Chromatography and Archaeological Materials Analysis

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Introduction

Chromatography is essential for the study of archaeological organic materials. Since most archaeological organic substances comprise complex mixtures of molecules with a wide range of chemical and physical properties, chromatography's analytical utility is essential to modern archaeological research practice and more broadly to heritage studies. Identifying and characterizing the compositions of archaeological organic mixtures helps archaeologists to interpret ancient people's lifestyles.

Organic materials recovered in archaeological contexts are composed of a mixture of molecules. Chromatography allows us to separate and identify these molecules, being a technique that "allows separating a mixture into its individual components and simultaneously determine quantitatively the amount of each component" (Scott 1995). It allows us to analyze gaseous, liquid, or solid samples, and the analysis can be carried out with expensive instruments or simple techniques.

The word chromatography derives from the Greek words for "color" and "writing." It owes its name to the Russian botanist Mijaíl Tswett, who first employed the technique at the beginning of the twentieth century to separate plant pigments. Chromatography has since developed rapidly and is now used for different separation processes of molecules. In 1952, Martin and Synge, who established the principles of modern chromatography, received a joint Nobel Prize in Chemistry for their contribution to the "invention of partition chromatography."

Chromatographic separation is achieved by distributing the substances to be separated between a moving phase (the so-called *mobile phase* which can be a gas or a liquid) and a *stationary phase* (a solid, or a liquid supported on a solid). In a simplified vision of the technique, the mobile phase flows through the stationary phase and carries the components of the mixture with it, while the stationary phase retains them.

The various constituents of the mixture travel at different speeds—based on differences in characteristics, such as their molecular weight and structure, as well as on their affinities to the stationary and mobile phases—and reach the end of the chromatographic system at different times (it is said that molecules "elute" with different "retention times"). These different speeds of "elution" allow us to separate the mixture into its constituents. The separation processes that use a gas as the mobile phase are called "gas chromatography," while the processes that use a liquid are called "liquid chromatography."

Samples of archaeological materials (e.g., resin, pitch, beeswax, dung, organic residues trapped in ceramic vessels) are usually analyzed as organic solutions and therefore must be extracted by a solvent before their analysis. Depending on the objectives of the analyses and the materials analyzed, different extraction methods can be followed. Chromatographic analysis includes different techniques such as gas chromatography (GC), high-temperature gas chromatography (HTGC), liquid chromatography (LC), and pyrolysis/gas chromatography. Gas chromatography (GC) (see GAS CHROMATOGRAPHY–MASS SPECTROMETRY (GC-MS)) is commonly used, but it is unsuitable for the analysis of high-molecular-weight biopolymers or proteins. Bigger molecules, such as triacylglycerols, can be identified by techniques such as HTGC. In pyrolysis GC, the sample is rapidly heated, and large molecules are fragmented into volatile particles that are later separated by GC. In LC, the mobile phase is a liquid. High-performance liquid chromatography (HPLC) utilizes a high pressure and for this reason is called also high-pressure liquid chromatography.

The Encyclopedia of Archaeological Sciences. Edited by Sandra L. López Varela.

DOI: 10.1002/9781119188230.saseas0092

Chromatography gives better results when it is coupled with mass spectrometry, a highly selective, specific, and sensitive technique that separates ions according to their mass charge (m/z) ratios. Combined, the two techniques allow for the reliable identification and characterization of a mixture of components. GC can be coupled with isotopic analyses in gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) to identify the relative ratio of stable isotopes of carbon, hydrogen, nitrogen, or oxygen in individual compounds and to pinpoint the origin of such substances (Evershed 2008). In combination with accelerator mass spectrometry (AMS), chromatography can make it possible to date the organic residues preserved in the samples (Berstan et al. 2008).

Prior to applying chromatographic techniques, it is important to establish whether or not the samples require any treatment prior to the analysis; which are the most suitable for extraction, derivatization, and analytical methods; and which instruments best suit the analysis of specific materials and best align with the objectives of the research. In archaeological research, good results depend on the application of specific techniques and sampling strategies.

Application

The application of chromatographic techniques to the study of ancient materials has opened new paths in the investigation of different fields, such as the identification of ancient tars, resins, pitches, and incenses, as well as of ancient dyes such as indigo; the understanding of the use and function of ceramic vessels, pipes, and stone tools; the function of rooms and buildings; and the identification of activity areas. These methods have also provided evidence for the early domestication of animals and plants, the introduction of specific foodstuffs in human diets, and the historic consumption of alcoholic beverages and drugs. More broadly, they have yielded information about food practices and diets in different archaeological sites and societies. Chromatography has also allowed archaeologists to explain ancient production processes and technologies and to ascertain the degradation processes of different substances. This knowledge has enabled the conservation of ancient materials, and, in some cases, it has been able to identify their forgery.

One of the most important applications of chromatography is the identification of organic residues (amorphous or absorbed by porous materials), which are usually preserved as a mixture of substances (see ORGANIC RESIDUE ANALYSIS). Cooking pots likely contained different foodstuffs. Many substances ended up on kitchen or temple floors while cooking or performing ritual activities. Different oils and animal fats might have been burnt as fuel in ancient lamps. Beeswax and resin might have been mixed to produce a glue; and amphorae containing wine or oil might have been coated with pitch. The possibilities yielded by chromatographic techniques to recognize these various materials have existed since the 1970s, when these were used to investigate amphorae contents and lamp fuels (Condamin et al. 1976).

The difficulty of identifying residues of wine, which, along with oil and fish sauces, was one of the most important commodities traded in the ancient world, has long hindered the study of amphorae contents. However, recent developments in the identification of wine residues with LC and GC coupled to mass spectrometry have given new impetus to this line of research. They have made it possible to study wine's origins, its production and consumption at different sites, and its use as an offering for the dead and for gods. The consumption of other beverages, such as pulque, chicha, and black drink (an early North American beverage), as well as chocolate and beer has also been established thanks to the identification of specific biomarkers through chromatographic techniques.

Lipids are among the compounds more commonly identified in organic residue analyses (Evershed 2008). By studying their distribution and isotopic signature, it is possible to establish the various species of animals consumed in different areas of the world, to distinguish between adipose fats and dairy products, and to identify evidence of ancient dairy product consumption. Proteins can also be identified with chromatographic techniques—albeit with due care in interpretation—and their study gives clues regarding many interesting aspects of ancient daily life. Proteins are often well preserved in dental calculus, and their recognition facilitates a deeper understanding of food consumption in different regions and periods.

In recent decades, organic residues analysis carried out by chromatographic techniques has concentrated mainly on the analysis of ceramic materials. However, the technique can be used to identify residues preserved in other porous materials, such as the plaster used to make floors in different areas of the world or to make the coatings of vats from production installations for wine, oil, or fish by-products. The analysis of such materials has often been carried out by means of spot tests, and the combination of spot tests with GC has helped to interpret data and to produce knowledge about the function of rooms, buildings, production structures, and spaces in general (Pecci 2013; Pecci, Cau, and Garnier 2013).

Chromatographic techniques have also been applied in the analysis of beaten earth floors, fireplaces, anthropogenic soils, and ancient cultivation fields, as well as in the identification of dung traces in the archaeological record. They likewise play a crucial role in the characterization of amorphous materials such as beeswax, resin, pitch, incenses, tars, bitumen, and gums. These are found as bulk materials transported and preserved in ancient vessels, such as incense burnt during rituals, as waterproof linings of vessels, boats, or buildings; as glues used to repair ceramics or to make other artifacts such as knives, projectile points, masks, and many other ritual and domestic tools; and as glues for body and teeth decoration. Such substances can also be identified in the pores of ceramic matrices, since they were used as waterproofing agents in ceramic vessels and as preservatives and flavorings. Chromatographic analysis sheds light on the use of these materials, their production processes, and their geographic origins (Stern et al. 2008).

Chromatography has found many more applications. It has been used to characterize fossil resins such as amber and to identify the polymers used to imitate these materials and others (such as precious stones). It can characterize waterlogged archaeological wood, making it possible to determine degradation processes and to develop consolidation and conservation procedures (Colombini et al. 2007). Finally, the application of chromatographic analyses to heritage can identify the original techniques used to paint and glue and the substances used in previous conservation processes.

Future directions

Chemical analyses in archaeological research should always be conducted in collaboration with a team comprising historians, archaeologists, chemists, archaeozoologists, and materials specialists such as botanists in order to accurately understand the materials investigated (and the degradation processes that they have undergone) and to contextualize the results obtained. The interpretation of chemical results must take into account the archaeological contexts where materials were recovered and answer the historical and archaeological questions that prompted the analyses. Likewise, ethnoarchaeology and experimental archaeology should be integrated in the study to better identify the archaeological substances investigated, their use, and their production processes.

SEE ALSO: Bioarchaeology; Food Residue Analysis; Mass Spectrometry (MS); Soil Chemistry in Archaeology

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