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# Modern analytical chemistry in archaeology and arts: An overview

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**ABSTRACT**

The relationship between analytical chemistry, arts, and archaeology and the role of the analytical techniques in archaeology and arts have been discussed. The analytical techniques have been divided and listed into sample destructive and non-destructive techniques. Each technique has been discussed briefly.

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## 1. Introduction

The historical relationship between scientific approaches and techniques and prevailing theoretical views regarding past human behavior has been reviewed by Trigger who states that *'archaeologists have asked different questions at different periods. Some of these questions have encouraged close relations with the biological and physical sciences, while other equally important ones have discouraged them.'* During the 1960s, archaeology embraced the sciences, not only the techniques but also the terminology of scientific methods for explaining human behavior. During the last decades, general attitudes in society towards science have been shifting towards a more critical point of view. Therefore, the contribution of scientific analysis to the study of the past has come under increasing inquiry (Pollard, 2011; Trigger, 1988; Pollard and Heron, 1996).

There is a strong practical requirement to extract the maximum information from the material remains recovered during archaeological investigations. The application of analytical chemistry includes the detection and quantification of the inorganic elements, and also, including methods of organic analysis, and isotopic abundances for a range of elements (Pollard, 2011).

Archaeology uncovers a variety of physical remains that vary from simple stone artifacts, to complex metal alloys, to food residues on pottery vessels, therefore, chemists have been giving their efforts to apply most sophisticated analytical techniques to these artifacts since the 18th century to get information where the raw materials came from, how materials were made, what diet ancient peoples consumed, or how alloy composition changed with time and place (Lambert, 1999).

Analysis of archaeological material presents a number of challenges, including the small amount of sample available, the presence of complex mixtures, chemical alteration due to processing or degradation, and contamination. Furthermore, every sample is unique. These factors are against simple interpretations of analytical results (Heron and Stacey, 2000).

There are four main steps in chemical analysis process, sampling, sample preparation, measurement, data analysis and interpretation. Whatever the technique used for analysis in archaeology, the most important step is the interpretation of the results in order to obtain complete information about the sample. This step needs a lot of requirements and information or colleagues involved in many different fields of sciences, but from analytical chemistry side, sample preparation is also of great interest.

Indeed, all materials, both organic and inorganic, changed and are permanently attacked and degraded by many different factors, including the environment (light, humidity, temperature, pollution, vibration, etc.), nature (flood, earthquakes), accidents (fire), and the human himself (handling, transporting, theft, the general public).

According to Lahanier (1991), a museum laboratory`s assignments can be broken down into five aims:

- Research into ancient techniques: their dating, origin and workmanship. Such research is reported on the publications and specialized conferences under the heading "archaeometry", which includes aerial and prospecting archaeological sites.
- Enlarging collections: problems of authentication, attribution and state of a work that determine its evaluation.
- Conservation- restoration: drawing up a work`s medical file by a laboratory.
- To distinguish the original parts from the later additions
- To determine the change in appearance and in physical properties due to ageing processes
- To discover the cause of deterioration and the mechanism involved prior to the restorer`s diagnosis and action.

– Preservation: study of conditions conducive to the durability of collections both in permanent and temporary exhibition halls and in reserve collection.

For many materials, characterization begins with macroscopic observations and measurements of physical properties such as color, density, hardness, and refractive index. The next step for many materials is microscopic examination (Lahanier, 1991). Although the increasing need for the scientific methods in field of archaeology, there is a lack in the literatures focusing on the application of analytical techniques in archaeology.

## 2. Analytical techniques

The selection of the analysis method or technique is dependent upon: (1) the type and the value of the sample, (2) the analyte(s), (2) the analyte concentration level(s), (3) the sample matrix, and (4) the precision and sensitivity of the instrumental measurement technique.

In the following, we are going to discuss briefly the most useful methods of analysis and most convenient for archaeological objects. From archaeology point of view, it is important to discuss the analysis techniques as destructive and non-destructive.

### 2.1. Techniques that destroy samples (Destructive):

In addition to the classical methods of analysis, there are many different simple and sophisticated instrumental methods for chemical composition analysis.

*UV and visible (UV/VIS) spectrophotometry.*

Organic or inorganic reagents are used for specific tests for many elements or compounds by forming a compound that absorbs at specific wavelengths. The products may or may not be colored. If the compounds are colored, analysis may be carried out visually (colorimetric analysis by eye) but use of a spectrometer is more accurate. Sensitive and selective methods have been developed for most elements and many functional groups (Robinson et al., 2005).

*Atomic absorption spectrometry*

It is a very accurate and sensitive method for the quantitative determination of metals and metalloids down to absolute amounts as low as picograms for some elements. It cannot be used directly for the determination of nonmetals (Bings and Bogaerts, 2010; Moretto et al. 2011).

*Flame atomic absorption spectrometry (FAAS)*

A mature analytical method, which is present in almost any analytical laboratory as a working horse for determinations of elemental metals (Bings and Bogaerts, 2010; Moretto et al. 2011).

*Atomic emission spectrometry (AES)*

It is an almost comprehensive method for qualitative elemental analysis for metals, metalloids, and nonmetals. Its sensitivity range is great, varying from parts per billion to percent levels. Many elements can be detected simultaneously. Spectral overlap is the major limitation. AES is used extensively for the quantitative determination of elements in concentrations from ppm levels down to ppb (Bader, 2011; Bader and Zimmermann, 2012).

*Flame photometry*

Flame photometry is particularly useful for the determination of alkali metals and alkaline-earth metals. It provides the basis for flame tests used in qualitative analysis schemes. It provides much simpler spectra than those found in other types of atomic emission spectrometry, but its sensitivity is much less (Pollard et al., 2011).

*Electrothermal atomic absorption spectrometry*

Especially with graphite furnaces (GFAAS), has developed in the past decades to an unrivaled method for ultra-trace analyses at an affordable price.

The analytical advantages of GFAAS are that its detection limits which is about two orders of magnitude better than either FAAS or ICP-AES (inductively coupled plasma – atomic emission spectroscopy) and its lower sample consumption (Bader and Zimmermann, 2012).

*The inductively coupled plasma (ICP)or inductively coupled plasma atomic emission spectrometry (ICP-AES)*

The most commonly used type of plasma techniques. Sample preparation methods for ICP analysis of trace metals can be found in many sources. The sample introduction for ICP applications requires that samples be in a liquid form so as to be aspirated through a nebulizer and that suspended solids must be removed to prevent clogging of the nebulizer. Therefore, solid samples such as soils and sludges must first be acid digested to extract the metals of interest from the solids, prior to analysis (Pollard et al., 2011; Bader, 2011; Bader and Zimmermann, 2012).

*Inductively coupled plasma-Mass spectrometry (ICP-MS)*

Similar to ICP-AES, except that after ionization in the plasma, the ions pass into a mass spectrometer for separation and measurement. There are few mass spectral overlaps, and for elemental analysis nearly all can be overcome by analyzing alternative isotopes (Bader and Zimmermann, 2012; Martini et al., 2004).

Application of ICP-MS in archaeology have mostly centered on determining geological provenance, where different elemental patterns or isotopic ratios have been taken as signatures of different geographical locations (Pollard,2011).

*Mass spectrometry (MS)*

It can be used to identify the molecular weight of organic and inorganic compounds, from very small molecules to large polymers and biological molecules. It is a powerful tool in the determination of the structure of organic compounds, can also identify elements, isotopes and polyatomic ions in solutions and solid samples at ppt concentrations or below.

Inorganic MS is used for simultaneous multielement analysis for metals and nonmetals. It provides the isotope distribution of the elements. Special mass spectrometers are used for accurate isotope ratio measurements used in geology and geochemistry (Martini et al., 2004).

*Gas chromatography (GC)*

Gas chromatography can be used to separate the components of complex mixtures of gases or of volatile compounds. By comparison with known standards, it can identify components based on retention time.

Gas chromatography is an accurate method for quantitative analysis using the peak area and compared with internal or external standards. Gas chromatography (and analytical techniques)is often coupled with the selective techniques of spectroscopy or electrochemistry, thus giving so-called hyphenated methods that provide powerful tools for analysis (Skoog et al., 1998).

GC with MS detection (GC-MS) is a powerful tool for quantitative analysis of organic compounds in environmental, biological and archaeological samples (Pollard et al., 2011; Robinson et al. 2005).

*Liquid chromatography (LC) or high performance liquid chromatography (HPLC)*

LC is used for the quantitative determination of components in mixtures, especially for high molecular weight or thermally unstable compounds. It is particularly useful for separating

complicated mixtures such as natural products derived from plants or animals and biological samples such as urine and blood. LC with MS detection (LC-MS) is also a powerful tool for quantitative analysis of organic compounds in environmental, biological and archaeological samples (Pollard et al., 2011; Robinson et al. 2005; Mantzouris et al., 2016).

It is used mainly in study of organic material from pottery and mummified human remains. Characterization of organic residues generally relies upon the principles of chemotaxonomy, where the presence of a specific compound or distribution of compounds in an unknown sample is matched with its presence in a contemporary natural substance (Heron and Stacey, 2000).

*Neutron activation analysis (NAA)*

Involves converting some atoms of the elements within a sample into artificial radioactive isotopes by irradiation with neutrons. The radioactive isotopes so formed then decay to form stable isotopes at rate, which depends on their half-life. Measurement of the decay allows the identification of the nature and concentration of the original elements in the sample. It is applicable to a wide range of archaeological materials (Kellner et al., 1998; Pollard et al., 2011). This method offer several advantages including high sensitivity, ease of calibration, and like other non-destructive techniques, minimal sample preparation. The major disadvantages of activation methods are their need for large and expensive equipment and special facilities for handling and disposing of radioactive materials and the long time required to complete analyses when long-lived radionuclides are used (Skoog et al., 1998).

### 2.2 Techniques that not destroy samples (non-destructive):

*Ultra violet lighting*

Ultra violet lighting of an object causes the emission of fluorescence in the visible spectrum of it is surface elements. The emission's heterogeneity reveals changes that often arise from occasional restorations (Lahanier, 1991).

*Infrared reflectance spectroscopy*

Because it can easily identify the -OH group in many materials, it has proved useful for the study of corroded glass and weathered obsidian, where the corrosion manifests itself as hydrated layer penetrating into the material from the surface. Collection of multiple reflections from the surface of a solid sample is suitable for the measuring of water content in glass surface as a dating technique (Pollard et al., 2011; Zidan et al., 2016).

*X-ray fluorescence (XRF)*

In addition to X-ray photography, X-ray fluorescence is useful for elements with atomic numbers greater than 4, including metals and nonmetals. For qualitative analysis, no sample preparation is required and the method is generally nondestructive. XRF is used extensively for quantitative determination of elements in alloys, glass, and mineral samples, particularly of elements with high atomic weights. Sample preparation is complex for quantitative analysis (Robinson et al. 2005; Bader and Zimmermann, 2012; Al-Bashaireh et al., 2016).

Since XRF meets a number of ideal requirements, analysis of objects of artistic and/or archaeological value with conventional XRF is fairly common; it is in fact one of the most often applied methods for obtaining qualitative and semi-quantitative information on the materials of which these objects are made (Pollard and Heron, 1996; Johansson and Campbell, 1988; Janssens, 2000).

This type of non-destructive analysis can be conducted very quickly. XRF is becoming an increasingly popular method for chemical analysis, and the portability of the system used here allows for the easy implementation of the method across the varying fields of art and archaeology, since sampling is in most cases restricted in view of the importance or uniqueness of the object. In-situ XRF analysis can provide answers to specific analytical problems and therefore, in many cases, offer unique data for archaeological research (Pantazis et al., 2002).

As archaeological and historical objects are often unique and may be not easily movable, a portable XRF detector system allowing in situ analysis is ideally suited for archaeometric applications (Hocquet, 2008). There are a large number of examples of the use of XRF in distinguishing pottery shards from different region, usually in combination with other methods (Pollard, 2011).

*Scanning electron microscopy*

It can refine the microscopic studies of metallographic sections, thin slices of ceramic or stone, stratigraphic sections of picture material not only by local analysis, but also by mapping the distribution of chemical elements (Lahanier, 1991).

*Proton activation*

This technique is particularly suited to the analysis of museum objects as the energy of highly accelerated particles (> 7 MeV) makes them penetrate deeply into the matter thereby reducing the errors due to contamination of the surface of archaeological objects (Lahanier, 1991).

### 3. Conclusion

There are many different techniques in analytical chemistry are related to archaeology and arts. The analytical methods can be divided into destructive and non-destructive techniques. Synergy between analytical chemistry and archaeology and arts will allow improving the quality and precision of the obtained information.

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