ARCHAEOLOGICAL CHEMISTRY: REVEALING TRACES OF THE PAST

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Abstract

The objective of the ARCHEM Project is twofold. First, to promote and reinforce the cooperation between the chemical and the archaeological sciences, the most important disciplines for effectively deriving the maximum amount of information from the analysis of materials recovered from excavation sites worldwide. Archaeological chemistry focuses not only on the study of ancient pottery, stone, metal, and glass, but also on new materials of interest such as archaeological soils, fibres, dyes, bone, DNA and, more recently, organic residues from ceramic sherds. In the last few years, scientists have focused on the use of analytical chemistry to identify the constituents of archaeological artefacts to find out what these objects were made from and even their provenance. The development of new analytical methods has enabled us to discern patterns of human behaviour in the past. The ARCHEM Project focuses on the characterization of the organic residues found in archaeological pottery. Therefore, this represents an innovative project that brings together two traditionally independent disciplines with the aim of obtaining high quality information about past societies.

The second objective of the ARCHEM project is the development of competencies and abilities in the field of archaeological chemistry through the production of Doctoral and Master's Theses. In this way, Master's degree students (members of the ARCHEM project) will learn a new perspective approach to the study of archaeological pottery including the aspects related to the chemical analysis. Basic knowledge of chemical analysis will provide students from humanities background with the abilities for a more complete professional development in Archaeometry. In this context, the idea of adapting the teaching of analytical chemistry to students of archaeology has led the team of researchers, members of the ARCHEM project, to consider including the subject of chemistry in the Archaeology degree curriculum. This early learning of chemistry will enable undergraduate students to unravel the secrets of archaeology through chemistry.

Keywords: archaeological chemistry, research project, organic residues.

1 INTRODUCTION

Disciplines such as geology, history, anthropology, materials science and chemistry have helped archaeology to explain past lifeways. In particular, chemistry can make a unique contribution to archaeology, often providing new information that is not apparent to the naked eye. Archaeology and chemistry are very important disciplines to extract the maximum information from the material remains recovered during archaeological excavations worldwide. Archaeological chemistry focuses on the study of ancient metal, stone, pottery and glass, but ceramic objects, such as pottery vessels, are the most common artefacts recovered in archaeological excavations. Their commonest functions appear to be as containers for storing and preserving food and drinks such as oil, wine and water, and as vessels for cooking and presenting meals.

Until recently, most of the previous research studies in the archaeological chemistry field focused primarily on the analysis of inorganic materials because of their stability over time. Increasing attention has been directed over the past 25 years towards the analysis of organic residues from ceramic sherds. The main focus has been on biological materials (waxes, resins, carbohydrates, proteins, lipids and, more recently, DNA) in residues found in ceramics, but also in soils and others matrix [1]. The analysis of these organic residues preserved in ceramic vessels is highly dependent on environmental conditions.

The development of new analytical methods has enabled us to obtain information on the original contents processed or stored in the vessels and even on their provenance. These data can help us to understand the traditions, customs, lifeways and dietary patterns of the people who used this material...
in the past. Food preparation and consumption are essential daily activities for the survival of any social group. These timeless practices generate residues that can be absorbed into the microporous structure of the fired-clay wall or preserved in visible surface deposits. Thanks to these remains one can know where (area) and what types of objects (ceramic vessels) people used to store, cook and eat food four thousand years ago, but answering questions as to what they cooked or what they ate remains difficult. In addition to foods, these vessels may also have contained drinks, medicines, dyestuffs, essential oil, wine, etc. Residues containing lipids are better preserved in favourable environments than proteins, carbohydrates, polyalcohol and other organic components and can survive for a long time in a ceramic matrix.

A scientific approach in archaeology is critical for extracting the maximum amount of information from the material remains recovered during archaeological excavations and, therefore, for the accurate reconstruction of past events. In this respect, the organic residue analysis is an important source of information for historians and archaeologists and is now an established discipline in archaeology, with increasing numbers of archaeologists beginning to consider organic residue analyses amongst the many scientific tools available to them.

What is the chemical composition of the organic residues? In order to identify the nature of organic compounds in pottery (either in visible deposits or occluded in another matrix), a specific method for extraction, purification and further analysis of the total lipid extract (TLE) has been developed. Spectroscopic methods, such as Infrared (IR), Raman and Nuclear Magnetic Resonance (NMR) spectroscopies, provide insights into bulk compositions that have proved useful in 'fingerprinting' the sources of certain classes of organic residues. Because of the chemical complexity of these types of residues (endogenous or exogenous constituents) and the low concentrations of organic compounds, especially where mixtures of natural products may be present, chromatographic methods should be used. Gas Chromatography-Mass Spectrometry (GCMS), Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS), Thermally Assisted Hydrolysis and Methylation Gas Chromatography-Mass Spectrometry (THM-GC-MS), High Temperature Gas Chromatography-Mass Spectrometry (HT-GC-MS), Liquid Chromatography-Mass Spectrometry (LC-MS), Direct Infusion Electrospray Ionization-Mass Spectrometry (ESI-MS) and isotopic analysis (GC-C-IRMS) have been used for the determination of organic residues [1,2,3,4].

What is the source of the organic compounds identified? The provenance of amorphous organic compounds identified in archaeological contexts can pose more problems. Nevertheless, this is the ultimate goal of archaeological research: the reconstruction of past events through the study of materials that have survived for long time periods. To achieve this it is necessary to establish a relationship between the molecular constituents that remain in the organic residues and the source from which they originated. To this end, several criteria were used. The simplest was the comparison of the “chemical fingerprints” of the molecules found in ancient ceramic objects with the reference materials. The ratios of some common fatty acids, the presence of specific archaeological biomarkers and the stable carbon isotope values of specific lipid components are also useful for characterization of residues [5].

2 ARCHAEOLOGICAL CHEMISTRY PROJECTS

An interdisciplinary group of colleagues from the departments of Analytical Chemistry, Prehistoric and Archaeology, Edaphology and Agricultural Chemistry from the University of Granada (Spain), and from the Centre for Scientific Instrumentation (CIC) from the University of Granada (Spain) as well as some experts in Archaeology participate in the multi-disciplinary research Project on Archaeological Chemistry since 2016, ARCHEM [6].

The objective of the ARCHEM Project is twofold. First to promote and reinforce the cooperation between the chemical and the archaeological sciences. Therefore, the Project will involve an interdisciplinary teamwork with a pluralistic approach to the research methods and common interests.

The second objective of the ARCHEM Project is the development of competencies and abilities for graduate students in the field of archaeological chemistry through the production of Doctoral and Master’s Theses. The learning benefit of analytical chemistry in the archaeological field is reflected in the robust training offered to our doctoral students in this area.
3 ARCHEM RESEARCH PROJECT

The current Project focuses on the analytical study of archaeological materials with a special emphasis on organic residues from ancient pottery. Chemical characterization of these residues could help in determining the sources of raw materials.

It should be noted that, because of the nature of archaeological materials, these analyses are rarely considered “routine analysis”. Each project has its own challenges because of the limited sample size available, the degradation of the organic compounds or contamination of the sample as a result of burial and excavation.

3.1 ARCHEM. Project objectives

Our interdisciplinary group faces two important challenges. First, the characterization of archaeological pottery vessels and of the organic residues preserved in them. Second, to determine the raw materials those were the sources of organic residues.

First, by applying appropriate analytical techniques, the preserved and even degraded biomolecular components of such residues can be revealed.

The second challenge involves the determination of the chemical nature of the raw materials from the identified residues. This is not an easy task, as the qualitative and quantitative composition of the residue differs significantly from that of the primary raw materials due to their biodeterioration. Our goal therefore is extracting the organic matter from the residue with a high recovery rate while being as representative of the original sample as possible. A correlation can be then established between the compounds identified in the extract and the raw material from which they are obtained. It is clear that the closer the qualitative and quantitative composition of the extract is to that of the organic matter in the residue, the more accurate the characterization of the original raw matter will be.

The study and discussion of the chemical results and the study of the archaeological context can provide us with an insight into the habits of the past population of the Peñalosa settlement (Fig. 1). In addition, we will contrast our results with those obtained from other Argaric sites located in the province of Granada (settlements of Castellón Alto in the municipality of Galera and Cerro de la Encina in Monachil). Table 1 shows the general objectives of the project. Each of these aims involves more specific objectives.

Figure 1. Argaric site of Peñalosa (Jaén, Spain)
1. Technological study of Peñalosa ceramics.
3. Application of the analytical method to the samples from Peñalosa vessels recovered from households and burial contexts.
4. Reconstruction of the habits and customs of the population of Peñalosa.
5. Contrasting the results obtained with data from other Argaric sites located in the province of Granada (Spain).

3.2 ARCHEM. Project goals

ARCHEM is an interdisciplinary project that involves a range of approaches, specific objectives and even case studies in archaeological pottery. Some of these objectives begin to be achieved and are discussed below.

The development of analytical methods for the determination of organic substances in the archaeological samples recovered for the Peñalosa settlement was divided into two groups.

First, a GC-MS analytical method was developed. Several instrumental parameters have been tested in order to select the optimal conditions for separation and identification of the compounds, including injection volume, temperature gradient, injector temperature, injection solvent, detector gain and solvent delay. Given the lipidic nature of the compounds analyzed, a previous derivatization step is required. Different derivatizing agents have been tested, with Trifluoromethylphenyl Trimethylammonium Hydroxide, 5% in methanol, showing the best performance. The variables associated to the derivatization reaction have been optimized, including temperature, reaction time, solvent and derivatizing agent concentration.

The second approach was the development of a method for the identification of polar organic substances by liquid chromatography coupled to a High Resolution Mass Spectrometry (UPLC-
HRMS) detector. Different types of chromatographic columns and different mobile phases have been tested with the HSS T3 1.8µm column (2.1 X 100 mm) selected as the working column. Additionally, different types of mobile phase combinations were tested, with water with 0.5% of acetic acid as channel A and acetonitrile as channel B selected as the preferred mobile phase. At present, extraction optimization of the polar organic compounds is being carried out. To do this, polar compounds of known behavior are used as standards whose results are compared to the polar compounds present in the archaeological samples. The proposed analytical methods have been used for the analysis of residues in archaeological samples recovered from settlements of Peñalosa (Jaén, Spain).

The first results of this research study have been published in journals listed in the ISI Web of Science [7,8]. Our students with predoctoral contracts from the Spanish Ministry of Education (FPU and FPI) have presented their work in a number of publications and oral presentations about archaeological chemistry before multidisciplinary audiences in specialized congresses. One of the ARCHEM project students has already completed her Master’s Thesis based on the analytical results from her research [9]. This shows the significance of the learning of archeological chemistry techniques and the importance of researcher-student interactions. Another doctoral student (FPI) has recently joined the ARCHEM project, and is currently investigating the inorganic matter in ceramic pastes from the Argaric site of Peñalosa. To approach the inorganic study supposes to improve the knowledge of these prehistoric artefacts. The skills acquired in analytical techniques will greatly help this student in the study of ancient objects and, in turn, in the reconstruction of past events which will provide us with a better understanding of the Argaric culture.

### 3.3 ARCHEM. Teaching project

A second objective of the ARCHEM project is the development of competencies and abilities in the field of archaeological chemistry through the production of Doctoral and Master’s Theses (Table 2).

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<th>Table 2. Teaching project</th>
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<tr>
<td>1. To write/publish paper in Journal indexed with ISI (International Scientific Indexing)</td>
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<td>2. To speak in multidisciplinary National and International Congresses</td>
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<tr>
<td>3. To defender Master Thesis (1/project year) and Doctoral Thesis (2)</td>
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<td>4. 2 predoctoral contract (FPU, FPI)</td>
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In this way, Master’s degree students (members of the ARCHEM project) will learn a new perspective approach to the study of archaeological pottery including the aspects related to the chemical analysis. This basic understanding of chemical analysis will provide students from humanities background with the skills and abilities for a more complete professional development in Archaeometry. In this context, the idea of adapting the teaching of analytical chemistry to archaeology students has led the team of researchers, members of the aforementioned project, to consider in the future the transmission of knowledge through teaching Chemistry in the Archaeology degree. In this way to consider including the subject of chemistry in the Archaeology degree curriculum so the early learning of this subject will enable undergraduate students from humanities background to unravel the secrets of archaeology through chemistry. This will enable them to understand the concepts and the application of the procedures used by the analytical chemistry experts as well as to understand and interpret the data provided by the analytical analyses. This will help students to extract the maximum amount of information from the ancient objects recovered from different archaeological contexts.

### 4 CONCLUSIONS

Upon successful completion of this project, students will:

1. Be familiar with the physical processes of pottery production and be able to give careful consideration to the social context in which the pottery was produced.

2. Have an overview of the most recent archaeological approaches, analysis and interpretation of ceramics.

3. Be introduced to a wide range of analytical techniques used in pottery studies.
4. Be able to evaluate the implementation of different methods of organic residues analysis in order to answer archaeological research questions about the habits and customs and other aspects of human activities in the past.

5. Learning to defend your PhD dissertation and Master Thesis, speak and defend your research in specialized congress, write your paper to be published in Journal indexed with ISI.

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