Total ion chromatogram of the resinous material contained in a *Kados* (sample 101) after extraction, transesterification and GC–MS analysis.

abundant in Monte Poro's area, is another proof which helps to identify the organic residues as pine pitch.

The FT-IR spectrum of a sample taken from the content of a *Kados* shows the typical transmittance profile of a diterpenoid resin extractable from Pinaceae family (Fig. 4), as observed for the waterproofing treatments samples. Some differences in the composition was observable by GC–MS analysis (Table 2 reports all the detected compounds). The chromatogram depicted in Fig. 5 shows the presence of methyl esters of abietic and diisopropylabietic acids, characteristic acids of Pinaceae family, and of isopimaric and palmitic acids, which are distinctive of other arboreal families although belonging to *Coniferae* group. Moreover, it is possible to observe the presence of methyl ester of dehydroabietic acid (DHAM) and, just in this case, of 6-methyl ester of dehydroabietic acid. Both the acids are produced during wood distillation and indicate therefore the pitch process production indicators that pitch was obtained from a process of wood distillation. As seen for the waterproofing treatments sample, in the chromatogram the presence of retene and phenanthrene was recorded as well, while the typical oxidation products were not found. Their absence might be due to the different conditions of conservation. In fact, organic residues of a waterproofing treatment consist in a thin layer of an organic substance; on the contrary the residues within the *Kadoi* are organic products stored in great quantity and therefore less exposed to ageing processes by oxidation.

Only in samples of waterproofing treatments methyl esters of miristic, stearic and succinic acids are present: this is probably due to amphora's utilization. It is possible, in fact, that dynamic use of amphoras as vessels for preservation of liquids may enriched the waterproofing treatment of the interior surfaces. These same considerations are not possible for samples collected from vessels (*Kadoi*) where pitch was stored and preserved for use and commercial exchanges.

For all the organic samples considered in this study, it was not possible to identify with accuracy the species of Pine used to prepare the pitch since the profile of diterpenoid acids of an aged and thermal treated resin is very different from the one of fresh resin. Nevertheless, the hypothesis about the use of *Pinus Laricius* and *Pinus Negrus* to prepare the pitch is plausible as these two species were and are both very abundant in Monte Poro's area.

4. Conclusions

The analytical analysis developed allowed the characterization and the comparison between the organic residues collected from the interior surfaces of amphoras appointed to preserve and transport wine and from *Kadoi* used to conserve pitch also for commercial purposes. The geographical area of provenance of these vessels is the Monte Poro's one, in Calabria. Although the localities of provenance are different in all cases, pottery come from sub-aqueous context which has permitted the conservation of organic residues studied in this paper (Serpico and White, 2000).

All samples studied showed the presence of pine resin and pine pitch or, more specifically, wood tar employed to prepare the pitch. This information is moreover confirmed by the presence of retene and of methyl ester of dehydroabietic acid (DHAM), which are products of the chemical reaction between gaseous methanol and diterpenic acids formed during the distillation of wood.

The use of pitch obtained by combustion of vegetal resins was largely documented in the past, not only as waterproofing treatment but also as medicine or ritual balsams (Colombini et al., 2004; Colombini et al., 2005).

The use of substances extracted from the exudates and/or from the wood of arboreal species of Pinaceae family agree upon the abundance of *Pinus Laricius* and *Pinus Negrus* in this area of Calabria region.

The high degree of oxidation of diterpenoids, present in the organic residue collected from waterproofing treatment, suggests that resin was cooked in an oxidant atmosphere and/or was subjected to ageing processes by oxidation.

The presence of pine pitch in these pieces of pottery is also confirmed by Plinius in the *Naturalis Historia*, and moreover support archaeological studies about the contents of some amphora's typologies like *Dressel 1*, *Keay III* and *Kadoi*. For this last typology the use is suggested also by impressed stamp *pix bruttia* (Sanginetto, 1992).

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