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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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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.

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 μg 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 °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.