



Setting up a natural resin collection to identify an archaeological black pitch sample

Marc Valls Mompo¹, Gianni Gallelo², Irene Sáez Giménez¹, Agustín Pastor García¹, Francesc Albert Esteve Turrillas¹, Oreto García Puchol², Consuelo Mata Parreño²

¹ Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner Street, 46100 Burjassot, Valencia, Spain

² Department of Prehistory, Archaeology and Ancient History, University of Valencia, Avda. Blasco Ibáñez, 28, 46010, Valencia, Spain

ABSTRACT

Natural resins are among the multiple organic materials that have been employed since the prehistory as an adhesive or varnish in the manufacturing processes and operative chains of several tool. For this study, a black pitch sample found inside an amphora was compared with several types of natural resins previously analysed by gas chromatography-mass spectrometry (GC-MS). Different preservation states resins were collected or acquired to be analysed by GC-MS. The results obtained show the reliability and strength of the developed method, while also giving a hint about the raw material employed to coat the amphora.

Section: RESEARCH PAPER

Keywords: Natural resins; GC-MS; pitch; amphora; fatty acids

Citation: M. Valls Mompo, G. Gallelo, I. Sáez Giménez, A. Pastor García, F. A. Esteve Turrillas, O. García Puchol, C. Mata Parreño, Setting up a natural resin collection to identify an archaeological black pitch sample, Acta IMEKO, vol. 13 (2024) no. 2, pp. 1-6. DOI: [10.21014/actaimeko.v13i2.1834](https://doi.org/10.21014/actaimeko.v13i2.1834)

Section Editor: Fabio Leccese, Università Degli Studi Roma Tre, Rome, Italy

Received February 28, 2024; **In final form** May 17, 2024; **Published** June 2024

Copyright: This is an open-access article distributed under the terms of the Creative Commons Attribution 3.0 License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Funding: Spanish Ministry of Science and Innovation for funding the project EvolMED "Evolutionary cultural patterns in the contexts of the neolithisation process in the Western Mediterranean" (PID2021-127731NBC21).

Corresponding author: Gianni Gallelo, e-mail: gianni.gallelo@uv.es

1. INTRODUCTION

In ancient times, natural resins were employed to waterproof ceramics, such as amphoras, to allow the storing or transport of different liquids such as wine, milk, or oils. In general, a ceramic is a porous material that makes it extremely permeable [1]. Organic residue analysis involves extraction of the compounds that are either absorbed within the ceramic matrix or preserved within visible encrustations on the surface.

The chemical composition of natural resins exuded by trees is diverse, but most are composed of terpenes made up of isoprene units [2], [3]. Furthermore, there are many different resins as they can vary a lot in the compounds found due to the type of tree, environment, and age, even the same species of resin can have differences in their chemical profiles [4]. Useful information about the resins employed in antiquity has been previously reported [5], reducing the number of natural resins to identify. In this work, a set of natural resins and bee wax (often used in the past as adhesives or as elements of oil-resin) were employed as reference materials to characterize unknown substances. Due to

the complexity of the samples, they were processed employing two different sample treatments to separate the neutral compounds from the acid fraction [6]. In the acidic fraction fatty acids and acidic terpenoids are recovered, thus reaching the identification of lipids and other resin components; in the neutral fraction hydrocarbons, sterols, and neutral terpenoids are determined, finally the presence of both resins and waxes is evaluated [1].

The characterization of the organic residues through analytical methods using chemical techniques can help the identification of the materials employed for medicines, adhesives, or also can give information about human diets presented in archaeological remains. These organic compounds are sensitive to ageing and the environment they are exposed to. These factors can cause the disappearance or modification of the compounds of interest and, consequently, different techniques such as liquid or gas chromatography are required for their identification.

Gas chromatography (GC) has a high capability of separating compounds, while mass spectrometry (MS) has a high sensitivity

and selectivity for their detection. GC-MS combination allows us to identify and quantify a large number of compounds that compose the different samples. This type of analysis usually requires a small portion of the sample (lower than 5 mg). Furthermore, the obtained chromatography retention time and mass spectra for each organic compound allows its potential identification by comparison with its Kováts retention index and spectra libraries [7].

The method employed is based on an initial saponification stage, followed by the extraction of acid fraction and neutral fractions. The acid fraction is derivatized with a silylating reagent, which makes the chemical compound more volatile, being trimethylsilylation specifically used in previous studies [4], [8]. This sample treatment allows us to determine hydrocarbons, sterols, and neutral terpenoids in the neutral fraction; while fatty acids, acid terpenoids and resinous components are determined in the acid fraction [9].

This study aims to present the organic compounds found in an archaeological sample and compare them to a previously developed database of natural resins to be able to know what resin was used during its manufacturing process.

2. MATERIALS AND METHODS

2.1. Samples

Some natural resins and waxes were purchased from AGAR while others were obtained through natural extraction. Their provenance is summarized in Table 1. A small sample of 5 mg black tar was taken from the pointed bottom of an amphora (Figure 1). The fragment of the amphora was found out of context in the shores of Pinedo beach located in the southern area of the city of Valencia (Spain).

Potassium hydroxide is used to carry out the derivatization of acidic compounds acquired from Panreac, and methanol (HPLC grade) from Scharlau (Barcelona, Spain). The acidic compounds are extracted from the sample with diethyl ether, sold by Scharlau (Barcelona, Spain). The derivatizing agent for acidic compounds is N,O-bis(trimethylsilyl)trifluoroacetamide with 1% Trimethylchlorosilane (BSTFA+TMS), sold by Honeywell Fluka (Madrid, Spain). As an acidifier for the sample prior to extraction, 37% HCl is used (Scharlau Barcelona, Spain).

Table 1. Description of the different samples with the brand and number

| Sample | Description |
|----------|---|
| RN1K/7 | Amber Rosin. Brown and brittle resin. |
| RN1K/4 | Sandarac Juniper Resin. Fragments of a yellowish-white color. |
| RN1K/16 | Burgundy resin. Large orange fragment. |
| RN1K/9 | Benzoin gum. In pieces. Small light orange fragments with some small dark-colored pieces. |
| RN1K/1 | Dammar resin. Fragments of a yellowish-white color. |
| RN1K/5 | Copal-Manila resin. Mixture of yellowish fragments and dark pieces. |
| AR | Natural prunus persica resin. |
| CR | Natural burnt coniferous resin |
| CRB | Natural coniferous resin that has been burnt |
| CRA | Natural coniferous resin aged |
| Z.Anfora | Sample of a dark pitch found covering the inside walls of an amphora |
| WAX | Bee Wax |



Figure 1. Photo of the amphora piece with a dark pitch covering the inside walls.

2.2. Gas chromatography-Mass Spectrometry

GC-MS analyses were carried out by a gas chromatograph, model 7890 A (Agilent Technologies, Santa Clara, CA, USA), incorporating a low polarity HP-5 (5%-phenyl)-methylpolysiloxane capillary column (30 m × 0.25 mm × 0.25 μm) for the efficient separation of compounds. Detection was carried out using a simple quadrupole mass spectrometer (5975C inert XL EI/CI MSD, also from Agilent Technologies), using electron impact ionization source at 70 eV. Injections were carried out using an Agilent 7683 autosampler. Agilent MSD Enhanced data analysis software was used for data acquisition.

A five milligrams sample was extracted with 1 mL methanol: water (1:1, v/v), sonicated for 10 min using a JP Selecta ultrasonic bath (Fisher Sci., Waltham, MA, USA) and heated at 70 °C for 2 h in a water bath.

The first fraction to analyse was separated by liquid-liquid extraction with 1 mL hexane, in triplicate, and the extract was evaporated to 0.5 mL using N₂ flow (neutral fraction). The remaining hydroalcoholic solution was acidified with 7 drops of HCl 37% and the acidic organic compounds, including terpenoid acids and fatty acids, were extracted three times with 1 mL diethyl ether. After solvent evaporation using N₂ flow, it was derivatized with N, O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMS) 1% and the sample was dissolved in 1 mL hexane (acidic fraction). Hexadecane was employed as an internal standard for this method being added to both neutral and acid fraction.

Sample blanks were also analysed to check the absence of interferent compounds.

The chromatograph oven was programmed as follows: 50 °C maintained for 2 min, 50-220 °C at 8 °C/min, 220 - 260 °C at 2 °C/min, and 260-300 °C at 10 °C/min maintained for 5 min. The volume of injection is 1 μL splitless and the range of acquisition of m/z is from 40-450.

3. RESULTS AND DISCUSSION

The most significant compounds identified in the neutral and acid fraction of the selected analysed samples are shown in Table 2. Figure 2 compares the extraction method and shows the chromatograms of the neutral and acid fraction from the archaeological amphora sample, while Figure 3 and Figure 4 compare the two fractions with selected pine resins based on common marker compounds. The organic compounds found correspond to terpenes and some fatty acids transformed in

Table 2. List of compounds identified in the neutral and acid fraction of the selected analyzed samples. The compounds found in the samples are marked with an X.

| Compound | CR | CRB | CRA | RN1K/5 | RN1K/1 | RN1K/9 | RN1K/4 | RN1K/16 | Z.Anfora |
|--|----|-----|-----|--------|--------|--------|--------|---------|----------|
| Hexadecane (PR) | X | X | X | X | X | X | X | X | X |
| Palmitic Acid, TMS (1) | X | X | - | - | X | - | - | - | X |
| Retene (2) | X | X | X | - | - | - | - | - | X |
| Stearic Acid, TMS (3) | X | X | - | - | X | - | - | - | - |
| Pimaric Acid,TMS (4) | X | X | X | X | X | - | - | X | X |
| Isopimaric Acid, TMS (5) | X | X | X | - | X | - | X | X | - |
| Palustric Acid, TMS (6) | - | X | X | - | - | X | - | X | X |
| Methyl Dehydroabietate (7) | X | X | X | - | - | - | - | - | X |
| Dehydroabietic acid, TMS (8) | X | X | X | X | X | - | - | X | X |
| Abietic Acid, TMS (9) | X | X | X | - | X | - | - | X | X |
| Neoabietic Acid, TMS (10) | X | X | - | - | X | - | - | X | - |
| Agathalic Acid, TMS | - | - | - | X | - | - | - | - | - |
| Methyl agathic acid, TMS | - | - | - | X | - | - | - | - | - |
| Acetoxy agatholic acid, TMS | - | - | - | X | - | - | - | - | - |
| Cinnamic Acid, Methyl ester | - | - | - | - | - | X | - | - | - |
| Sandaracopimaric Acid, TMS | - | - | - | - | - | - | X | - | - |
| Dehydroagatholic Acid, TMS | - | - | - | - | - | - | X | - | - |
| Dihydroagathic Acid, TMS | - | - | - | - | - | - | X | - | - |
| Alpha-pinene (11) | X | X | - | X | - | - | X | - | - |
| Camphene (12) | X | X | X | X | - | - | - | - | - |
| Beta-pinene (13) | X | X | X | - | - | - | X | - | - |
| Ortho-cymene (14) | X | X | - | X | - | - | - | - | - |
| D-Limonene (15) | X | X | X | X | - | - | - | - | - |
| Camphor (16) | X | X | X | - | - | - | - | - | - |
| Borneol (17) | X | X | - | - | - | - | - | - | X |
| Alpha-terpineol (18) | X | X | X | - | - | - | - | - | - |
| Palmitic Acid, Methyl ester (19) | X | X | - | - | X | - | - | X | - |
| 10,18-Bisnorabieta-5,7,9(10),11,13-pentaene (20) | - | X | X | - | - | - | - | - | X |
| Stearic Acid, Methyl ester (21) | X | X | X | - | X | - | - | X | X |
| Methyl abietate (22) | X | X | X | - | X | - | - | - | X |
| 7-oxodehydroabietic acid, methyl ester (23) | - | X | X | - | - | - | - | - | X |
| Copaene | - | - | - | X | - | - | - | - | - |
| Alpha-cubebene | - | - | - | - | X | - | - | - | - |
| Alpha-murolene | - | - | - | - | - | X | - | - | - |
| Alpha caryphyllene | - | - | - | - | X | - | - | - | - |
| D-germacrene | - | - | - | - | X | - | - | - | - |
| Alpha-selinene | - | - | - | - | X | - | - | - | - |
| Delta-cadinene | - | - | - | - | X | - | - | - | - |

methyl esters due the reaction of transesterification, but the signals obtained are lower than the fatty acids obtained derivatized with BSTFA-TMS in the acidic fraction.

During the extraction of terpenes and fatty acids most of their fatty acids were extracted in the acid fraction. The conditions of the sample also affect their compounds, as the fresh and burnt sample had higher ratio of fatty acids and it also had a higher ratio of abietic acid to abietic derivatives compared to the aged sample. Abietic acid is the most important compound in pine resins, but this compound suffers from degradation [10].

Abietic acid is a cyclic diterpene produced especially in conifers. The treatment of these plants gives rise to a modification of the composition (i.e through combustion and environmental factors) and, therefore, the analysis of this gives us information about the treatment of their corresponding resins

[2], [3]. Some of the compounds identified, despite being neutral, or methylated derivatives, have been detected in the acid fraction (such as methyl dehydroabietate). On the other hand, fatty acids have also been identified. These last fatty acids (stearic acid, palmitic acid) and terpenic acids (abietic acid) are present in oils in this case belonging to coniferous species resins [11]. These molecules are insoluble in water and very stable at high temperatures. The characterization of these fatty acids can be classified and form taxonomic groups [10]. It has been identified derivatives of palmitic acid (C16:0) and stearic acid (C18:0), which are quite common in plant and animal oils and other acids that could be used as biomarkers such as abietic acid for coniferous resins, but no other biomarkers have been found that are common in other resins such as sandaracopimaric acid for sandarac resins or cinnamic acid for benzoin gum [12]. Another

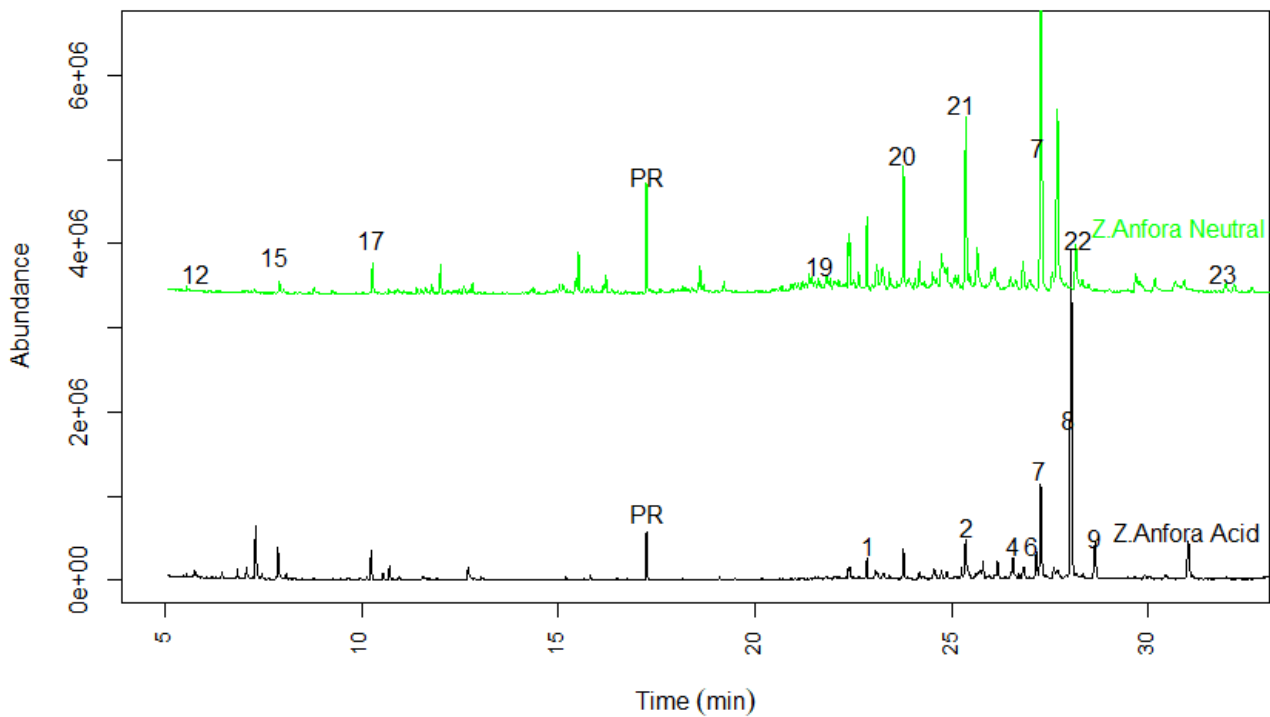


Figure 2. Chromatograms of the amphora Z. Anfora acid and neutral fractions

analysed resin includes the dammar resin from the dipterocarpaceae family, composed mainly of polysesquiterpenes whose molecules follow the cadinene skeleton [13], but also had some common compounds such as abietic acid. After a thorough comparison, most of the biomarkers of the different resins were not found so they could be discarded, only remaining the pine resins, burgundy resin, and dammar resin, due the presence of abietic acid through the acid fraction results. The neutral fraction had a higher similarity in chemical profile with pine resins compared to the other two resins.

Roman amphora fragment has been analysed and several compounds have been identified; they are related to the pine resins previously studied. On the one hand, monoterpene compounds, such as beta pinene and borneol, were detected. On the other hand, very representative compounds, such as abietic acid, dehydroabietic acid, and retene have been identified. Therefore, we may have indications that the resin of the amphora could have been made of pine resin.

The compounds identified in the pine resins were compared with the amphora. The greatest part of relevant compounds in

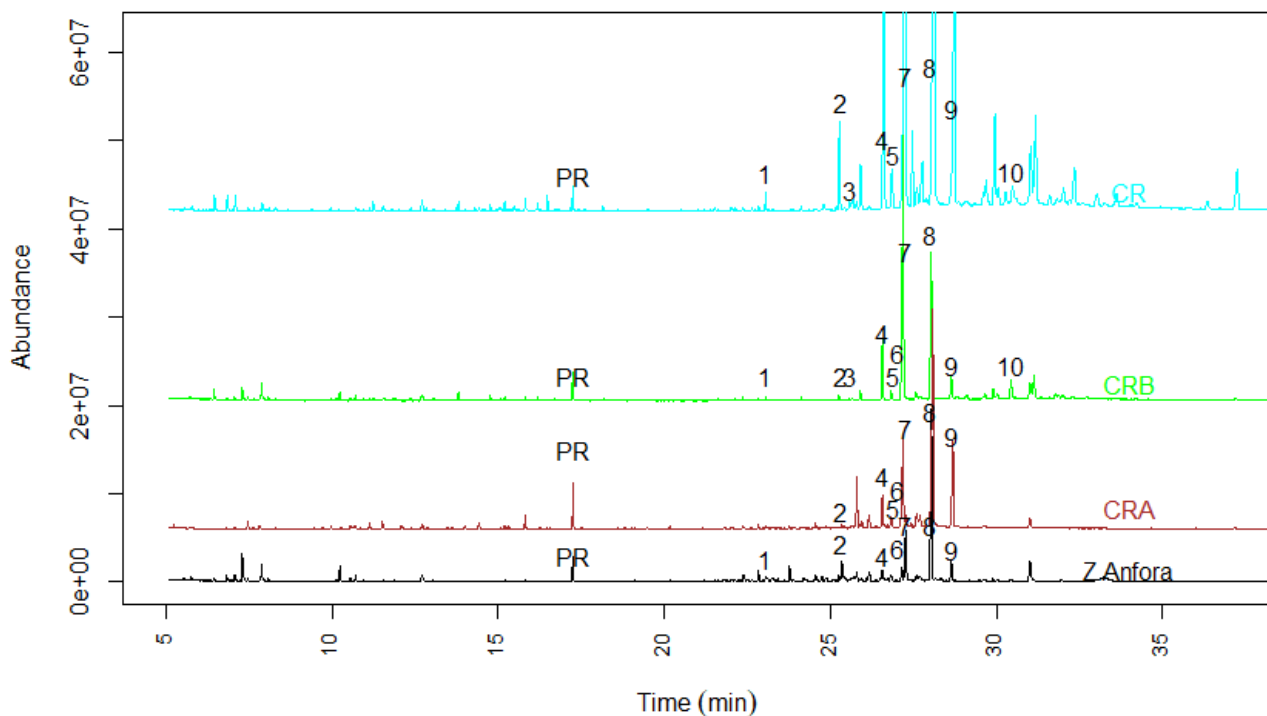


Figure 3. Chromatograms of the acidic fraction of the resin samples CR, CRA, CRB and the archaeological sample Z.Anfora

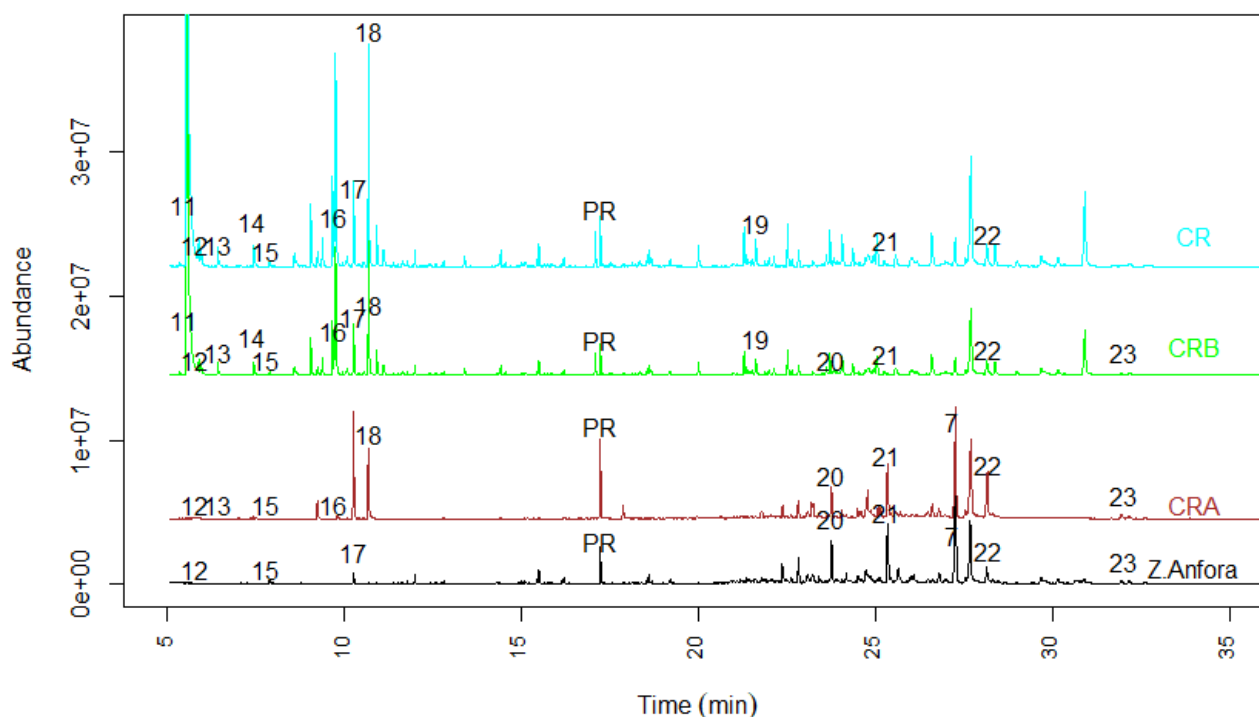


Figure 4. Chromatograms of the neutral fraction of the resin samples CR, CRA, CRB and the archaeological sample Z.Anfora.

pine resins found in the CRB resin were detected in the amphora, such as retene or 10,18- bisnorabieta-5,7,9(10),11,13-pentaene and other abietic acid derivatives, such as 7-oxodehydroabietic acid. This indicates that environmental factors have given rise to the oxidation of compounds derived from abietic acid, probably due the varnish preparation having a heating procedure.

The compounds that were found within the acid fraction of Z.Anfora are extremely common in coniferous trees such as abietic acid and its derivatives (i.e dehydroabietic acid and oxodehydroabietic acid). In this sample, the closest natural resins results were the pine resins as they had a similar chromatogram, and the biggest difference is due to the higher presence of derivatives of abietic acid due to probably oxidation and other chemical reactions. Dehydroabietic acid was found in higher proportion than the abietic acid, being a byproduct of oxidative process. Polyunsaturated fats were not found, as other resins, and this is in accordance with previous studies: they are rarely found in archaeological samples, being degraded after a long period [14].

Abietic acid is the one of the main components to identify archaeological materials made from pine resins, as can be shown in the coniferous resin, being one of the most abundant peak signals. This component can be transformed with a heating process or ageing into dehydroabietic acid due a dehydrogenation reaction. There are other components that can be obtained with abietic acid such as dehydroabietic acid by a decarboxylation reaction. These components can be transformed into different derivates, depending on the chemical reactions that can happen during the heating process. Two of the most important components are the norabietane and retene which are compounds that can be found in the amphora sample as can be shown in Figure 3 [15].

Most of the volatile compounds were found either in extremely small peaks or not found at all in the neutral fraction corresponding to natural resins (Figure 4). This is probably due to the ageing of the sample. Several identified compounds matched with the pine resins and common coniferous trees, such as the presence of alpha-pinene [16]. This compound is usually

found in higher quantities, but the results in the amphora are negative, probably because of the nature of the sample and to its extreme volatility as well.

Our results are in accordance with other studies in which Roman amphorae have been studied and derivatives of abietic acid that come from the Pinaceae family have been found [15], [16], [17], [18], [19].

Finally, the beeswax is a material that was also used in the past mixed with resins for adhesives [17], despite not being a resin of vegetable origin, objects made by natural wax are of great interest in archaeology. Wax is a natural product whose composition is based on hydrocarbons, fatty acids, alcohols, and esters. Most of the peaks identified are linear hydrocarbons with a higher ratio of compounds and several odd carbons [20]. The amphora sample doesn't show any high signal in odd hydrocarbons, discarding the employment of this material in the studied black pitch.

4. CONCLUSIONS

The characterization of the natural resins and waxes has been satisfactory since the most intense peaks have been identified in the chromatograms, which provide a complete information about each of the resins allowing the comparison with the studied ancient material. The greatest similarity between the archaeological sample and the natural resin in the database occurs between the Pinaceae family due to the abietic acid and with the resins of conifers species.

The differences between the archaeological pitch analysed and the pine resins indicate that the sample has suffered degradation as the chemical profile changed due either to the aging or the thermal alterations. Abietic acid can be degraded in multiple chemical compounds due to extended environmental exposure, but thermal degradation cannot be ruled-out as part of the manufacturing process.

In relation to the amphora pitch, compounds derived from abietic acid that have previously been identified in pine resins

confirm that this resin could have been used for waterproofing. The presence of methyl 7-oxodehydroabietate and retene indicates that environmental factors or heating procedures have caused the oxidation of compounds derived from abietic acid.

ACKNOWLEDGEMENT

The authors acknowledges the financial support of the Beatriz Galindo Fellowship (2018) funded by the Spanish Ministry of Science and Innovation and Ministry of Universities (Project BEAGAL18/00110 “Development of analytical methods applied to archaeology”), the financial support of the Ministry of Innovation, Universities, Science and Digital Society of the Valencian Government for funding the projects NeoNetS “A Social Network Approach to Understanding the Evolutionary Dynamics of Neolithic Societies (C. 7600-4000 cal. BP)” (Prometeo/2021/007), and the Spanish Ministry of Science and Innovation for funding the project EvolMED “Evolutionary cultural patterns in the contexts of the neolithisation process in the Western Mediterranean” (PID2021-127731NBC21).

REFERENCES

- [1] M. P. Colombini, F. Modugno, S. Giannarelli, R. Fuoco, M. Matteini, GC-MS characterization of paint varnishes, *Microchemical Journal* 2000, 67, 385396. DOI: [10.1016/S0026-265X\(00\)00098-9](https://doi.org/10.1016/S0026-265X(00)00098-9)
- [2] K. J. Berg, J. J. Boon, I. I. Pastorova, L. F. Spetter, Mass spectrometric methodology for the analysis of highly oxidized diterpenoid acids in Old Master paintings, *Journal of Mass Spectrometry*. 2000, 35(4), pp. 512-533. DOI: [10.1002/\(SICI\)1096-9888\(200004\)35:4<512::AID-JMS963>3.0.CO;2-3](https://doi.org/10.1002/(SICI)1096-9888(200004)35:4<512::AID-JMS963>3.0.CO;2-3)
- [3] N. Marchand-Geneste, A. Carpy, Theoretical study of the thermal degradation pathways of abietane skeleton diterpenoids: aromatization to retene. *Theochem*. 2003, 635(1-3), pp. 55-82. DOI: [10.1016/S0166-1280\(03\)00401-9](https://doi.org/10.1016/S0166-1280(03)00401-9)
- [4] M. P. Colombini, G. Giachi, F. Modugno, E. Ribechini, Characterisation of organic residues in pottery vessels of the Roman age from Antinoe (Egypt), *Microchemical Journal, Devoted to the Application of Microtechniques in All Branches of Science*, 2005, 79(1-2), pp. 83-90. DOI: [10.1016/j.microc.2004.05.004](https://doi.org/10.1016/j.microc.2004.05.004)
- [5] G. Cartoni, M. V. Russo, F. Spinelli, F. Talarico, GC-MS characterisation and identification of natural terpenic resins employed in works of art, *Annali Di Chimica*, 94(11), 2004, pp. 767-782. DOI: [10.1002/adic.200490098](https://doi.org/10.1002/adic.200490098)
- [6] D. Cnuts, S. Tomasso, V. Rots, The Role of Fire in the Life of an Adhesive, *J Archaeol Method Theory* 2018; 25: pp. 839-862. DOI: [10.1007/s10816-017-9361-z](https://doi.org/10.1007/s10816-017-9361-z)
- [7] I. Kononenko, L. de Viguier, S. Rochut, P. Walter, Qualitative and quantitative studies of chemical composition of sandarac resin by GC-MS, *Environmental Science*. 2017, 24(3), pp. 2160-2165. DOI: [10.1007/s11356-016-7261-5](https://doi.org/10.1007/s11356-016-7261-5)
- [8] L. Osete-Cortina, M. T. Doménech-Carbó, Analytical characterization of diterpenoid resins present in pictorial varnishes using pyrolysis-gas chromatography-mass spectrometry with on line trimethylsilylation. *Journal of Chromatography A*, vol. 1065, Issue 2, 2005, pp. 265-278. DOI: [10.1016/j.chroma.2004.12.078](https://doi.org/10.1016/j.chroma.2004.12.078)
- [9] F. Modugno, E. Ribechini, GC/MS in the Characterisation of Resinous Materials, *Organic mass spectrometry in art and archaeology*, pp. 215-235. DOI: [10.1002/9780470741917.ch8](https://doi.org/10.1002/9780470741917.ch8)
- [10] R. L. Wolff, L. G. Deluc, A. M. Marpeau, B. Comps, Chemotaxonomic differentiation of conifer families and genera based on the seed oil fatty acid compositions: multivariate analyses, *Trees*, Springer, Berlin, Germany, 1997, 12(2), 57. DOI: [10.1007/s004680050122](https://doi.org/10.1007/s004680050122)
- [11] M. Resano, *Organic Mass Spectrometry in Art and Archaeology*, *Journal of the American Society for Mass Spectrometry* 2011, 22, 947. DOI: [10.1007/s13361-011-0096-x](https://doi.org/10.1007/s13361-011-0096-x)
- [12] X. Fernandez, L. Lizzani-Cuvelier, A.-M. Loiseau, Chr. Périchet, C. Delbecque, Volatile constituents of benzoin gums: Siam and Sumatra. Part 1, *Flavour and fragrance journal* 2003, 18, pp. 328-333. DOI: [10.1002/ffj.1230](https://doi.org/10.1002/ffj.1230)
- [13] M. Mallick, S. Dutta, P. F. Greenwood, Molecular characterization of fossil and extant dammar resin extracts: Insights into diagenetic fate of sesqui- and triterpenoids, *Int. Journal of Coal Geology*, 2014, 121, pp. 129-136. DOI: [10.1016/j.coal.2013.11.013](https://doi.org/10.1016/j.coal.2013.11.013)
- [14] J. Eerkens, The Preservation and Identification of Piñon Resins by GC-MS in Pottery from the Western Great Basin. *Archaeometry* 2002, 44, pp. 95-105. DOI: [10.1111/1475-4754.00045](https://doi.org/10.1111/1475-4754.00045)
- [15] I. Jerkovic, Z. Marijanovic, M. Gugic, M. Roje, Chemical Profile of the Organic Residue from Ancient Amphora Found in the Adriatic Sea Determined by Direct GC and GC-MS Analysis. *Molecules*. 2011; 16(9): pp. 7936-7948. DOI: [10.3390/molecules16097936](https://doi.org/10.3390/molecules16097936)
- [16] E. A. Dimitrakoudi, S. A. Mitkidou., D. Urem-Kotsou, K. Kotsakis, J. Stephanidou-Stephanatou, J. A. Stratis, Characterization by gas chromatography-mass spectrometry of diterpenoid resinous materials in Roman-age amphorae from northern Greece. *European Journal of Mass Spectrometry (Chichester, England)*. 2011, 17(6), pp. 581-591. DOI: [10.1255/ejms.1155](https://doi.org/10.1255/ejms.1155)
- [17] F. Dorrego, F. Carrera, M. P. Luxan, Investigations on Roman amphorae sealing systems, *Materials and Structures* 2004, 37(5), pp. 369-374. DOI: [10.1007/BF02481686](https://doi.org/10.1007/BF02481686)
- [18] J. Font, N. Salvado, S. Buti, J. Enrich, Fourier transform infrared spectroscopy as a suitable technique in the study of the materials used in waterproofing of archaeological amphorae, *Analytica Chimica Acta*. 2007, 598(1), pp. 119-127. DOI: [10.1016/j.aca.2007.07.021](https://doi.org/10.1016/j.aca.2007.07.021)
- [19] F. C. Izzo, E. Zendri, A. Bernardi, E. Balliana, M. Sgobbi, 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), *Journal of archaeological science* 2013, 40, pp. 595-600. DOI: [10.1016/j.jas.2012.06.017](https://doi.org/10.1016/j.jas.2012.06.017)
- [20] E. Was, T. Szczesna, H. Rybak-Chmielewska, Determination of Beeswax Hydrocarbons by Gas Chromatography with a Mass Detector (GC-MS) Technique, *Journal of Apicultural Science* 2014, 58, 145157. DOI: [10.2478/jas-2014-0015](https://doi.org/10.2478/jas-2014-0015)