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Identifying wine markers in ceramics and plasters using gas chromatography–mass spectrometry. Experimental and archaeological materials

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ABSTRACT

The identification of the organic residues preserved in archaeological materials yields good insights into understanding food production, trade and consumption. Wine is one of the most important beverages produced, traded and consumed in the Mediterranean area. Consequently, it is important to identify its presence in ancient materials. Nevertheless, the identification of wine markers is still an object of discussion. We present here the results obtained from analysing different materials using gas chromatography/mass spectrometry (GC/MS), which allowed for the identification of tartaric acid and other markers of wine. The method was first tested on experimental and traditional materials that have been used until recently to store and/or produce wine and was then used for investigating archaeological materials. The experiments also involved the degradation of wine through cooking, drastic heating and burial for seven years. The results from the analysis of ceramic and plaster materials are discussed.

The importance of the proposed methodology is that it allows the identification of traces of wine using the same facilities that are usually employed for the study of the organic residues preserved in archaeological samples (GC/MS), with no need for HPLC, LC/MS/MS or THM/GC/MS, thus allowing a larger number of laboratories to detect traces of wine.

1. Introduction

Wine is one of the most important beverages that has been produced, consumed and traded in the Mediterranean area. Many ceramic vessels have been used to store, trade and serve wine, with the *amphorae* as the most common transport container. To delve further into the study of the history of wine and to provide archaeological evidence of its distribution, it is necessary to know whether these containers actually contained wine or its derivatives. To accomplish this goal, it is necessary to identify the traces of wine in archaeological materials (Barnard et al., 2011; Garnier et al., 2003; Garnier, 2007; Guasch-Jané et al., 2004; McGovern, 2003; Miller, 2008).

Since the 1970s, the chemical analysis of organic residues has been used to identify the contents of ceramic vessels (Condamin et al., 1976; Evershed, 1993, 2008). Nevertheless, the identification of wine markers has always been difficult because of its degradation. Formenti has used gas chromatography to identify tartaric acid (which is abundant in grapes) in residues of wine in Roman *amphorae* (Formenti et al., 1978; Formenti and Duthel, 1996). McGovern has used the identification of tartaric acid and its salts as markers of wine, using the Feigl spot test, infrared spectroscopy and high performance liquid chromatography (HPLC) (McGovern, 2003; McGovern and Michel, 1990, 1996; Michel et al., 1993), although Stern et al. (2008) have identified problems arising from the use of these methods. To overcome the difficulties generated by the identification of tartaric acid, Guasch Jané and co-authors suggested the use of HPLC/MS/MS for the identification of tartaric acid and syringic acid (considered a marker of red wine) (Guasch-Jané et al., 2004, 2006; Stern et al., 2008). Barnard et al. (2011) indicated problems that can arise in the identification of tartaric acid with HPLC due to its short retention time and improved the method developed by Guasch-Jané et al. (2004) to identify syringic acid deriving from malvidin in the grapes. Finally, Garnier has developed an alternative method, studying polyphenols to identify the presence of wine in

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archaeological samples by thermally assisted hydrolysis and methylation/gas chromatography/mass spectrometry (THM/GC/MS) (Garnier, 2007; Garnier et al., 2003).

The aim of this study is to analyse different materials with a new methodology that involves a new extraction method and to analyse the extract with gas chromatography–mass spectrometry (GC/MS); these analyses may be useful for the identification of wine in archaeological materials. The method of this study allows the identification of tartaric acid and other markers of wine and its derivatives. Tartaric acid is usually considered the biomarker for wine because it is abundant in grapes. Nevertheless, tartaric acid is associated not only with wine, but also with grape juice, syrup or wine derivatives (Barnard et al., 2011; Miller, 2008). In addition, it is present in fruits other than grapes (e.g., tamarind, star fruit and yellow plum), as different authors have noted (Barnard et al., 2011; Garnier, 2007; Singleton, 1996). In the Mediterranean area, these plants did not play an important role, especially in the production of fermented beverages. Nevertheless, it is important to stress, as those authors did, that the interpretation of the chemical results must always be related to the archaeological context of the findings. Although tartaric acid is soluble in water, when it is identified, it can be considered a marker of wine or its derivatives. Moreover, the method proposed here allows the identification of more acids that are characteristic of wine, in addition to tartaric acid.

This method was first tested on experimental and traditional materials that were in contact with wine or its derivatives and was then used for the analysis of archaeological materials. Examples of the analysis of ceramic and plaster materials are shown.

This work has been carried out over several years following different steps. The first efforts were directed at verifying the possibility of identifying wine traces in materials that have been experimentally enriched with wine and in traditional modern materials that had a known function related to wine production or storage ("experimental" and "traditional materials"). The experiments also involved the degradation of wine through cooking, drastic heating and burial for seven years.

After verifying that the method yielded good results for these types of samples, we tested it on archaeological materials. Ceramic vessels were chosen because they were commonly used for the storage and transport of wine, as well as for serving, cooking and heating wine. In addition, plasters were analysed, as they were generally used for the floors of the installations where wine was produced, as well as for the coatings of the vats where wine was kept to decant and ferment. The experiments had the objective of recognising the absorption of wine in different kinds of materials and the possibility of identifying wine.

2. Materials and methods

2.1. Materials

Experiments were undertaken to verify the possibility of identifying wine markers in materials enriched with wine; afterwards, some traditional materials were chosen to test the method. Finally, some archaeological materials were analysed.

2.1.1. Experimental materials

For the experiments, materials that are usually found at archaeological levels and that are related to wine production, storage, trade and consumption were chosen.

Since *amphorae* were the main transport vessels for wine in the ancient Mediterranean, we chose to analyse a small amphora in which wine was stored for a month. The *amphora* was not coated (Fig. 1), and it was filled with 500 mL of red wine and left for a month at room temperature. After a month, a sample was taken from the bottom of the vessel (sample 1, Table 1).

Fig. 1. Small *amphora* in which wine was kept during a month. Notice the blackish colour (scale bar is 20 cm).

Wine was not only consumed at room temperature, but was also heated and sometimes cooked, as described in the recipes of Apicius for the Roman period and in Medieval treatises. Therefore, an experiment was carried out by cooking wine in a coarse ware pan (Fig. 2). The pan was not coated with an organic lining such as resin or pitch, nor was it glazed. For the experiment, the protocol developed for a bigger experimental project was followed (Pecci, 2005), consisting of cooking 150 mL of red wine in the pan until it evaporated and repeating the cooking twenty times. After twenty cycles of cooking, a sample was taken from the bottom of the pan (sample 2).

To induce the degradation of the compounds present in "fresh" wine to obtain data that could be useful for the interpretation of the analyses of archaeological materials, two different experiments were

Table 1
Samples analysed.

Sample	Sample n.	Material	Experimental/ Traditional/ Archaeological samples
Amphora	1	Ceramic	Experimental
Pan	2	Ceramic	Experimental
Buried pan	3	Ceramic	Experimental
Pan kept in the oven for 18 days	4	Ceramic	Experimental
Plaster brick	5	Plaster	Experimental
Terracotta tile of the floor of the wine celler	6	Tile	Traditional
Orcio (jar)	7	Ceramic	Traditional
Dolium at Augustus villa, Somma Vesuviana	8	Ceramic coating	Archaeological
Basin coating at Son Peretó (Mallorca, Balearic Islands)	9	Plaster	Archaeological