Microchemical Journal 207 (2024) 112088

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

"Natural or synthetic":The identification history of an object in an archaeological context

Gianni Gallello [a,*], Jesús Setien [b], Miguel Cisneros [c,*], Marc Valls-Mompó [d], Pablo Martín-Ramos [e], Maria Esperanza Ortiz Palomar [f], Juan Ángel Paz Peralta [g], Agustín Pastor [d], Ana B. Marín-Arroyo [h]

[a] *Department of Prehistory, Archaeology and Ancient History, University of Valencia, Avda. Blasco Ibáñez, 28, 46010 Valencia, Spain*
[b] *Laboratory of the Science and Engineering of Materials Division (LADICIM), University of Cantabria, Avda. de Los Castros, 44, 39005 Santander, Spain*
[c] *Department of Historical Sciences, University of Cantabria, Interfaculty Building, Avda. Los Castros s/n., 39005 Santander, Spain*
[d] *Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner Street, Burjassot, 46100 Valencia, Spain*
[e] *Advanced Materials Laboratory, ETSIIAA, University of Valladolid, Avda. de Madrid 44, 34004 Palencia, Spain*
[f] *Archaeologist, Zaragoza, Spain*
[g] *Museum of Zaragoza, Pl. de los Sitios, 6, 50001 Zaragoza, Spain*
[h] *EvoAdapta Research Group, Department of Historical Sciences, University of Cantabria, Interfaculty Building, Avda. Los Castros s/n, 39005 Santander, Spain*

ARTICLE INFO

Keywords:
Non-invasive methods
Plastic fragment
Archaeological site
Natural resins
Data interpretation
Misleading characterisation
Out of place artefact

ABSTRACT

Materials characterisation by non-invasive analytical methods is already a standardised practice in Archaeology. However, problems may arise in the chemical identification of certain materials that lead to erroneous interpretations. In this study, we address the case of a fragment found in the well-documented archaeological site of *Colonia Celsa* (Velilla de Ebro, Zaragoza, Spain), first labeled during fieldworks as a glass fragment, subsequently this hypothesis was descarted by macroscopic archaeological recognition, then it was analyzed and identified as a natural resin, and finally, as a polymer blend upon a reinterpretation of the chemical characterisation. Based on this case of study, a methodological protocol for characterising unknown materials using non-invasive analytical methods was developed. A set of reference samples from natural resins were analysed using a portable X-ray fluorescence spectroscopy, Raman spectroscopy, Fourier-transform infrared spectroscopy, and finally, gas chromatography-mass spectrometry as a reference method. The obtained data were statistically processed to assess affinities and differences between the analysed samples, and the results of the different techniques were compared, indicating that the sample was a blend of high-density polyethene with ethylene vinyl acetate, (i.e., an out-of-place artefact). The reported procedure may be useful for specialists working in archaeological science and a warning signal in archaeometry studies.

1. Introduction

During the last century, significant development of analytical methodologies applied to archaeological contexts and their materials has been developed, opening new lines of research that support classical archaeological methods by providing new valuable information (e.g., shading light about the composition and raw material origin of ancient remains). The characterisation of ancient objects through physicochemical analyses was first documented in the late eighteenth century [1]. It was during the 1960s when new archaeological materials, such as glass, resins, rocks, sediments, and others began to be analysed, providing a relevant development in archaeological sciences [2]. The new challenges in this research field are associated with the need of developing and optimising non-invasive devices due to the scarcity and high cultural value of the archaeological findings. The use of non-destructive and portable analytical techniques, such as X-ray fluorescence (pXRF), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy, allows archaeologists to obtain data on-site and on unique archaeological materials that otherwise would be impossible [3–6]. However, in some cases, employing portable and less sensitive non-invasive devices (instead of benchtop equipment or invasive techniques) can make the physicochemical identification of materials

---

* Corresponding authors.
E-mail addresses: gianni.gallello@uv.es (G. Gallello), miguel.cisneros@unican.es (M. Cisneros).

https://doi.org/10.1016/j.microc.2024.112088
Received 26 October 2024; Accepted 31 October 2024

challenging. This situation raises a relevant question: Are we as researchers aware that erroneous interpretations of the physicochemical analysis can lead to wrong archaeological interpretations? Are we aware that the most straightforward identification is sometimes not always the correct one?

This work presents, for the first time, a critical analytical case regarding the archaeological fragment (MZ 58299) found in the well-documented Roman site of *Colonia Celsa* (Velilla de Ebro, Zaragoza, Spain). The fragment was labeled as a glass during archaeological fieldwork (Fig. S1) and at the Museum of Zaragoza a misinterpretation about the origin of the fragment was identified. In 2021, a new project to reassess Roman glass materials led to the implementation of archaeometric analyses to characterise its composition and manufacture. However, the first chemical analyses were non-conclusive due to the similarity of the obtained spectra (80–90 %) to amber and later beeswax compounds. Thus, based on this archaeometric experience, we propose a methodological approach for identifying unknown archaeological materials combining portable and non-destructive analysis techniques such as pXRF, FTIR, and Raman.

A set of natural resins, beeswax and pitch (often used in the past as adhesives or as elements of oil-resin media) were employed as reference materials to characterise the unknown archaeological remain. In this regard, it should be noted that the use of non-invasive analytical methods to characterize archaeological and natural resins and waxes are quite problematic due to the scarce information about their chemical features [7]. Natural resins chemical compositions are complex and diverse, and their compounds considerably undergo ageing due to oxidation or polymerisation processes. Furthermore, there is an important number of resins that were used by ancient populations, to be identified. Helpful information about the resins employed in antiquity has been reported by Cartoni et al. [8]. In the end, some synthetic materials (types of plastics) were also added to the reference sample set due to their similarities in the FTIR and Raman spectra with those of the other materials. Finally, the data obtained from the different non-invasive techniques were compared, evaluated and cross-checked with those obtained using gas chromatography-mass spectrometry (GC–MS) as a reference method. The results were statistically processed to observe affinities and differences between archaeological, natural, and syinthetic samples.

1.1. Archaeological background

The fragment under study was found during the archaeological fildwork in 1985 at the site of *Colonia Celsa* (Velilla de Ebro, Zaragoza, Spain), *Hispania Tarraconensis*, founded in 44 BC by Marcus Aemilius Lepidus under the name of *Colonia Victrix Iulia Lepida*. The fall from grace of Lepidus led to the colony's name being changed to the Latinised indigenous (*Celse*) *Colonia Victrix Iulia Celsa* in 36 BC (Fig. S1).

The archaeological context where the fragment was found is a stratum dated to the time of the abandonment of the colony, in the year of the three emperors (69–70 AD) [9]. The room corresponds to space 22 of the so-called 'House of Hercules', located in Insula VII and characterised by its Tuscan atrium [10].

Among the ceramics associated with the archaeological level, the presence of *terra sigillata* in its Italic, South Gallic, and Hispanic varieties stands out, the latter coming from the potteries of the current Spanish Autonomous Community of La Rioja and being the one that provides the chronology of the level [9]. These productions were widespread in *Colonia Celsa* in 69–70 AD. The ceramic marker corresponds to the wall of a Dragendorff 37, mould-decorated with geometric decorative motifs aligned in friezes, wavy-line circumferences, and a schematic laurel wreath.

The methodology applied to this site was rigorous, including intensive archaeological collection in the excavated areas. During the fieldwork, the artefacts and ecofacts were subjected to an initial triage due to their different degrees of fragility and conservation conditions (e.g., ceramics, construction, metal, glass, bone, and miscellaneous). The studied fragment was deposited as a glass sample, given to its fineness, translucency and related features.

The fragment was among those studied by the LAPISVITRUMQUE research project (2021) aimed to analyse glass from the Roman period that could imitate stones. A first macroscopic recognition was conclusive and allowed us to determine that it was not glass. The colour, thickness and morphology of the studied fragment were similar to a glass, however the specific material weight and the observed texture employing a stereomicrospe were not compatible with this material. It was also ruled out that it could be stone, teeth or bone. However, due to the fragment shape and its archaeological context, chemical analyses were carried out to identify its origin.

2. Materials and methods

2.1. The archaeological sample

The studied fragment (MZ 58299), currently housed in the Museum of Zaragoza (inventory number 58299), corresponds to a coloured [11] (2.5Y 8/3) material (Fig. 1). It is in a good state of preservation, with vertical fracture marks and net cracking over the entire surface. The preserved dimensions are 21 mm wide × 13.3 mm high × 2.06–2.35 mm minimum–maximum thickness, 4.06 mm at the rim, and 75–80 mm Ø rim; 0.396 g weight.

Three characteristics define the object. Firstly, the thin wall thickness; second, the size of a potential vessel; and thirdly, the rim's shape, creating a characteristic profile different from those of *terra sigillata*, glass, bone, and wood. In the technical assessment, the neatness of the workmanship, the precision of the lines, the symmetry of the forming, and the homogeneity of the satin finish stand out.

2.2. Reference samples

A set of sample references was created to be compared with the archaeological fragment (Table 1).

2.3. Thermal analyses

TG–DSC curves of the sample were obtained in a SetSys Evolution – 1750 TG–DSC equipment (SETARAM Instrumentation, Cailure, France). The sample was heated from room temperature up to 300 °C at a 5 °C/

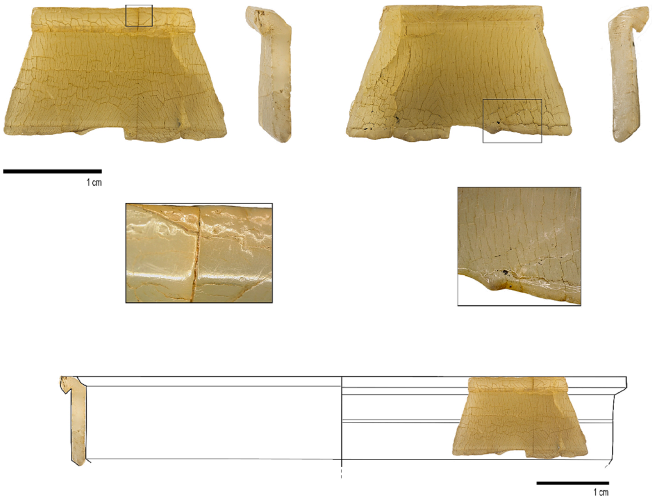

Fig. 1. Macrophotography: J. Garrido. Museo de Zaragoza. Archaeological drawing of the archaeological fragment (MZ 58299): E. Ortiz. Microphotography and assembly of the figure: Lucía Agudo (Evoadapta Research Group – UC).

Table 1

Description of the different samples with the brand and number in the case of acquired samples (RN).

Sample	Description
RN1K/7-100	Amber Rosin. Brown and brittle resin. This sample was purchased.
RN2K/9-100	Pure Shellac in pearls. Gum granules of a dark reddish colour. This sample was purchased.
RN1K/4-100	Sandarac – Juniper Resin. Fragments of a yellowish-white colour. This sample was purchased.
RN1K/16-100	Burgundy resin. Large orange fragment. This sample was purchased.
RN1K/9-100	Benzoin gum – In pieces. Small light orange fragments with some small dark-coloured pieces. This sample was purchased.
RN1K/1-100	Dammar resin. Fragments of a yellowish-white colour. This sample was purchased.
RN1K/5-100	Copal-Manila resin. A mixture of yellowish fragments and dark pieces. This sample was purchased.
CR	Natural conifer resin.
Wax	Beeswax.
Pitch	Glossy black fragment provided by the Museum of Fine Arts of Castellón
PE	Piece of high-density polyethene.
PP	Piece of polypropylene.
MZ 58299	Archaeological sample under study.

min rate in an argon atmosphere. Heat flow and weight variation of the archaeological sample were recorded.

2.4. *Portable X-ray fluorescence spectroscopy (pXRF)*

X-ray fluorescence spectra were collected using a portable S1 Titan X-ray fluorescence spectrometer (Bruker, Kennewick, WA, USA) equipped with a rhodium X-ray tube and an X-Flash® SDD detector. For the instrument control, the S1RemoteCtrl (Geochem-trace program) was used. In addition, S1Sync software by Bruker was employed to measure the MgO, Al_2O_3, SiO_2, P_2O_5, S, K_2O, CaO, and Fe contents of all the samples.

2.5. *Raman spectroscopy*

To measure the Raman spectra, an i-Raman plus portable device (BWTEK, Newark, NJ, USA) was used together with the BWSpec program, which allows the measurement variables and data extraction to be modified. Raman measurements were performed with three repetitions, integration times of 1000 ms, and different laser intensities for each sample, with an excitation wavelength of 785 cm^{-1}. An intensity optimisation was performed for each sample. The data were processed by subtracting the baseline and the dark spectrum.

2.6. *Fourier-Transform infrared (FTIR) spectroscopy*

To obtain infrared vibrational data, a 4300 Handheld FTIR was utilised (Agilent Technologies, Santa Clara, CA, USA). ATR measurements were performed. Spectra were collected with a measurement time of 60 s over the 4000–650 cm^{-1} range. Before each measurement, the ATR diamond interface accessory was cleaned with an isopropanol-soaked swab. Each point was analysed three times and averaged.

2.7. *Gas chromatography–mass spectrometry (GC–MS)*

Gas chromatography-mass spectrometry analyses were carried out employing a 7890 A (Agilent Technologies) gas chromatograph, 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. The detection was carried out using a simple quadrupole mass spectrometer (5975C inert XL EI/CI MSD, also from Agilent Technologies), using an electron impact ionisation source at 70 eV. The autosampler coupled to the system was a 7683 model. The MSD Enhanced data analysis software was used for data acquisition.

Analyte extraction for chromatographic analysis was performed by weighting about 5 mg of powdered sample into a test tube adding 1 mL of solvent (MeOH/H_2O, 1:1), followed by sonication for 10 min. The sample was heated at 70 °C for 2 h. The first fraction to analyse (neutral fraction) was separated by liquid–liquid extraction with hexane, using 1 mL for each sample in triplicate. The hydroalcoholic solution was saved. The hexane solution was evaporated to 0.5 mL under N_2 flow. The basic hydroalcoholic solution was acidified and the acidic organic compounds, including terpenoid acids and fatty acids, were extracted three times with 1 mL of diethyl ether. After solvent evaporation, it was derivatised with BSTFA + TMS 1 %. The sample was dissolved in 1 mL hexane. Hexadecane was employed as an internal standard for this method.

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 45 to 600.

2.8. *Data analysis*

Data analysis was carried out using RStudio (version: 1.4.1106) [12]. Principal component analysis (PCA) was used to explore the pXRF elemental results of analysed samples to evaluate the role of the variables (chemical elements) in complex datasets. Ggplot2 (version: 3.3.5) was employed for data visualisation of Raman results. Finally, FTIR spectra were plotted with Spectragryph (Oberstdorf, Germany).

3. Results

3.1. *Thermal analysis*

A determination of the specific weight of the sample by a hydrostatic balance was carried out, as a previous step to the thermal analysis, obtaining a value of 0.97 g/cm^3.

Fig. S2 (supplementary information) shows the TG (green) and DSC (blue) curves resulting from the thermogravimetric and calorimetric analysis of the archaeological sample (MZ 58299). It started to melt at 75 °C and exhibited a sharp melting peak at around 110 °C. From this temperature, a slight mass loss was observed (green signal) up to 300 °C. The presence of a smooth shoulder at a lower temperature region of the melting peak suggests that more than one compound was present in the sample.

3.2. *Multielement analysis*

Results of pXRF analyses are reported in Table S1 (Supplementary information). Exploratory data analysis was carried out by PCA on the natural samples employing all the elemental concentrations as variables (Fig. S3, top). The samples/scores plot shows that the sample from pitch can be distinguished from the others on PC1 positive direction due to the high concentrations of SiO_2, Al_2O_3, CaO, and S, as suggested by PC1 loadings (Fig. S3, bottom left). The archaeological sample under analysis (MZ 58299) is similar to the resins in PC1 negative direction. However, this sample and shellac resin sample are characterised by very high contents of P_2O_5, CaO, and K_2O and are located in PC2 negative direction (Fig. S3, bottom right).

3.3. *Raman spectra*

Fig. S4 shows the benzoin gum, amber, Shellac, sandarac, Burgundy, dammar, pine resin and copal resins spectra, including the pitch sample spectra. Amber, Shellac, sandarac, and Burgundy resin spectra share with MZ 58299 (Fig. 2) the shift at 1440 cm^{-1}but not those at 1180 and 1125 cm^{-1}. Benzoin gum spectrum shows changes at 1440, 1125, and

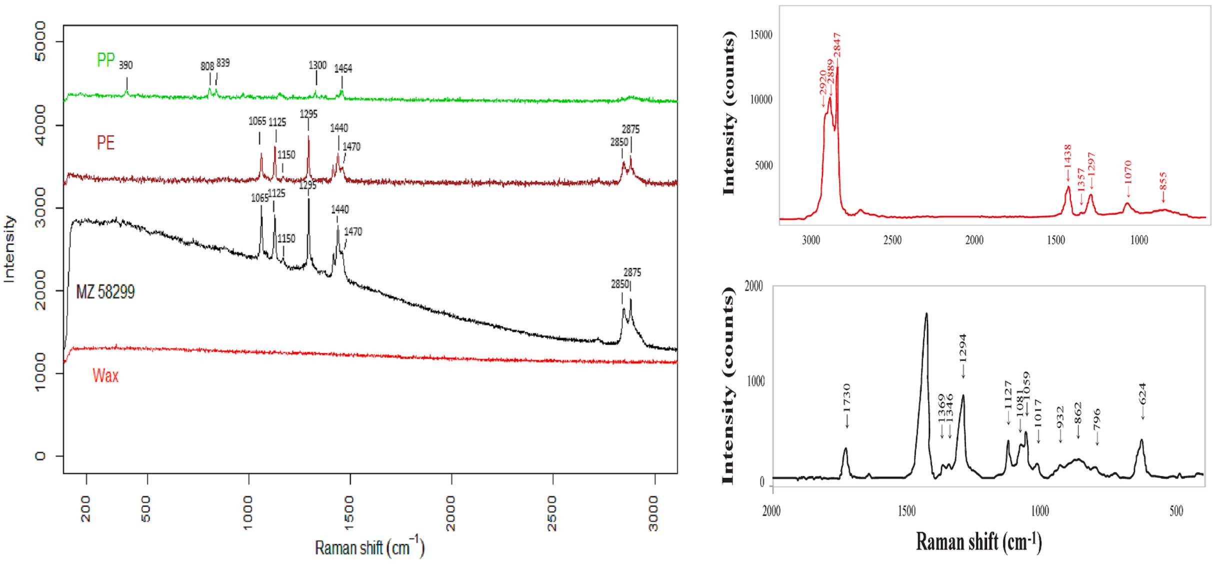

Fig. 2. Left: Raman spectra of the archaeological sample (MZ 58299), polypropylene (PP) and polyethylene (PE), samples over the 0–3000 cm^{-1} range. Offsets in the y-axis have been added to the polyethylene (+2000) and polypropylene (+3000) spectra to avoid overlapping. Right: Raman spectra of high-density polyethylene (top) and ethylene vinyl acetate (bottom) [13].

1065 coincident with those of the archaeological sample, but it has additional shifts at 1640, 1610, 1285, 1200, and 1000 cm^{-1}not observed in MZ 58299. As regards other samples, minor coincidences were observed for the shifts at 1440 and 1125 cm^{-1}, with those observed in dammar resin (1122 cm^{-1}), copal resin (1447 cm^{-1}), beeswax (1117 cm^{-1}), and pitch (1119 cm^{-1}) spectra. No peak was found in the pitch sample.

The Raman spectra of the archaeological sample (MZ 58299) and those of the PE and PP plastics and wax are shown in Fig. 2. The MZ 58299 sample show shifts at 1440 cm^{-1} ($\supset$CH$_2$ deformation), 1125 and 1065 cm^{-1} (doublet, νC–C), and 808 cm^{-1} (νC–C, backbone polymer), but also additional shifts at 1295 cm^{-1} (assigned to the P=O vibration superposed with O–P–O), and at 1125 cm^{-1} (due to P–O–stretching) [13]. It may be observed that polypropylene has different Raman shifts (at 1220, 1168, 995, 972, 898, and 840 cm^{-1}) than those of the unknown sample and polyethene, ruling out that the archaeological sample is polypropylene.

No spectra are identified in the beeswax sample. An interpretation of the Raman shifts in the polypropylene spectrum may be found in [14]. When the comparison of the Raman spectrum of MZ 58299 is extended to the spectra of high-density polyethene (HDPE) and ethylene vinyl acetate (EVA) [13] (Fig. 2), it is observed that the characteristic shifts at 1440 and 1065 cm^{-1} appear in HDPE at 1438 and 1070 cm^{-1} and in EVA at 1438 and 1060 cm^{-1}, respectively.

3.4. *Infrared spectra*

The spectra comparison of the archaeological sample with those of

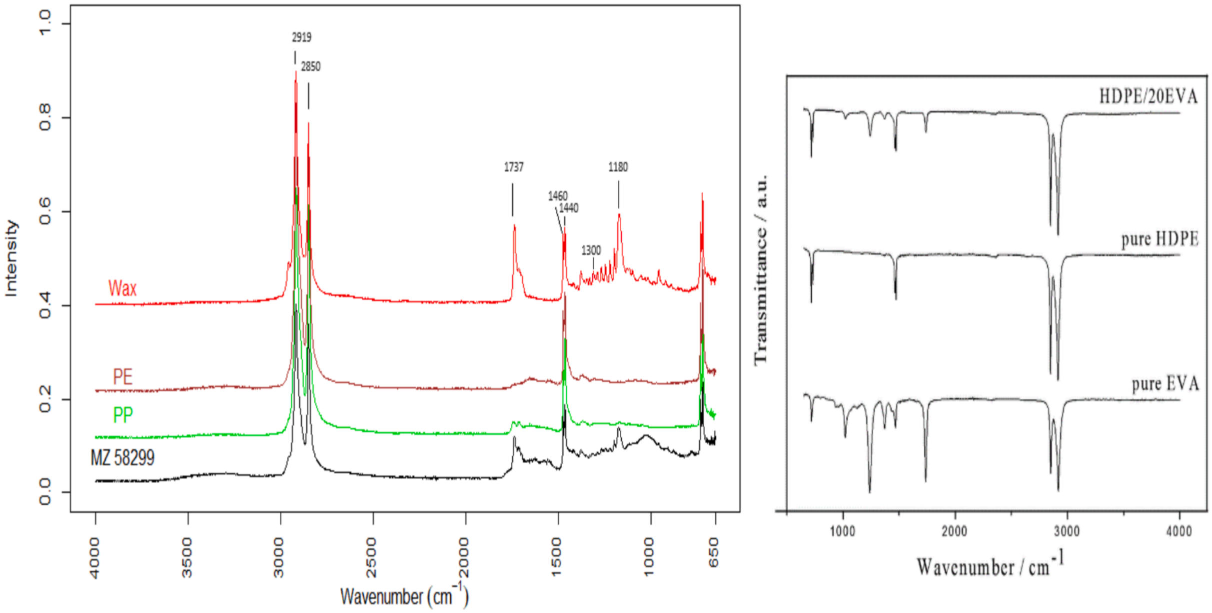

Fig. 3. Left: FTIR spectrum (reflectance) of the alleged archaeological sample, together with the spectra of the polyethylene (PE) (+0.1 offset) polypropylene (PE) (+0.2 offset), and beeswax (Wax) (+0.3 offset) samples. Right: FTIR spectra (transmittance) of the HDPE, EVA, and HDPE/20EVA blend samples. Reproduced from Albano de Morais et al. [21], under CC license.

the resins and pitch (Fig. S5 and Table S2, Supplementary information) shows that the unknown material does not share the bands that are commonly found in resins and that it does not resemble the spectrum of pitch either.

On the other hand, looking at the MZ 58299 (Fig. 3) polyethene (absorbance bands at 2919, 2850, 1470, 1440, 1300, 1070, and 718 cm^{-1}) polypropylene (characteristic peaks at 2950, 2918, 2847, 1464, 1376, 1168, and 972 cm^{-1}), and beeswax (peaks at 2923, 2840, 1464, 1070 cm^{-1}) spectra, some similarities may be observed in the high-intensity bands at 2919 and 2850 cm^{-1} (corresponding to the asymmetric and symmetric stretching of CH_2 group, respectively), and in the lower intensity bands at 1465 cm^{-1} (which corresponds to a C-H bending deformation) and 721 cm^{-1} (oscillating deformation, $\delta_{rocking}$ C–H(–CH_2–)N) [15,16]. Nevertheless, the main difference between the sample under study and the two plastics lies in the 1737 and 1180 cm^{-1} bands arising from C=O bond stretching (which indicates the presence of an aldehyde, ester, or ketone group in the sample) and in the stretching mode vibration at 1024 cm^{-1} (ν[–O–C–]). Moreover, characteristic minor bands of polyethene (PE) and polypropylene (PP) are missing in the MZ 58299 sample: e.g., those at 1463 and 1300 cm^{-1} from polyethene (PE); and those at 2950, 1376, 1168, and 972 cm^{-1} from isotactic polypropylene (PP). The MZ 58299 spectra are very similar to those of HDPE and EVA (Fig. 3): the unassigned bands at 1737 cm^{-1} and 1180 cm^{-1} can be attributed to pure EVA or an HDPE/EVA blend. This can be seen in Table S2, where the bands of these materials are similar.

3.5. GC–MS

Concerning the GC–MS analysis, several compounds were found in all natural resins, while no peaks were registered in the chromatograms of MZ 58299 and the two plastics (PE and PP), as shown in Fig. S6 and Fig. S7 (Supplementary information). The only peak that can be observed is the reference standard employed (hexadecane, RT = 17.25 min). The obtained results show that the archaeological sample

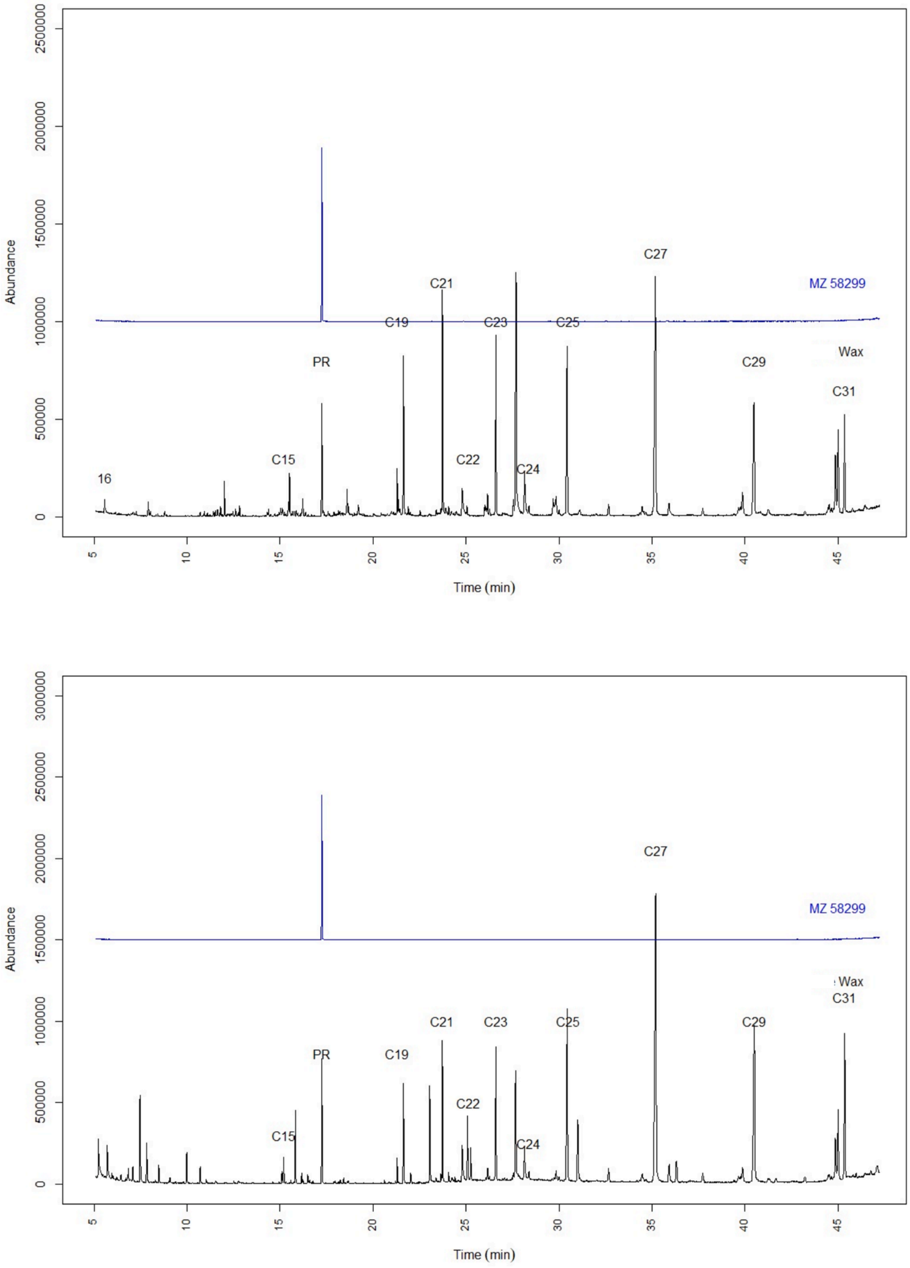

Fig. 4. Chromatograms of the neutral (*top*) and acid (*bottom*) fractions of the archaeological sample (MZ 58299) and beeswax samples (Wax).

chromatogram is not compatible with a beeswax based composition or coating (Fig. 4).

4. Discussion

4.1. Telling the analytical history of the archaeological fragment

As aforementioned in this study the characterization of an unknown archaeological material is a really challenging issue, especially when only non-invasive analytical methods are employed. A naked-eye material identification can be mislading, even though it has been the principal method for archaeological objects identification for many decades.

The identification of the MZ 58299 fragment should be understood in its historical analytical process. First, the fragment was analysed employing micro-invasive and non-invasive methods by measuring the melting point (110 °C), obtaining FTIR and Raman spectra and running microscopic analysis. After comparing the obtained results, the initial hypothesis proposed was related to a material such as amber and beeswax. The FTIR spectrum obtained from the beeswax was highly similar (between 80 and 90 % of similarity) to the archaeological fragment, as well as the texture and the observation under the high-resolution digital microscope. However, additional peaks found in the spectra, differences in melting point and the Raman spectra were interpreted as a consequence of the postdepositional processes that might have affected the MZ 58299. Therefore the initial work and the finding of the object in a well-documented archaeological context reinforced the initial hypothesis that it was a fragment corresponding to a beeswax vessel.

Nevertheless, doubts about some residues observed in the internal part of the vessel drove the investigation to discern what the vessel could have contained. Thus, no invasive techniques were applied to identify the residue content. So, for the second time a FTIR analysis was carried out in the MZ 58299 fragment and this time it was observed that some identified peaks were not related to beeswax. Therefore, a test in a lab polyethene bottle to observe instrumental mistakes was run. Suddenly we could observe the impressive similarity between the lab bottle and the archaeological material under study.

At this point, the analytical process started again from zero developing a specific protocol to understand if this sample could be a synthetic material such as simple piece of plastic. A set of natural resins, pitch and plastics was assembled and pXRF to observe inorganic matter, followed by Raman and FTIR for organic material. A reference method such as GC–MS was also employed. Concerning the information obtained by XRF, it was of limited usefulness in this case, as alredy known elements with atomic number $\leq Z = 11$ are not properly measured with this technique. Considering that major elemental constituents of resins, waxes, and plastics (viz. C, H, O, N) cannot be detected. Nonetheless, pXRF results showed that the multielement analysis of natural samples differed from that of the sample under study. In this latest sample, results of pXRF analyses showed high levels of P_2O_5, CaO, and K_2O, compatible with the presence of calcium potassium phosphate, an excellent retarder in cement and plastic-based materials.

The two vibrational spectroscopy techniques (Raman and ATR-FTIR) were the most effective in identifying the studied material, but showing very similar spectra within beeswax, plastic and the archaeological sample that makes difficult a proper interpretation of the obtained data. However, those are the rights tecniques to be employed for the archaeological fragment toghether with the resin, wax, and pitch samples used for comparison purposes. The results indicate they can be differentiated more easily using Raman spectroscopy than ATR-FTIR. While it is possible to use this latest technique [17], authors such as Prati and colleagues [18] noted that data from the far infrared spectrum would be required to discern resin samples more efficiently.

Nevertheless, vibrational and thermal data toghether are in accordance with fact that the fragment found at *Celsa* is not an original archaeological material but an allochthonous synthetic material such as a plastic. Besides, we believe that it does not correspond to polyethene or polypropylene, but it may be an high-density polyethene (HDPE) and ethylene vinyl acetate (EVA) or an HDPE/EVA blend. The melting point of the piece under study (110 °C) is closer to the melting point of HDPE (110–140 °C) than to EVA (<96 °C), but is also compatible with the one of an HDPE/EVA blend, while the beeswax melting point rage between 62 and 64 °C. On the other hand, it cannot be ruled out that the incorporation of a retarder and/or post-crystallisation could have altered the melting point of the material, thus providing an alternative explanation for the difference from the expected temperature value. As regards the information obtained from the FTIR spectrum, it should be emphasised that HDPE and EVA share the bands at 2919, 2850, 1465, and 721 cm^{-1}, and those at 1737 and 1180 cm^{-1} by HDPE/EVA blend. The Raman shifts at 1440 and 1065 cm^{-1} of the sample also seem to correspond to HDPE or EVA plastics. Hence, to the best of the authors knowledge, the plastic material under study is an HDPE/EVA blend mixed with inorganic phosphate ($CaKPO_4$) as a flame retardant, affected by post-crystallisation and cracking. Moreover, it should not be over 60 years old (it has been on the Spanish market since 1960).

Finally, GC–MS analysis employed as a reference method –with the chosen extraction procedures– was able to identify the chemical constituents of resins, beeswax, and pitch. No peaks were obtained for MZ 58299, PE, and PP, which would require using, for instance, 1,2,4-trichlorobenzene (TCB) as a solvent and a pyrolysis-GC–MS apparatus, unless only compounds migrating from the plastic are to be analysed [19]. Nonetheless, it allowed us to rule out that the sample of the study had any coating.

4.2. A conceptual reflection on the archaeological material misleading interpretation

Based on the analytical data collected, which provided new interpretive insights, it is important to emphasise several key points (Fig. 5). From a conceptual point of view, the piece could be an oopart (an acronym for “out of place artefact”). Unfortunately, it is unlikely to know the origin of this intrusion in the archaeological layers, although some hypotheses can be proposed. The most common explanations would be an identification labels swapping during the excavation, a contaminated material collected in the environment or a human error in any phase of the handling (finding, transfer, cleaning or during storage).

The laboratory work consisted in cleaning and manually classifying the remains with their acronym, count, and inventory number. Erroneous attributions or incomplete data occur during the visual description of the remains in the fieldwork. Often, researchers and specialists find an inadequate cleaning of the archaeological materials, or a poor technical drawing to characterise a material during the inventory or the material origin can affect the proper identification of the unearthed objects.

As aforementioned, it should be noted that the naked-eye aspect of the MZ 58299 was similar to that of glass and other translucent substances, such as amber, precious stones, or wax, for example. Although, the tracking control protocol from the archaeological site to the final repository is well-established and well-known, its application is not always feasible. Therefore, even when a safety practice takes action, it must be noted that everything that happen before the archaeological excavation, whether due to natural or anthropogenic processes, is out of control, and these postdepositional activities are not always (clearly) identified [20].

5. Conclusions

This study presents a critical reflection on the methodological aspects of archaeological and archaeometric studies by examining a small fragment of an indeterminate material initially classified as a glass (Fig. 5), found during the excavation of *Colonia Celsa*. It has been proved

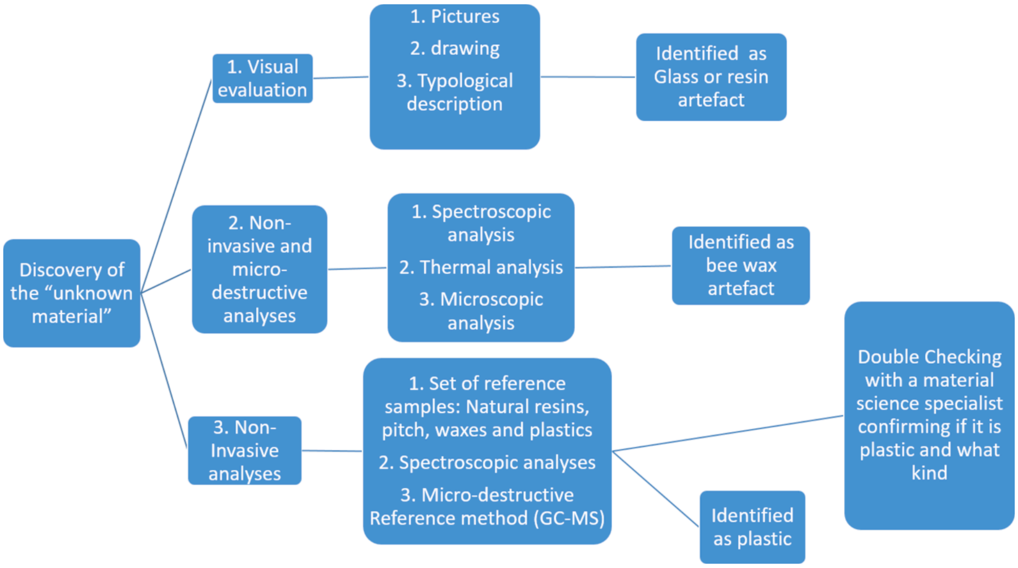

Fig. 5. Graph of concept. Unknown material characterization during its interpretation process.

that non-destructive techniques are often not fully elucidative and are subject to potential interpretative errors, mainly when only a limited set of material is used for comparison. This underlines the need to analyse a broad selection of reference materials and the significance of building reference collections for characterising unknown matters. Furthermore, combining multiple complementary techniques was highlighted as necessary to avoid similar misleading interpretations and correctly identify samples. With the use of three commonly available non-destructive techniques (pXRF, FTIR, and Raman) plus thermal and GC–MS it was determined that the archaeological sample was an out of place artefact, which did not correspond to the abandonment date of the Roman colony. This example also highlights the importance of controlling the operational chain. The reported procedure and findings may be help other archaeologists facing with the arduous task of characterising unknown remains.

CRediT authorship contribution statement

Gianni Gallello: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Jesús Setien:** Conceptualization, Data curation, Investigation, Methodology, Validation, Writing – review & editing. **Miguel Cisneros:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Marc Valls-Mompó:** Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – review & editing. **Pablo Martín-Ramos:** Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Writing – review & editing. **Maria Esperanza Ortiz Palomar:** Data curation, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. **Juan Ángel Paz Peralta:** Data curation, Investigation, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Agustín Pastor:** Data curation, Investigation, Methodology, Supervision, Validation, Writing – review & editing. **Ana B. Marín-Arroyo:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Funding

Research, Culture and Sport of the Valencian Generality for funding the project PROMETEO 2019-056.

Grant PID2020-117299GB-I00 (Glass Imitations of Stones in the Roman Period and their Reinterpretation in the Modern Era. Acronym: LAPISVITRUMQUE), funded by MCIN/AEI/10.13039/501100011033.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gianni Gallello and Miguel Cisneros, as corresponding authors of the manuscript and the other authors declare no competing interests..

Acknowledgements

G.G. acknowledges the Spanish Ministry of Science and Innovation and Ministry of Universities for the grant BEAGAL18/00110.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2024.112088.

Data availability

Data will be made available on request.

References

[1] A.M. Pollard, C. Heron. Archaeological chemistry, The Royal Society of Chemistry, Cambridge, 1996. ISBN-13978-0854045235.

[2] A.M. Pollard, C.M Batt, B. Stern, S.M.M. Young. Analytical Chemistry in Archaeology, Cambridge University Press, 2007, https://doi.org/10.1017/CBO9780511607431.

[3] J.M. Madariaga, M. Maguregui, K. Castro, U. Knuutinen, I. Martinez-Arkarazo, Portable Raman, DRIFTS, and XRF analysis to diagnose the conservation state of two wall painting panels from pompeii deposited in the Naples National Archaeological Museum, Apply Spectroscopy 70 (2016) 137–146, https://doi.org/10.1177/0003702815616589.

[4] V. Di Tullio, G. Sciutto, N. Proietti, S. Prati, R. Mazzeo, C. Colombo, E. Cantisani, V. Romè, D. Rigaglia, D. Capitani, 1H NMR depth profiles combined with portable and micro-analytical techniques for evaluating cleaning methods and identifying original, non-original, and degraded materials of a 16th century Italian wall

painting, Microchem. J. 141 (2018) 40–50, https://doi.org/10.1016/j.microc.2018.04.034.

[5] M. Ramacciotti, G. Gallello, J. Jiménez-Puerto, J. Bernabeu, T. Orozco Köhler, S. Rubio-Barberá, A. Pastor, Non-destructive characterisation of dolerite archaeological artefacts, Microchem. J. 183 (2022) 108080, https://doi.org/10.1016/j.microc.2022.108080.

[6] L. Alapont, G. Gallello, M. Martinón-Torres, M. Osanna, V. Amoretti, S. Chenery, et al., The casts of Pompeii: Post-depositional methodological insights, PLoS One 18 (2023) 8, https://doi.org/10.1371/journal.pone.0289378.

[7] I. Jerković, Z. Marijanović, M. Gugić, 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 16 (9) (2011) 7936–7948, https://doi.org/10.3390/molecules16097936.

[8] G. Cartoni, M.V. Russo, F. Spinelli, F. Talarico, GC-MS characterisation and identification of natural terpenic resins employed in works of art, Anal. Chim. 94 (11) (2004) 767–782, https://doi.org/10.1002/adic.200490098.

[9] M. Beltrán Lloris, La concurrencia de la terra sigillata en la Colonia Victrix Iulia Lepida Celsa (Velilla de Ebro, Zaragoza), in: X. Aquilué, J. Beltrán de Heredia, À. Caixal, J. Fierro y H. Kichner (eds.), Estudis sobre ceràmica i arqueologia de l'arquitectura, Homenatge al Dr. Alberto López Mullor, Barcelona (2020), pp. 177-186.

[10] M. Beltrán Lloris, La Colonia Celsa, in: M. Beltrán Lloris (ed.), La casa urbana hispanorromana. Ponencias y comunicaciones, Zaragoza (1991), pp. 131-164.

[11] Munsell, Munsell Soil Color Charts (Year 2000 Revised Washable Edition), Munsell Color Company - x-rite; 1994a edición (1 de enero de 2000) (2000).

[12] R Core Team, R: A language and environment for statistical computing. R Foundation for Statistical Computing, 2021, Wien, Austria.

[13] F. Adar, Raman analysis of ethylene vinyl acetate copolymers-using 2D-COS for identifying structural changes, Spectroscopy 34 (11) (2019) 12–21.

[14] A.S. Nielsen, D.N. Batchelder, R. Pyrz, Estimation of crystallinity of isotactic polypropylene using Raman spectroscopy, Polymer 43 (9) (2002) 2671–2676, https://doi.org/10.1016/s0032-3861(02)00053-8.

[15] J.I. Weon, Effects of thermal ageing on mechanical and thermal behaviors of linear low density polyethene pipe, Polym. Degrad. Stab. 95 (1) (2010) 14–20, https://doi.org/10.1016/j.polymdegradstab.2009.10.016.

[16] J.V. Gulmine, P.R. Janissek, H.M. Heise, L. Akcelrud, Polyethene characterisation by FTIR, Polym. Test. 21 (5) (2002) 557–563, https://doi.org/10.1016/S0142-9418(01)00124-6.

[17] P. Martín-Ramos, I.A. Fernández-Coppel, N.M. Ruíz-Potosme, J. Martín-Gil, Potential of ATR-FTIR spectroscopy for the classification of natural resins, Biol. Eng. Med. Sci. Rep. 4 (1) (2018) 03–06, https://doi.org/10.5530/bems.4.1.2.

[18] S. Prati, G. Sciutto, R. Mazzeo, C. Torri, D. Fabbri, Application of ATR-far-infrared spectroscopy to the analysis of natural resins, Anal. Bioanal. Chem. 399 (9) (2010) 3081–3091, https://doi.org/10.1007/s00216-010-4388-y.

[19] F. Akoueson, C. Chbib, S. Monchy, I. Paul-Pont, P. Doyen, A. Dehaut, G. Duflos, Identification and quantification of plastic additives using pyrolysis-GC/MS: A review, Sci. Total Environ. 773 (2021) 145073, https://doi.org/10.1016/j.scitotenv.2021.145073.

[20] S. García Fernández-Villa, Los plásticos en el arte y el diseño hasta 1945: historia, tecnología, conservación e identificación. Tesis doctoral, Universidad Complutense, Madrid, 2010.

[21] J. Albano de Morais, R. Gadioli, M.A. De Paoli, Curaua fiber reinforced high-density polyethene composites: Effect of impact modifier and fiber loading, Polymers 26 (2016), https://doi.org/10.1590/0104-1428.2124.