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# ARCHAEOLOGICAL CHEMISTRY: A BRIDGE BETWEEN CHEMISTRY AND ARCHAEOLOGY

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**Abstract:** The review takes into consideration the importance of chemistry in the study of the human past, mainly, for the authentication and the provenience determination as well as the characterization of archaeological artifacts. Archaeological chemistry is an unbreakable linkage between archaeology and chemistry and has rapidly grown in the last few decades. The use of chemistry in archaeology can help archaeologists provide valuable information for the learning of archaeological sites and artifacts. Over the years, new chemical techniques have been improved, and the vital role of chemists in evaluating the development of technology and other activities of ancient civilizations has been increased. In addition to discovering the past, chemists should consider the physicochemical and analytical degradation procedures for preserving the heritage of humanity for our children and the next generations to enjoy, benefit, and learn from the legacy of the past. Furthermore, here, some commonly used analytical techniques such as neutron activation analysis (NAA), inductively coupled plasma (ICP), gas chromatography-mass spectrometry (GC-MS), X-ray diffraction (XRD), and X-ray fluorescence (XRF) are briefly described regarding their use for archaeological artifacts. We hope that this article will be helpful for students who are new to the field, in addition to interesting productive argument among experienced researchers.

**Keywords:** Archaeological chemistry, Analytical methods, inductively coupled plasma (ICP), neutron activation analysis (NAA), X-ray diffraction (XRD), X-Ray fluorescence (XRF).

**چکیده:** این کار اهمیت شیمی را در مطالعه گذشته بشر، عمدتاً برای احراز هویت و تعیین منشأ و همچنین توصیف آثار باستان‌شناسی را نشان می دهد. شیمی باستان‌شناسی پیوندی ناگسستنی بین باستان‌شناسی و شیمی است که در چند دهه اخیر توسعه یافته است. کاربرد شیمی در باستان‌شناسی به محققین کمک می‌کند تا اطلاعات ارزشمندی از مکان‌ها و آثار باستانی بدست آورند. با گذشت زمان، روش‌های شیمیایی تکامل یافته و نقش کلیدی شیمیدانان در مطالعه تمدن‌های باستانی افزایش یافته است. علاوه بر کشف گذشته، شیمیدانان باید به فرآیندهای فیزیکی، شیمیایی و تجزیه‌ای که می‌توانند موجب تخریب آثار بازماندگان شود توجه کنند و آن را برای فرزندان ما و نسل‌های بعدی به درستی حفظ کنند. در این مقاله، همچنین برخی از تکنیک‌های شناسایی متداول آثار باستانی مانند آنالیز فعال‌سازی نوترون (NAA)، پلاسمای جفت شده القایی (ICP)، طیف‌سنجی جرمی-کروماتوگرافی گازی (GC-MS)، پراش اشعه ایکس (XRD) و فلورسانس اشعه ایکس (XRF) به‌طور مختصر توضیح داده شده است. امیدواریم این مقاله برای دانشجویان و محققان رشته شیمی و باستان‌شناسی مفید واقع شود.

**کلیدواژه:** شیمی باستان‌شناختی، روش‌های آنالیزی، پلاسمای جفت شده القایی (ICP)، تجزیه و تحلیل فعال سازی نوترون (NAA)، پراش اشعه ایکس (XRD)، فلورسانس اشعه ایکس (XRF).

## I. Introduction

Archaeological chemistry, as a subclass of archaeometry, is the study of the human past, mainly, the authentication and the provenience determination, and characterization of archaeological objects through the analysis of material leftovers. Cultural evolution can be tracked in the continuing growth of the stone implements manufactured and the materials used by early humans. In the course of time, objects were prepared from native metals like gold, silver, and copper. As time passed, fire was applied to modify the physical features and the composition of some materials. Accordingly, solid objects including pottery, glass, and metals have chemical compositions that come from the natural or synthetic chemicals used through the development of human skills. Analytical methods can provide the data to answer many critical scientific questions in archaeological research. The usage of chemical analysis to improve our understanding of ancient materials, culture, technology, and society is not new. Archaeological chemistry was begun by chemists (Pollard, 2007; Price & Burton, 2010; Nigra et al., 2015). John W. Mallet (1852) was the pioneer of chemical investigations of Celtic artifacts, in the 1880s. Mallet investigated the chemical compositions of the sources of the raw materials used and evaluated the data with his geological information. Accordingly, he established that through the early Christian period, the Celts utilized just native gold before it was possible to extract silver from ores. Since these early days, analytical methods have been developed, and the key roles of chemists in archaeology have been highlighted. A lot of elements and isotopes have been considered in the study of provenience. For instance, for a long time, Lead isotopes have been considered to identify the sources of bronze artifacts (Liu et al., 2018; Oudbashi et al., 2021). In general, bronze is comprised mostly of copper with about 12-12.5% tin and other metals. Copper or tin can separately include a small amount of highly radiogenic lead with the different rations, which permits to identify of their possible areas. Using the carbon and nitrogen isotopes from organic residues (e.g. wood, hide, bone, antler, and thatch, etc.) human diets, climate, and other aspects of the past can be studied. There are various other examples of the application of archaeological chemistry in exploring and understanding the past.

Archaeological chemistry is a continually developing field, and with new techniques and instruments come new information in detailed chemical studies of archaeological objects, helping to decrease the problems of data management and the deterioration of value added artifacts and materials. For careful analysis, the condition of the sample as very rare or valuable ingredients, the sample preparation procedure, the use of destructive or non-destructive testing techniques must be considered before the experiment run. Many apparatuses involve destructive sample preparation methods in powder or liquid forms. For instance, neutron activation analysis (NAA) and XRD use samples in powder forms. In addition, some instruments such as ICP and GC-MS are intrinsically destructive analytical techniques. In archaeological chemistry, it is vital to have a balance between key aspects of protecting and maintaining the heritage of humanity for the next generation and the importance of learning as much as we can about them.

In the following section, we give an overview of the most used and efficient tools in archaeological chemistry.

## II. Neutron Activation Analysis (NAA)

Neutron activation analysis, discovered in 1936, is an instrumental technique for determining the concentration of elements through the measurement of gamma rays emitted from temporarily radioactive elements of a sample that was irradiated by neutrons. The energies of gamma rays are specific for each element and allow the identification and measurement concurrently. Various types of stone are analyzed by means of NAA, but since it is needed to grind samples into powder forms for analysis, this technique is destructive. There are a number of different neutron sources, but nuclear (uranium fission) source with high fluxes is the most sensitive mode. However, there are some obstacles such as the convenient use of NAA and disposing nuclear waste which limit the application of such reactors.

### III. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma (ICP) can generate a torch with temperature between ~6,000 K and ~10,000 K (~6 eV – ~100 eV), which results in the degradation of the samples to individual elements and hence, this technique can be used for the rapid determination of trace element concentrations and elemental (or isotope) ratios. ICP systems are capable of analyzing most elements (~82 elements) in the periodic table simultaneously. Based on the detection method, it can be classified into inductively coupled plasma optical emission spectroscopy (ICP-OES), of which the quantitation is based on measurements of the intensity of characteristic wavelength of the goal element, and inductively coupled mass spectrometry (ICP-MS) (Al-Hakkani, 2019) which measures an atom's mass. ICP-MS can be applied to sense very low concentrations (as low as parts per trillion, ppt) in comparison to ICP-OES (as low as parts per billion, ppb). For both techniques, the solid must be completely digested (dissolved) before injection into the instrument. As a hybrid mass spectrometer, multi-collector ICP-MS (MC-ICP-MS) can be used for high-precision measurements of isotopic compositions even at lower levels than those of ICP-MS.

### IV. Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS instrument combines two powerful techniques to separate and identify volatile organic compounds (approximately boiling points below 350°C) by the mass of each molecule/fraction as a function of retention time. It is one of the common tools for analyzing organic archaeological materials such as visible and absorbed pottery residues, pigments, blinders, and other organic residues (Reber, 2020). It is important that the identity of the material is verified by comparing the GC-MS chromatograms with those of known materials.

### V. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns are produced by the interaction of incident X-ray and power crystal samples (Holder & Schaak, 2019). The crystal planes in crystalline materials have distances equal to the X-ray wavelength and yield diffraction of X-rays with regions with increased or decreased X-ray intensity (Ali et al., 2022). XRD is one of the most powerful methods to investigate structures and composition of crystalline materials (inorganic and organic materials), crystalline orientation, crystal size (Scherrer equation), phase transformation, and crystal defects. The position of diffraction peaks associates with the interplanar distance based on Bragg's law:

$$n\lambda = 2d\sin\theta$$

where n is an integer number, $\lambda$ is the wavelength of the X-ray source, d is the distance of near diffracting planes, and $\theta$ is the incent angle of the X-ray source.

Sample phase purity can be confirmed by comparing the experimental powder pattern with a reference pattern that is either simulated or achieved from an existing one. In archaeology, XRD is usually used to identify the minerals existing in ceramics, rock, and sediment samples. The next advantage of the XRD technique is that the instrument is portable and allows simultaneous and real-time monitoring. However, it is needed to prepare powdered samples for careful analysis.

## VI. X-Ray Fluorescence (XRF)

The X-ray fluorescence technique is the most common non-destructive tool for the identification of the type and amount of elements in an archeological sample of various forms through the determination of the wavelength and intensity of the X-ray fluorescence (or secondary waves) emitted from different atoms in the solid induced by X-ray beams (Pushie et al., 2014). However, elements lighter than magnesium are difficult to measure directly by XRF. XRF portable instruments permit fast and in-situ analyses.

## VII. Conclusion

In summary, we have outlined an overview of the chemistry in archaeology and the most common techniques used in the field. Indeed, archaeological chemistry is the study of the past through chemistry, art, and geology. Portable XRD and XRF are now available as small and light units for fast and in-situ characterizations. Archaeological chemistry is a developing and growing field, and with new techniques/portable instruments come new developments and information updates.

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