

Contents lists available at ScienceDirect

Microchemical Journal

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

Determination of selected polyaromatic hydrocarbons by gas chromatography–mass spectrometry for the analysis of wood to establish the cause of sinking of an old vessel (Scauri wreck) by fire



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ARTICLE INFO

Article history:

Received 23 May 2014

Received in revised form 16 June 2014

Accepted 16 June 2014

Available online 25 June 2014

Keywords:

Archaeological

Vessel

Fire

PAHs

ABSTRACT

The aim of this paper was to establish the cause of sinking of an old wooden vessel by polycyclic aromatic hydrocarbon (PAH) analyses because wood combustion is a source of PAHs. In particular, the molecular PAH patterns generated by each source are like fingerprints and it is possible to determine the processes that generate PAHs by studying their distribution in wood samples. The relative abundance of high molecular weight PAHs, together with the PAH compound ratios and with total index (proposed by us) has demonstrated that samples owe their PAHs in wood archaeological material to a predominant single mode of origin, i.e. combustion processes, therefore we can say that the sinking of the vessel was caused by a fire.

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1. Introduction

During the archaeological excavation carried out in 2010, at the port of Scauri, in the Island of Pantelleria (Italy), by a team from the Soprintendenza del Mare, the remains of a sunken vessel were discovered, at a depth of about 8 m. Inspections of retrieved materials by archaeologists, which are kept in the Arenella Sea Museum in Pantelleria, showed that it was a flat-bottomed barge, at least 20 m long and have provided a confirmation of the ancient sailing routes for trading to and from the island [1]. The area was located on the ancient transport route between the Italian Peninsula and African coasts.

Aquatic environments and wetlands represent a unique matrix for the preservation of wooden archaeological objects, especially in the absence of marine borers. Under anaerobic or near anaerobic conditions wooden archaeological finds are protected from the fast biological decomposition that occurs in terrestrial environments and can be found seemingly intact despite centuries of exposure. However, the discovery of the wreck near Pantelleria, gave rise to questions regarding the cause of its sinking. Considering that, some wooden parts of the vessel were damaged, as well as several objects (vases, amphorae, etc.), archaeologists speculate that the sinking was caused by a fire. In this context, scientific confirmation is crucial to add a further element to the data already collected by archaeologists and other researchers [1].

Recent developments in the new frontiers of archaeometry and analytical chemistry are providing important contributions towards

a better understanding of cultural heritages. The use of analytical techniques [2–8] to the study of historical and cultural heritage has led to a considerable improvement in the knowledge of human civilizations [9–12].

Wood combustion is a source of polycyclic aromatic hydrocarbons (PAHs). In particular, PAHs are a class of aromatic compounds that are formed during incomplete combustion. Once engaged in the materials they accumulate [13] and are likely to be retained for a long time due to their persistence, low water solubility and hydrophobicity, especially in organic matrices such as wood. PAHs can be found, to different extents of concentration, in the atmosphere [14,15], water [16,17], soil [18,19], sediments [20], food [21,22] and other matrices [13].

Some studies were carried out on the concentrations of PAHs in different matrices but unfortunately, information about the distribution of PAHs in ancient materials is rare [13].

Pyrogenic polycyclic aromatic hydrocarbons are produced during the combustion of vegetal material, such as organic material during forest fires, and are predominantly unbranched, mostly 3–6 ring PAHs [23]. Previous research shows that the concentration of pyrogenic PAHs increases in sediments following forest fires and pyrogenic PAHs are different from petrogenic PAHs [24]. Other researches use PAHs as indicators of fire in the paleorecord in Triassic, Jurassic or Cretaceous age sediments, often in conjunction with charcoal or pollen analysis [25].

One of the analytical difficulties that may occur with archaeological materials is the complexity of matrices. Therefore, every time, it is necessary to check the validity of analytical method by using the material to be analyzed.

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The aim of this paper was to establish the cause of sinking of an old vessel by PAH determination in the wood of the ship. The investigations have been performed on the seventeen PAHs recommended by US-EPA as priority pollutants to be monitored in the framework of the environmental quality control [26]. Perylene, a non-US-EPA listed PAH, has been investigated with the aim to obtain additional information on PAH origin [27,28].

The molecular patterns generated by each source are like fingerprints and it is possible to determine the processes that generate PAHs by studying their distribution in samples [23]. Pyrolytic sources are characterized by the occurrence of PAHs over a wide range of molecular weights, while low temperature (petroleum, etc.) sources are dominated by the lowest molecular weight (3 rings) PAHs.

2. Experimental part

2.1. Laboratory equipment

All glassware and sample containers were thoroughly washed with hot detergent solution followed by rinsing with Milli-Q water and acetone (analytical grade), respectively. These were finally kept in the oven at 85 °C overnight. To avoid the contamination of samples, different glassware and syringes were used for standards and for solutions extracted from samples.

2.2. Quality assurance

The procedural blanks were analyzed with samples. Limits of quantifications (LOQs) were determined as ten times the noise level of the chromatogram in blank sample (IUPAC Criterion). LOQs were in the range from 0.1 to 0.5 $\mu\text{g kg}^{-1}$ dry weights.

Perdeuterated PAH surrogate standards were added to the samples to monitor the procedures of sample extraction, treatment and analysis. The mean recoveries of surrogate standards ranged from 85% to 103%. The variation of PAH concentrations in triplicate analyses of samples was less than 10%. All results were expressed on dry weight basis.

2.3. Chemicals

Analytical reagent grade dichloromethane and pentane (Carlo Erba, Milano) were used as solvents. A PAH standard solution containing 17 PAH compounds (100 mg L^{-1}) (Supelco, Milano, Italy) was used. Four deuterated compounds were used as internal standards (acenaphthene d_{10} ; phenanthrene d_{10} , chrysene d_{12} and perylene d_{12}) chosen because of isotopic similarity with the analytes of interest. The solution of two surrogate PAHs (anthracene- d_{10} and benzo[a]anthracene- d_{12}) and internal standards was supplied by Supelco (Milano, Italy). The calibration stock solution was prepared by a 1:200 dilution of the custom PAH calibration standard solution. Further dilutions of the calibration stock solution were made to prepare four standards that spanned the expected working concentration range.

2.4. Site and sampling

Pantelleria (Fig. 1) is the fifth largest island in Sicily and it represents the outcrop of a submarine volcano rising about 2000 m. Given its historical and geographic central location in the Mediterranean, the isle has constantly represented a key point for sea trade thus favouring strong commercial affairs and safe navigation along different routes and the Scauri wreck, can be a confirmation of these relations.

On the basis of the current recovery of its load and given the few diagnostic wooden remains pertaining the boat, some authors [1] affirm that it can be a small-sized merchant ship, dating to the first half of the 5th century A.D., which was likely to carry a load of Pantellerian ware produced in the neighbouring village of Scauri Bay, towards the near African coasts.

Three samples were taken, during 2010, from wooden parts. The samples were refrigerated at 4 °C, avoiding the exposure to light, and taken to the laboratory where they were frozen ($-20 \text{ }^{\circ}\text{C}$) until the analysis was performed.

About 10 g of homogenized sample (Fig. 2) of wood was dried overnight at 105 °C. The water content was determined by weight loss and was utilized to correlate all the results with dry weight. Before each analysis the samples were finely pulverized by using a mortar.



Fig. 1. Area of sinking.



Fig. 2. Wood samples.

2.5. Extraction of PAHs

Among different techniques, available in our laboratory, and various solvents, tested in previous works to find the better extraction conditions [20], about the matrix considered in this work, we used the ultrasound bath extraction because it allowed us to obtain the highest recovery percentage of PAHs.

About 0.5 g of dried and pulverized sample, was mixed with pre-cleaned (Soxhlet purified with dichloromethane: pentane 1:1 for a night) anhydrous Na_2SO_4 (Carlo Erba, Milano), spiked with 250 μl of a solution containing two surrogate PAHs (anthracene d_{10} and benz[a]anthracene d_{12}).

The samples were extracted, three times, in ultrasound bath for 30 min by using 20 mL of dichloromethane-pentane 1:1 mixture. The extracted samples were filtered through a pre-cleaned pipette filled with solvent-rinsed glass wool and pre-cleaned anhydrous Na_2SO_4 , rinsed and concentrated in a rotary evaporator with the thermostatic bath at $T = 35 (\pm 0.5)^\circ\text{C}$. The final volume was about 2.5 mL. Finally the solution containing PAHs was dried under a weak nitrogen flow. The dry residue was dissolved in 200 μl of internal standard solution containing acenaphthene d_{10} ; phenanthrene d_{10} , chrysene d_{12} and perylene d_{12} (500 mg L^{-1} each).

2.6. GC–MS analyses

The quantitative analyses were performed by using a gas chromatograph, connected to a mass spectrometer (Shimadzu QP 2010 plus) and equipped with a capillary column as described in previous papers [13,15,18,21]. Target and surrogate analytes were quantified against the internal standard belonging to the same group (Table 1).

A total of 4 calibration standards were available to provide a concentration range from 0.5 to 5 ppm. The mean correlation coefficients of the

calibration lines from the different MS runs were >0.999 for all compounds, attesting the high linearity of the calibration curve for this concentration range.

The identification of the components in the standard mixture was carried out by comparing retention times of each component with those of pure components, analyzed under the same experimental conditions. Identification was confirmed by comparing the mass spectra of the single components with those stored in the library of the acquisition system. The identification of PAHs in solutions originating from the sample extract was carried out on the basis of previously determined retention times and confirmed using mass spectra. The PAHs in the samples were quantified relative to per-deuterated PAHs added to dry residue.

The analyses were performed on three different samples in three replicates in selected ion monitoring (SIM) mode.

3. Results and discussion

The results for the three different wood samples were very similar, therefore, we indicate the result as the average of the three samples analyzed individually three times. Total PAH concentrations, calculated as sum of 18 PAH analyzed, is $1747 \mu\text{g kg}^{-1}$. The single and total PAH concentrations are shown in Table 2 and in Fig. 3. Considering the results of our analyses, among individual PAHs, fluoranthene (26%) and indene(1,2,3 cd)pyrene (16%) are the most abundant components (Fig. 4). Phenanthrene (3 rings) is always much more abundant than the isomeric anthracene. About 4% of perylene was found. The origin of perylene is controversial, some authors argue that a perylene contribution of more than 10% indicates a diagenic process [27,28]. Perylene occurs only in small amount in the products of combustion processes, probably due to its thermal instability or reactivity, but there is also significant evidence that it can be produced biologically under anaerobic conditions [16]. Several authors reported PAH formation through plant and microbial metabolism [29] and showed that wood from the forest contained naphthalene, phenanthrene and perylene. Thiele and Brummer [30] reported that biological formation of 3,4,5 and 6-ring PAHs was observed after incubation of fresh plant material and of soil mixed with fresh plant material under reducing conditions. Perylene quinones (pigments found in several organisms) are suspected to be degraded to perylene by anaerobic microbial metabolism [28,30,31].

In the case of the wood studied in this research, part of the perylene can have a biological origin because the samples were taken from the not exposed to air surface and therefore can include reducing environments.

Table 1

List of groups of PAHs formed for analysis, the deuterated standards employed (underlined), the quantification ion and confirmation ion for SIM GC–MS mode.

Group	Chemical	Quantification ion	Confirmation ions
1	Acenaphthylene	152	76, 151
	Acenaphthene	154	152, 76
	Fluorene	166	164, 165
	Acenaphthene d_{10}	164	
	Phenanthrene	178	188, 89
2	Anthracene	178	188, 89
	Fluoranthene	202	101, 200
	Pyrene	202	101, 200
	Benzo[a]anthracene	228	114, 226
	Phenanthrene d_{10}	188	
	Chrysene	228	114, 226
	Benzo[b]fluoranthene	252	126, 250
3	Benzo[k]fluoranthene	252	126, 250
	Benzo[a]pyrene	252	126, 250
	Chrysene d_{12}	240	
	Perylene	252	126, 250
	Indeno[1,2,3-cd]pyrene	276	277, 138
4	Dibenzo[a,h]anthracene	278	279, 139
	Benzo [g,h,i]perylene	276	138, 124
	Perylene d_{12}	264	
	Anthracene d_{10}	188	
	Benzo[a]anthracene d_{12}	240	

Table 2

Results of analysis of individual and total PAHs (mg/kg).

Compound	Concentration (mg/kg)
Acenaphthylene	0.2
Acenaphthene	3.6
Fluorene	7.8
Phenanthrene	64
Anthracene	16
Fluoranthene	448
Pyrene	32
Benzo(a)anthracene	48
Crysene	38
Benzo(b)fluoranthene	82
Benzo(k)fluoranthene	76
Benzo(e)pyrene	77
Benzo(a)pyrene	96
Perylene	70
Indeno(1,2,3-cd)pyrene	274
Dibenzo(a,h)anthracene	216
Benzo(ghi)perylene	198
Total (mg/Kg)	1747

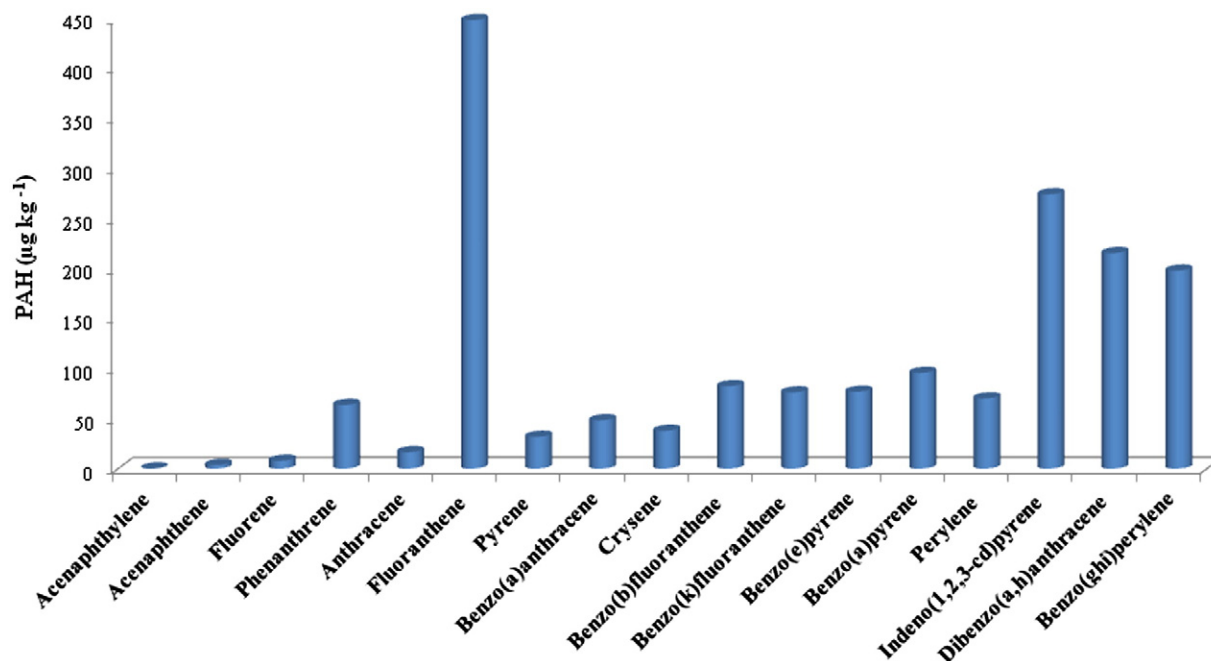


Fig. 3. Distribution of single PAHs.

3.1. Speciation and origin of PAHs

By grouping the polycyclic aromatic compounds in different classes, depending on the number of aromatic rings present in their structure, it can be observed (Fig. 5) that three-aromatic compounds are only present at trace levels while PAHs having 4,5 and 6-rings, found in samples under investigation, contribute about 95% of the total. This evidence suggests that PAH presence in the archaeological find might originate

mainly from high temperature sources, for example from combustion of wood.

In agreement to literature [32,33], we value the ratio of low and high molecular weight PAHs (Acph + Ace + Fl + Phen + Ant)/(BaA + Cry + BbF + BkF + BaP + InP + DBA + BgP), as a consistent instrument for discriminating the petrogenic/pyrolytic origin of compounds. Research [32,33] has shown that high ΣLPAHs/ΣHPAHs ratios (>1) often indicate PAHs with low temperature predominate sources

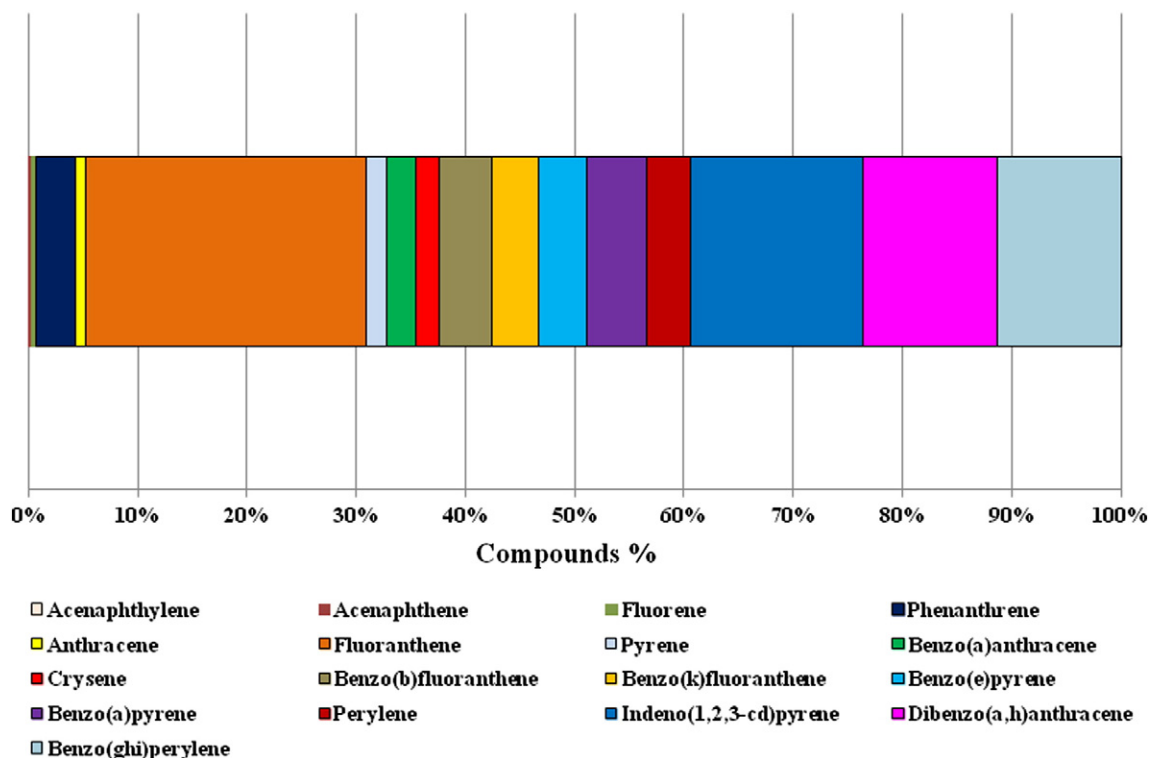


Fig. 4. Contribution of single compounds to total PAHs.

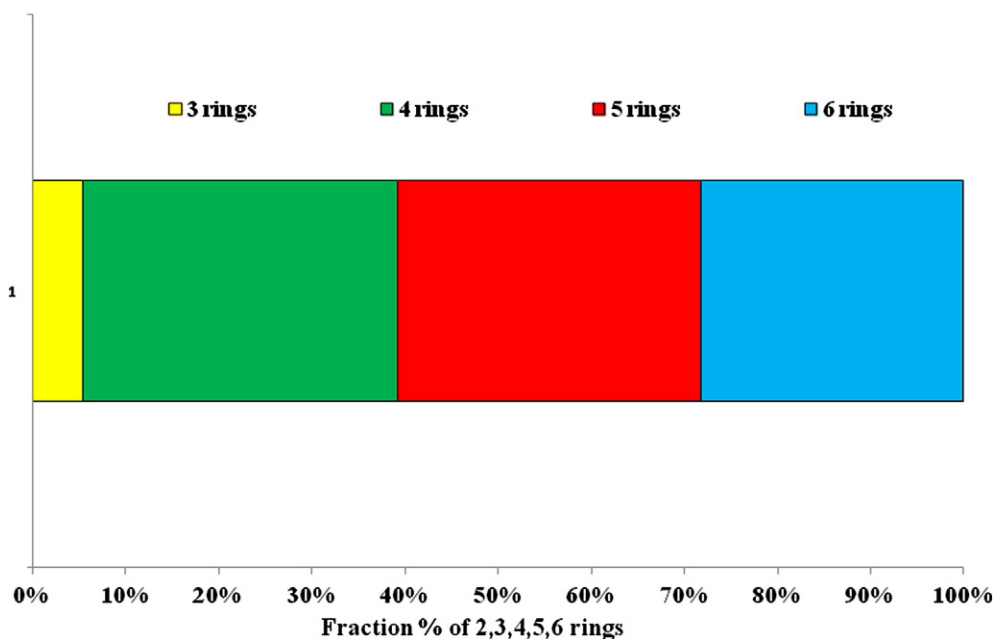


Fig. 5. Fraction % of 3–4–5–6-rings.

(petrogenic) while low $\Sigma\text{LPAHs}/\Sigma\text{HPAHs}$ ratios suggest PAHs of pyrolytic origin [34]. Considering the value of the ratio, in wood sample, the $\Sigma\text{LPAHs}/\Sigma\text{HPAHs}$ ratio was lower than 0.1. This value suggests that the sample has been subjected to a high temperature process.

Sources of the PAHs in the matrix under investigation have been estimated by using distribution indexes relative to concentration ratios of some single compounds. PAH isomer pair ratios have extensively been used to explain the possible sources [3,13,15–22]. These indexes are based on thermodynamic stability of compounds. The ratios of anthracene to anthracene plus phenanthrene ($\text{An}/\text{An} + \text{Ph}$), fluoranthene to fluoranthene plus pyrene ($\text{Fl}/(\text{Fl} + \text{Py})$) and benz[a]anthracene to benz[a]anthracene plus chrysene $\text{B[a]A}/(\text{B[a]A} + \text{Chr})$ have been frequently used in several papers [23,27]. PAHs of molecular mass 178 and 202 are normally used to distinguish between combustion and petroleum sources.

For mass 178, an anthracene to anthracene plus phenanthrene ($\text{An}/\text{An} + \text{Ph}$) ratio < 0.10 is taken as an indication of low temperature processes (petroleum) while a ratio > 0.10 indicates a dominance of combustion [23,27]. In the samples studied, the $\text{An}/\text{An} + \text{Ph}$ ratio is 0.21.

In this study $\text{Fl}/(\text{Fl} + \text{Py})$ ratio has been used to identify sources of PAHs. Yunker [23] suggested that a $\text{Fl}/(\text{Fl} + \text{Py})$ ratio < 0.4 indicates petroleum input, ratio between 0.4 and 0.5 liquid fossil fuel (vehicle and crude oil) combustion and ratio > 0.5 grass, wood or coal combustion. In the wood of the ship, the values of $\text{Fl}/(\text{Fl} + \text{Py})$ ratio is 0.95 indicating combustion as the main PAH source. In this study the values of $\text{B[a]A}/(\text{B[a]A} + \text{Chr})$ ratio is 0.56. Yunker [23] suggested that values < 0.2 and > 0.35 were indicative of petroleum and combustion origin respectively. Therefore, PAHs in the wood of ship might be mainly of combustion origin.

$\text{IP}/(\text{IP} + \text{B}[g,h,i]\text{P})$ ratios for our samples ranged is 0.66. Accordingly to literature data, $\text{IP}/(\text{IP} + \text{B}[g,h,i]\text{P})$ ratios higher than 0.50 imply

combustion [23]. In addition, we calculated a total index [15,20,35] as the sum of single indices (previously discussed) respectively normalized for the limit value (low temperature sources-high temperature sources) reported in the literature [23]:

$$\text{Total index} = \text{An}/(\text{An} + \text{Ph})/0.1 + \text{Fl}/(\text{Fl} + \text{Py})/0.4 + \text{B[a]A}/(\text{B[a]A} + \text{Chr})/0.2 + \text{IP}/(\text{IP} + \text{B}[g,h,i]\text{P})/0.5.$$

We assume that PAHs originating prevalently by high temperature processes (combustion) have a total index that is > 4 while lower values indicate prevalently low temperature sources (petroleum product). The obtained mean value (4.8) (Table 3) confirms that most of the PAHs identified in the wood samples originate from combustion processes.

4. Conclusions

The relative abundance of high molecular weight PAHs, together with the PAH isomeric ratios, has demonstrated that samples owe their PAHs in wood archaeological material to a predominant single mode of origin, i.e. combustion processes. The total index, proposed by us, permits to avoid the different responses of single indexes and identify the predominant sources of PAHs in a matrix. Therefore we can say that the sinking of the vessel was caused by a fire.

The knowledge of the cause of sinking of the old vessel (Scauri wreck) might be of crucial interest for archaeologists, restorers and museum conservators in order to adopt the most suitable treatment for the specific case study. Also, the results of this research offer a scientific basis for risk analysis, especially for archaeologists and restorers, caused by carcinogenic PAHs deriving by the wood presence. Finally, it seems very likely that the methodology used in the present study on the Scauri Ship may be extended to many archaeological objects (pottery dishes, amphorae, vases, etc.) found in the same area.

Acknowledgements

This study was made possible by the financial support of Palermo University (5236 2007-ATE-1046) that has funded the author (Grants ex 60% 2007). Also, we thank Dr. Sebastiano Tusa and Dr. Roberto La Rocca from Soprintendenza del Mare della Regione Siciliana.

Table 3
Isomeric ratios and total index.

Compound	
$\text{Fl}/(\text{Fl} + \text{Py})$	0.934
$\text{An}/(\text{An} + \text{Ph})$	0.205
$\text{Ba}/(\text{Ba} + \text{Cr})$	0.561
$\text{IndP}/(\text{Ind} + \text{Bghi})$	0.663
Total index	10

References

- [1] S. Tusa, S. Vinciguerra, R. La Rocca, Il relitto tardo-antico di Scauri a Pantelleria, http://issuu.com/stefanovinciguerra/docs/il_relitto_di_scauri_impaginato.
- [2] F. Caruso, S. Orecchio, M.G. Cicero, C. Di Stefano, Gas chromatography-mass spectroscopy characterization of the varnish and glue of an ancient 18th century double bass, *J. Chromatogr. A* 1147 (2007) 206–212.
- [3] S. Orecchio, Analytical method, pattern and sources of polycyclic aromatic hydrocarbons (PAHs) in the stone of the Temples of Agrigento (Italy), *J. Hazard. Mater.* 176 (2010) 339–347.
- [4] M.R. Mannino, S. Orecchio, Chemical characterization of ancient potteries from Himera and Pestavecchia necropolis (Sicily, Italy) by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES), *Microchem. J.* 97 (2) (2011) 165–172.
- [5] S. Orecchio, Speciation of iron in ancient pots from Sicily (Italy), *Microchem. J.* 99 (2011) 132–137.
- [6] I. Martinez-Arkarazo, M. Angulo, L. Bartolome, N. Etxebarria, M.A. Olazabal, J.M. Madariaga, An integrated analytical approach to diagnose the conservation state of building materials of a palace house in the metropolitan Bilbao (Basque Country, North of Spain), *Anal. Chim. Acta.* 584 (2007) 350–359.
- [7] S. Orecchio, Microanalytical characterization of decorations in handmade ancient floor tiles using inductively coupled plasma optical emission spectrometry (ICP–OES), *Microchem. J.* 108 (2013) 137–150.
- [8] M.R. Mannino, S. Orecchio, G. Gennaro, Microanalytical method for studying paintings by use of fluorescence spectroscopy combined with principal component analysis, *Microchem. J.* 110 (2013) 407–416.
- [9] E. Tomasini, G. Siracusano, M.S. Maier, Spectroscopic, morphological and chemical characterization of historic pigments based on carbon. Paths for the identification of an artistic pigment, *Microchem. J.* 102 (2012) 28–37.
- [10] M. Menu, Analysis of works of art down to the nanometric scale, *Microelectron. Eng.* 83 (2006) 597–603.
- [11] R.J.H. Clark, Pigment identification on medieval manuscripts by Raman microscopy, *J. Mol. Struct.* 347 (1995) 417–428.
- [12] A. Yoshinari, H. Rodan, K. Tadashi, Y. Ken, N. Akiko, K. Nozomu, Y. Sakuji, N. Izumi, Transition in the use of cobalt-blue colorant in the New Kingdom of Egypt, *J. Archaeol. Sci.* 39 (2012) 1793–1806.
- [13] A. Gianguzza, M. Governanti, S. Orecchio, D. Piazzese, Identification of polycyclic aromatic hydrocarbons (PAHs) in the black crusts of Sicilian stone monuments: distribution and sources, *Sci. Technol. Cult. Herit.* 13 (2004) 53–61.
- [14] E. Bodnar, J. Hlavay, Atmospheric deposition of polycyclic aromatic hydrocarbons on the Lake Balaton, Hungary, *Microchem. J.* 79 (2005) 213–220.
- [15] M.R. Mannino, S. Orecchio, Polycyclic aromatic hydrocarbons (PAHs) in indoor dust matter of Palermo (Italy) area: extraction, GC–MS analysis, distribution and sources, *Atmos. Environ.* 42 (2008) 1801–1817.
- [16] S. Orecchio, S. Cannata, L. Culotta, How building an underwater pipeline connecting Libya to Sicilian coast is affecting environment: polycyclic aromatic hydrocarbons (PAHs) in sediments; monitoring the evolution of the shore approach area of the Gulf of Gela (Italy), *J. Hazard. Mater.* 181 (2010) 647–658.
- [17] M. Howsam, K.C. Jones, Sources of PAHs in the environment, PAHs and Related Compounds: The Handbook of Environmental Chemistry – PAHs and Related Compounds, 3-I, Chemistry, Springer, Berlin, 1998, pp. 137–174.
- [18] S. Orecchio, Contamination from polycyclic aromatic hydrocarbons (PAHs) in the soil of a botanical garden localized next to a former manufacturing gas plant in Palermo (Italy), *J. Hazard. Mater.* 180 (2010) 590–601.
- [19] S. Orecchio, Assessment of polycyclic aromatic hydrocarbons (PAHs) in soil of a Natural Reserve (Isola delle Femmine) (Italy) located in front of a plant for the production of cement, *J. Hazard. Mater.* 173 (2010) 358–368.
- [20] S. Barreca, A. Mazzola, S. Orecchio, N. Tuzzolino, PAHs and PCBs in sediments from Sicilian coastal area (Scoglitti) using automated soxhlet, GC–MS and principal component analysis, *Polycyclic Aromat. Compd.* 34 (3) (2014) 237–262.
- [21] S. Orecchio, V. Papuzza, Levels, fingerprint and daily intake of polycyclic aromatic hydrocarbons (PAHs) in bread baked using wood as fuel, *J. Hazard. Mater.* 164 (2009) 876–883.
- [22] S. Orecchio, V. Paradiso Ciotti, L. Culotta, Polycyclic aromatic hydrocarbons (PAHs) in coffee brew samples: analytical method by GC–MS, profile, levels and sources, *Food Chem. Toxicol.* 47 (2009) 819–826.
- [23] M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre, PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, *Org. Geochem.* 33 (2002) 489–515.
- [24] D.S. Page, P.D. Boehm, G.S. Douglas, A.E. Bence, W.A. Burns, P.J. Mankiewicz, Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: a case study in Prince William Sound, Alaska, *Mar. Pollut. Bull.* 38 (1999) 247–260.
- [25] M.I. Venkatesan, J. Dahl, Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary, *Nature* 338 (1989) 57–60.
- [26] US-Environmental Protection Agency, Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons, USEPA EPAR600/r-93/r089, 1993.
- [27] M. Venkatesan, Occurrence and possible sources of perylene in marine sediments – a review, *Mar. Chem.* 25 (1988) 1–27.
- [28] C. Jiang, R. Alexander, R. Kagi, A. Murray, Origin of perylene in ancient sediments and its geological significance, *Org. Geochem.* 31 (2000) 1545–1559.
- [29] A.R. Bakhtiari, M.P. Zakaria, M.I. Yaziz, M.N. Hj Lajis, X. Bi, M. Che Abd Rahim, Vertical distribution and source identification of polycyclic aromatic hydrocarbons in anoxic sediment cores of Chini Lake, Malaysia: perylene next term as indicator of land plant-derived hydrocarbons, *Appl. Geochem.* 24 (2009) 1777–1787.
- [30] S. Thiele, G. Brummer, Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficient conditions, *Soil Biol. Biochem.* 34 (2002) 733–735.
- [31] C.A. Jiang, R.I. Kagi, A.P. Murray, Origin of perylene in ancient sediments and its geological significance, *Org. Geochem.* 31 (2000) 1545–1559.
- [32] H. Budzinski, I. Jones, J. Bellocq, C. Pierard, P. Garrigues, Evaluation of sediment contamination by polycyclic aromatic hydrocarbon in the Gironde estuary, *Mar. Chem.* 58 (1997) 85–97.
- [33] M.A. Sicre, J.C. Marty, A. Salio, X. Aparicio, Grimalt, J. Albaiges, Aliphatic and aromatic hydrocarbons in different size aerosols over the Mediterranean Sea: occurrence and origin, *Atmos. Environ.* 21 (1987) 2247–2259.
- [34] G. De Luca, A. Futonio, R. Leardo, G. Micera, A. Panzanelli, P.C. Piu, G. Sanna, Polycyclic aromatic hydrocarbons assessment in the sediments of the Porto Torre Harbor (Northern Sardinia, Italy), *Mar. Chem.* 86 (2004) 15–32.
- [35] S. Frenna, A. Mazzola, S. Orecchio, N. Tuzzolino, Comparison of different methods for extraction of polycyclic aromatic hydrocarbons (PAHs) from Sicilian (Italy) coastal area sediments, *Environ. Monit. Assess.* 185 (2013) 5551–5562.