APPLICATION OF SCIENTIFIC METHODS FOR THE CHARACTERISATION OF ARCHAEOLOGICAL MATERIALS

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The restoration of cultural heritage objects can be addressed both by traditional methods and by modern techniques, involving transdisciplinary studies and knowledge of scientific methods. Many scientific disciplines contribute with their specific methods of investigation, to the formation of a real image of the "state of health" of different objects, and in this context, to the prevention of degradation, curative or restoration, analytical techniques can offer a special participation in special studies. It is well known that every technique can offer different types of results, but the use of more than one method in the analytical process can offer better results. Also, every technique *present advantages and disadvantages regarding the measurements of the samples and the obtained results. Herein there are described some cases of ceramic objects analytical characterization (materials often requiring the application of several techniques for a correct characterization), and, in the same time, presenting the advantages and disadvantages of using these techniques.*

Introduction

The degradation of cultural heritage is the effect of destructive agents, the result of a succession of physicochemical processes that gradually alters the shape, the aesthetic of support materials to the stage that makes it impossible to use them as testimonies of history of human civilization. The restoration of cultural heritage objects can be addressed both by traditional methods and by modern techniques, involving transdisciplinary studies and knowledge of scientific methods.

Many scientific disciplines contribute with their specific methods of investigation, to the formation of a real image of the "state of health" of different objects, and in this context, to the prevention of degradation, for curative or restoration approaches, analytical techniques can offer a special participation in special studies. In the last decades, most of the published studies involve the application of various analytical techniques for obtaining relevant information; in many cases, chemical composition is the first necessary criterion.

Generally, for the preservation and restoration of cultural and historical value materials and artifacts, a range of analytical methods are used to provide information on:

• chemical composition/nature of the analyzed materials; this information can often be used to elucidate their provenance;

• the state of degradation (on the surface and/or internal) of objects as a result of exposure over a certain period to environmental conditions;

• the effect/effectiveness of conservation/restoration strategies during their application.

Each individual application requires a thorough study, evaluating the advantages and disadvantages of each micro-destructive or non-destructive method, and selecting the appropriate ones for achieving the desired results. The criteria for choosing the methods of investigation of the artifacts are: a minimum sample volume; the sensitivity of the method and quantitative results. Also, they must be non-destructive, versatile, precise and multi-elemental.

For ceramic materials, the use of analytical methods presents a great importance: they can offer information regarding the raw materials, human traditions and regional history. Analytical methods can offer complex information when are used *in tandem*; usually, methods based on ionizing radiation (X-Ray Diffraction – XRD, X-Ray Fluorescence – XRF, Particle Induced X Ray Emission – PIXE, etc.) can be used with microscopical and spectrometric techniques (Raman or μRaman spectrometry, IR spectrometry, Inductively coupled plasma mass spectrometry – ICP-MS, etc.).

Advantages and disadvantages of the main classes of analytical techniques

Methods based on ionizing radiation are well established methods used for the characterization of Cultural Heritage artifacts. These techniques can be applied for samples from different artifacts offering information regarding phase identification and quantification of crystalline compounds and complex polyphase mixtures, atomic and molecular structure of phases, texture and orientation of crystalline phases, and microstructural physical state of the material regarding the size of the crystallites. It can also be used as a portable technique. One advantage of the method is that the size of the sample required for the analysis can be extremely small – mm^2 or a few granules of powder, and with some types of equipment, the analysis can be performed directly on the surface of small and flat objects.

For the portable X-rays equipment has been developed a great interest in the last period, especially for the characterization of ancient objects. These types of equipment are considered the most effective tools for a successful *in situ* non-destructive elemental analysis. XRF technique is often applied for such estimation, elemental composition being usually the first step towards the identification of the materials[1]. A quantitative analysis is rather hard to perform using this type of equipment, due to the instrumental limitations and particular properties of the analyzed materials; however, the qualitative analysis is reliable, and in some cases, if correlated with other techniques, can prove to be sufficient. If for some type of artifacts (such as the metallic ones), X-ray fluorescence can prove to be very efficient for their characterization[2], for other types (i.e. ceramic artifacts), several limitation must be considered: first of all, the nature of the analyzed material (low density, poor homogeneity, etc.) can offer misleading results, if the technique is not adapted to the sample (for example, in order to gain more information from heterogeneous samples, a mapping of the sample may be achieved, using multiple analysis points); more than that, the intrinsic characteristics of the technique (such as limited penetration of the incident radiation) can lead to an over-estimation of the elements found mainly in the surface layers. This is extremely important for the artifacts with significant differences between the surface and bulk composition. This phenomenon can be overcome by sample treatment (such as grinding, melting) or by performing cross-section analysis. If these types of treatments can not be applied, other techniques should be used for reliable results[3].

Microscopic and associated techniques (such as Scanning or Transmission Electron Microscopy – SEM/TEM, Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy – SEM-EDS, Electron Backscattering Diffraction – EBSD, etc.) are useful techniques, often used in cultural heritage studies for powdered and bulk samples, combining high-resolution images with elemental chemical analysis. The limitations of these techniques are regarding the complexity of the structure and difficult surface preparation. For example, EBSD technique may require the polishing of the analyzed object. For applying microscopical methods a good surface state is needed, in order to obtain good information. By the application of EBSD to the analysis of ceramic or vitreous materials, it can be defined the crystalline particles (otherwise impossible to distinguish by other methods, such as XRD or SEM-EDS, in bulk samples), particles that can be related to the production technology. From all the microscopic techniques, EBSD can offer crystallographic information over a wide enough area and phase-identification that can be added to the chemical information of the ancient material[4].

Spectroscopic methods are very useful in characterization ancient objects. These methods can be used to characterize the composition and structure of a wide range of substances: organic and inorganic molecules, are micro-destructive or even

[1] Fierascu *et al.* 2017, p. 18.
[2] Fierascu, Ion, Fierascu 2015, p. 107.
[3] Ion *et al.* 2015, p. 487.
[4] Pérez-Arantegui, Larrea 2015, p. 193.

non-destructive when using non-contact instrumentation, and some of the spectroscopic equipment are portable.

From this category the most frequent and accessible technique is infrared spectrometry. FTIR spectrometry is essential in characterization of archaeological artefacts. This approach was pioneered by Weiner, who used FTIR spectroscopy for the analysis of archaeological samples[5]. For analysis of ceramic objects, FTIR spectroscopy is used especially for offering information regarding the manufacture of ceramics, analyzing extremely small samples[6]. The disadvantages of IR methods, are related to the sensitivity to luminescence also in the NIR and to light absorption for colored and opaque samples[7].

Methods based on inductively coupled plasma techniques are also methods used frequently for the archaeological samples. Even it is micro destructive, this method can provide information regarding trace elements, at the *ppm* level, with multi elemental quantification with only one measurement. The disadvantages of this methods usually relate to the sample preparation, being a micro destructive method, and requiring supplementary equipment for sample preparation. When ICP methods are combined with laser ablation (for example in instruments like Laser Ablation Inductively Coupled Plasma Mass Spectrometry – LA-ICP-MS), it can be determined elements with concentrations in the range of *ppm*, minimizing visible damage on the ceramic samples, using a laser beam with a certain diameter, laser energy and a pulse frequency.

From the spectroscopic methods using lasers, the laser induced breakdown spectroscopy (LIBS) is the most important for ceramic artefacts. These methods can be used to identify both the inorganic and organic components with high sensitivity and reproducibility. LIBS represent a rapid technique, capable of *in situ* analyses, micro-destructive (nanograms of material are ablated). The method can analyze various objects with high spatial resolution at the surface and in-depth, in air and at room temperature, even they are heterogenous samples. LIBBS coupled with other techniques (as Raman spectroscopy) can offer information regarding dating and provenance[8]. Laser-induced-fluorescence (LIF) spectroscopy is a specific class of fluorescence or luminescence spectroscopy which use a monochromatic laser source, in pulsed or continuous operation, as an excitation source. The fluorescence of natural minerals is usually due to intrinsic defects in their structure or trapped impurities. LIF can be used for the characterization of different minerals which contain ions from transition metals or rare elements[9].

Thermo analytical methods has been developed in the last decades, offering complex approaches for the study of cultural heritage objects. From these techniques we can mention differential scanning calorimetry (DSC), thermogravimetry (TG), thermomechanical analysis (TMA), dielectric analysis, dynamic mechanical analysis (DMA), and micro-thermal analysis (μ-TA). Especially for ceramic artifacts, these techniques can offer information related to their manufacture procedures and provenance of raw materials. Also, these techniques are able to present the

[5] Weiner, Goldberg, Bar-Yosef 1993, p. 613.
[6] Maniatis, Tsirtsoni 2002, p. 229.
[7] Cîntă Pînzaru, Pop, Nemeth 2008, p. 31.
[8] Lopez *et al.* 2006, p. 695.
[9] Mason, Clouter, Goulding 2011, p. 169.

characteristics and levels of pollution in the surrounding environment in which are kept the artefacts[10].

Case studies

Methods based on ionizing radiation, like X-Ray diffraction, X-Ray fluorescence, PIXE, etc., can offer important information regarding the major or trace and rare earth elements through a complete the mineralogical and chemical characterization. The level of concentration of certain elements can be considered a “chemical fingerprint” of the ceramic sample. The determination of the trace element concentration is very useful to approach the origin of the materials. Mineralogical studies, often completed with the geological information, can provide information regarding the provenance of the raw materials, as well as on the manufacturing conditions (such as firing temperature for the ceramic artifacts)[11]. For example, some authors associated the presence of calcite with firing temperatures below 800-850 °C, whereas the presence of gehlenite (formed at 900-950 °C from the reaction of calcite or dolomite with the clay minerals[12]) would suggest appropriate firing temperatures; other elements that can be used for the estimation of the firing temperature (such as quartz and illite) may remain stable up to almost 1000 °C[13].

In the case of objects analyzed from Cuatrovitas archaeological settlement (Bollullos de la Mitación, Seville, Spain), mineralogical analyses were performed with XRD technique. The mineralogical composition of the field samples shows variable content of calcite and quartz and minor feldspars and phyllosilicates, dividing samples into two categories: samples with presence of high temperature minerals such as diopside-anorthite-gehlenite and low contents in calcite and samples with low contents of calcite and without diopside and gehlenite[14]. In the described case, the XRF analysis was used to evaluate the calcium content of the ceramic paste. Two groups can be differentiated in ceramic sherds: samples with high Ca (> 5.5%) and Mg (> 1%). The analysis by micro-XRF on the surface of the ceramics revealed some heterogeneity of the samples, due, according to the cited authors, to presence of paintings or efflorescence. The results of the performed analysis in this research paper revealed at least, two different types of raw materials: those with a high Ca and Mg and those with low Ca and Mg content, also suggesting that the objects raw material was from a different area to the one where the objects were discovered.

These methods were successfully applied in the case of the vessels from a pottery assemblage recovered in the excavations conducted in 2008 at the site of Kurganzol, the Hellenistic fortress in ancient Bactria[15]. The conclusions of the cited study were that most of the wares can be associated with a single clay source, while the being identified two specific technological processes. The study suggests that the fortress was mainly supplied by pottery produced locally.

A complex couple of methods was used in the case of Islamic and post Islamic ceramic recovered from the town of Santarém[16]. The multi-analytical approach involved

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[10] Ghedini, Sabbioni, Pantani 2003, p. 105.
[11] Palanivel, Kumar 2011, p. 56.
[12] González García *et al.* 1990, p. 361.
[13] Miras *et al.* 2018, p. 176.
[14] González *et al.* 2018, p. 38.
[15] Martínez Ferreras *et al.* 2018, p. 1044.
[16] Beltrame *et al.* 2019, p. 910.

the application of optical microscopy (OM), powder and micro X-ray diffraction (PXRD and μ-XRD), μ-Raman spectroscopy and attenuated total reflection-Fourier transform infrared spectroscopy (ATR FT-IR) for determining the mineralogy and petrography of the samples. Bulk chemical analysis was obtained by XRF and ICP-MS, while by SEM-EDS was obtained the microanalysis of the ceramic paste and of the decorative layers.

XRD results indicate that the mineralogical composition of the samples under investigation is very similar. The presence of illite/muscovite and mullite allowed the authors to propose the temperature range 700-950 °C as operating temperature for the kilns of the town of Santarém. μ-XRD and SEM-EDS analysis of the decorations also established the composition of the pigments: calcite in white pigments, hematite in the red, and magnetite and hematite in the black enamel. μ-Raman and ATR FTIR spectroscopy identified a schorlitic iron-rich tourmaline which is present in several ceramic samples from different fabric, chronological periods and archaeological sites indicate the same raw materials for all the samples. SEM-EDS microanalysis also established an insignificant contribution of the calcium to the bulk chemical composition. Results indicated that the samples were locally produced, suggesting, a continuity in the raw material exploitation during the Islamic period and during the Reconquista by Portuguese king, confirming that a modification in the political power did not correspond to a change in ceramic technology.

XRD, XRF and Environmental Scanning Electron Microscopy, coupled with Energy Dispersive X-ray system (ESEM-EDX) were used for the determination of the morphological, chemical and mineralogical characteristics of the potsherds from Aiani western Macedonia (Greece)[17]. The raw materials used to manufacture the ceramic objects correlated to the specific utilization of each vessel. The presence of different minerals (like gehlenite or pyroxene) indicated higher firing temperatures, while other minerals (phyllosilicate) indicate lower temperatures.

Conclusions

These are few examples of using analytical techniques in the characterization of ancient ceramic artefacts. It is well known that every technique can offer different types of results, but the use of more than one method in the analytical process can offer better results. Also, every technique present advantages and disadvantages regarding the measurements of the samples and the obtained results. Using these techniques coupled it can be analyzed stages of the degradation process; the nature of the products resulted from degradation processes, and influence of different factors on the structure and morphology of the investigated samples, which determines the degradation behavior. Our present work represents, besides a short overview of the scientific basis of the analytical investigations of historical artifacts, an invitation and an encouragement for trans-disciplinary studies, that can lead to an increase of knowledge in this very important area.

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[17] Iordanidis, Garcia-Guinea, Karamitrou-Mentessidi 2009, p. 292.

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Aplicarea metodelor științifice pentru caracterizarea materialelor arheologice

Rezumat

Restaurarea obiectelor de patrimoniu cultural poate fi abordată atât prin metode tradiționale, cât și prin tehnici moderne, care implică studii transdisciplinare și cunoașterea metodelor științifice. Multe discipline științifice contribuie cu metodele lor specifice de investigare, la formarea unei imagini reale a „stării de sănătate” a diferitelor obiecte și, în acest context, prevenirii degradării, curativ sau pentru restaurare, tehnicile analitice pot oferi participare specială la studiile de specialitate. Este bine cunoscut faptul că fiecare tehnică poate oferi diferite tipuri de rezultate, dar utilizarea mai multor metode în procesul analitic poate oferi rezultate mai bune. De asemenea, fiecare tehnică prezintă avantaje și dezavantaje privind măsurătorile probelor și rezultatele obținute. În prezenta lucrare sunt descrise câteva cazuri de caracterizare analitică a obiectelor ceramice (materiale care adesea solicită aplicarea mai multor tehnici pentru o caracterizare corectă), și, în același timp, prezentând, de asemenea, avantajele și dezavantajele utilizării acestor tehnici.