METHODS OF ANALYSIS USED IN CERAMICS AS AN EFFECTIVE PROCEDURE IN THE CONSERVATION OF TERRACOTTA SCULPTURES

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The analytical techniques used in ceramics should be considered an essential procedure in research of terracotta sculptures. The application of these methods may contribute decisively to the preservation of this artistic heritage, by providing an insight into the composition, technology and behaviour over time of this material.
Studies remain scarce and incomplete when referred to terracotta as main material for sculpture. Terracotta has been used as a medium for sculpture since prehistoric times, and was especially important in the Renaissance and Baroque periods, when it was used to create complete pieces. As these pieces often have their own particular finishes and surface treatments, the methods of analysis must be adapted in order to ensure that relevant information can be obtained.
We have focused on the specific methods that help us to identify the geographical origin of the piece, to date it, to analyse the intrinsic characteristics that can lead to long term damage, and to assess the behaviour of the material through that of test samples.

Introduction

Although terracotta has frequently been used in different art forms over the centuries, there have been relatively few studies of its use in sculpture. This contrasts with the wide range of technical studies of other materials typically used in sculpture such as wood, stone, metal, etc. These studies have focused, for example, on the identification of the wood type, the degree of resistance of the stone or the level of deterioration of the support measured by different analyses, among other useful information. However, in the case of terracotta sculpture, most research has centred on its polychrome finish, while the study of its composition, nature and evolution has been somewhat neglected. This kind of study provides in-depth technical knowledge of the artworks and their current condition from the material point of view. However, this subject has been largely ignored by most of the research centres of this area. To our knowledge, only some few publications have included some attempt to assess terracotta as sculptural support material through technical analysis [1-4].

It would be wrong, however, to suggest that terracotta is an unknown material once it has been widely studied in other historical contexts, such as in architecture (bricks, tiles, etc.), archaeology (pottery), and even in the modern construction sector at quality control centres for building materials. The problem, therefore, is not the lack of knowledge of the material itself but rather of a certain neglect of its artistic value as a sculpture material. Our research at the University of Granada (Spain) aims to fill this gap by conducting all the necessary analysis required to gain a deeper insight into this material, and place it on the same level as other sculptural media with accurate, reliable results.

As previously mentioned, different types of scientific analysis have been used in other research fields to study ceramics, clay or terracotta. There are many examples where both the nature and origin of the clay and the composition of the fired ceramic have been thoroughly investigated. Other results include the characterisation of the technology used in their creation in terms of granulometry, pre-manufacturing treatments, types of finishes, quality studies, etc. The physical and chemical condition of the material can be accurately defined with this type of studies, as well as the effects of any material introduced during restoration interventions, assessing its impact and effectiveness. This research process is perhaps mostly developed in the field of architectural heritage [5, 6] and archaeology. In both disciplines we find methods for analysing the characteristics of the different building materials, and others that focus more on their technical quality and optimal functionality. In other studies, these methods have been applied from an artistic perspective to decorative or ornamental objects or from the point of view of preventive conservation [7, 8]. They have also been used in anthropological and historical studies.

Application of analytical techniques to terracotta sculptures

The information these studies are giving us is significant when applied to sculpture in polychrome terracotta. Undoubtedly, the scientific methods of analysis offer the most reliable and accurate way of studying the material components of an artwork and its chemical and physical properties, both on atomic and microscopic scale. They contribute to a full understanding of all the aspects of the object, including its state of conservation. These studies also provide the scientific evidence to confirm or not the results of other empirical techniques such as those used in art history which are based on observation, deduction, intuition, induction, experience, the principle of causality, etc. These techniques use stylistic, historical, artistic or aesthetic criteria as a reference, but lack the solid base provided by scientific results. When techniques based in observation are used alone, undue importance may be given to certain aspects inducing misleading results, hence the importance of conducting these studies in any type of material, including terracotta. In our case, we have performed an in-depth study using different methods of scientific examination that have produced significant, accurate results for more than 250 sculptures form different collections currently undergoing restoration. Many of these belong to the Museum of the Monasterio de la Concepción of Granada, which has over 200 terracotta sculptures.

The analytical techniques that provide useful information for terracotta artworks include Thermoluminescence, supported by α and β particle counting to date the material, Polarized Optical Microscopy - one of the methods used to study the texture and to locate the possible source of the raw material used in the sculpture, and Scanning Electron Microscopy which is used, among other things, to characterize the micro-texture, the firing temperature, and the presence and morphology of salts.

Thermoluminescence with α and β particle counting

The scientific methods used to determine the age of the materials from which an artwork is made can be of great importance when it comes to attributing it to a particular artist or trying to date it accurately. This is especially true in cases in which it is necessary to establish the authorship of the artwork and to detect possible forgeries, or if we want to find out at what stage in the artist's career the work was produced. It has been shown that thermoluminescence (TL) supported by α and β particle counting, is the most effective method for dating terracotta (even more than Carbon-14 dating) [9-11] and it is considered the most reliable physical technique to study materials that have undergone a significant heating or firing process during manufacturing, such as terracotta.

In order to be able to date these sculptures with a low margin of error, it was necessary to adapt methodologies to our specific needs. This type of analysis is used more frequently on archaeological objects. This study is performed at the site where the objects were found in order to compare the findings and confirming the age of the pieces in a conclusive way. According to Arribas [12], in the case of objects that do not come from archaeological sites for which we cannot obtain radiation data from the extraction site, such as museum objects, a combination of analytical techniques must be used. In the case of terracotta, the radiation received by the quartz present in the terracotta can be taken as reference. Although this increases slightly the margin of error (in this case around 5%), it is still possible to date the sculpture. This percentage can be further reduced by combining TL with α and β particle counting.

Another method would be to compare the object in study with other objects whose age and authors are already well-documented.

The main problem with this type of analysis is that it is a destructive technique that requires large amounts of sample material for testing, usually about 2 g in dust particles for α and β particle counting and an additional 0.2 g with a grain size between 4 and 10 μm for TL analysis. Sometimes when the piece is small, it is impossible to take so much material for sampling. This is very common in terracotta sculpture, which is typically used in folk artwork, test objects and figurines, most of which are under 40 cm tall. Thus, 2.2 g is too much quantity for pieces of that size. Fortunately, in many cases these pieces were created without a base, allowing access to take samples from the inside part. In our case, other logistical drawbacks would be that only very few laboratories perform these tests in Spain, it takes two to three months to obtain the results, and it is a very expensive technique.

Direct application on sculpture

Some of the analytical techniques widely used in the study and conservation of artworks focus on the detection of certain components that are only present in the polychrome layers, such as pigments, fillers and binders, or only on particular elements that can be effectively dated. The dating results of these elements are sometimes not sufficiently precise, and we cannot use them on plain, undecorated sculptures, or on sculptures with non original polychromies which can be difficult to detect at first glance. This situation is more common than we think, and it often leads to confusion or doubts making an artwork becoming known as "school of" or "style of" without specifying further. However, TL dating techniques allow us to authenticate a material from the sculpture that has hardly changed or completely changed since its original creation: the terracotta.

The dating results provided by these methods can be conclusive in the attribution of a work to a particular artist, or in defining the different stages in the artist development or career, etc. This technique is very effective to detect high-quality counterfeits, to identify copies or works with a style and technique that sometimes make detection by other means very difficult. It can also help to resolve debates in which authorship is attributed to various artists that have similar stylistic characteristics, such as with teachers and students. Thus, it provides important answers not only for the work of the artists in question, but also for History of Art in general.

Polarized Optical Microscopy (POM)

From the various methods used to characterise the materials present in clays and ceramics, polarized optical microscopy provides the most reliable information about the site from which the clay was extracted, giving us clues from the geographical location of the work and/or its creator. This technique is completely reliable in the identification of mineral phases through their optical properties using polarised light; the location and recognition of marker-substances with which we can conclusively identify a specific site; the study of the textural pattern of the clay mass and of each of its components; and the observation of the type and distribution of pores.

This is also a destructive method of analysis once it requires the extraction of a sample of material, albeit very small (similar to the amount required for analysing the polychrome), in order to prepare a thin section that can be observed under the microscope.

Geographical location of origin sites

There have been several archaeological studies based on comparative geographic location [13-16] that demonstrate the effectiveness of this technique in identifying the source area of the raw material. In the past, and particularly in the case of sculpture in which large amounts of raw material were required, this was normally sourced locally. The geographical location of the material can help to identify the sculptor or in cases where his identity is already known, it can provide information about his career. In our studies of the Granada school, it was common for sculptors to move to other cities to perform commissions using local materials. By identifying the geographical source of the raw material and contrasting it with the information obtained from our observational/documentary study of the work, we can make an attribution of it more confidently to a particular stage of the artist's career. This was the case of Spanish sculptors such as Pedro de Mena, who worked in the provinces of Granada or Málaga, or Luisa Roldan (La Roldana), who worked in Cadiz and Madrid. For example, it would also confirm if the sculpture of the Fallen Christ by the Granada artist José de Mora dates from his time in the town of Baza (province of Granada), where he worked initially in his father's studio, or if it belongs to his later period in the city of Granada, etc.

In a wider territorial range, this identification process could enable a more accurate geographical attribution of works than that offered by purely observational evidence which can sometimes be misleading. This is the case of sculptures in which the anthropological evidence, such as clothing, accessories, and even hairstyles and customs all point towards a specific time or geographical area when in fact they are of a completely different origin. That is the case of the sculpture shown in Figure 1. At first glance it would appear to be of Italian Renaissance origin when in fact it is almost certainly the work of a neoclassical Spanish or Latin American sculptor. The results provided by this analysis, combined with those from thermoluminescence would allow us to confirm or reject our initial assumption.

As previously mentioned, polarized optical microscopy offers us an insight into the specific physical characteristics of the texture and shape of the constituent elements of a clay paste, characteristic of a particular extraction site, and to locate marker elements.

A terracotta mural relief believed to be from the province of Jaén was studied by the authors. Its composition was analysed and compared with clayey material from a site near the town of Bailen by specialist company Innovarcilla [17]. A marker element common to both samples was located, a specific type of the microfossil Globigerina, confirming the origin of the material source (Figures 2 and 3).

Knowledge of the techniques used in the creation of an object

The physical observation of a sample by optical microscopy provides very specific qualitative information regarding the components of the clayey mass, in terms of the shape and size of specific elements, and the characteristics of the porous system.

Figure 1 (right). An angel sculpture in polychrome terracotta. Piece belonging to the sculptural group "Presentation in the Temple", Scenes from the Life of the Virgin Mary. Monastery-Museum of the Conception of Granada (Spain). It features attributes of Italian Renaissance and Hispanic Neoclassic. The final atribution will be determined by studies of TL.

Figure 2 (below). Images obtained by POM showing the presence of Globigerina as a marker, in the sample made with clay from the site of origin (left) and the sample taken from the terracotta wall relief (right).

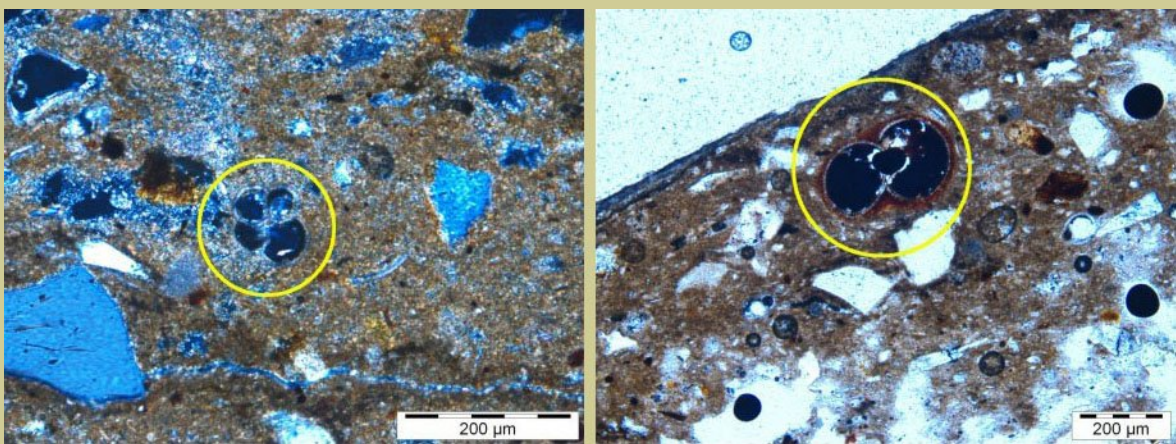
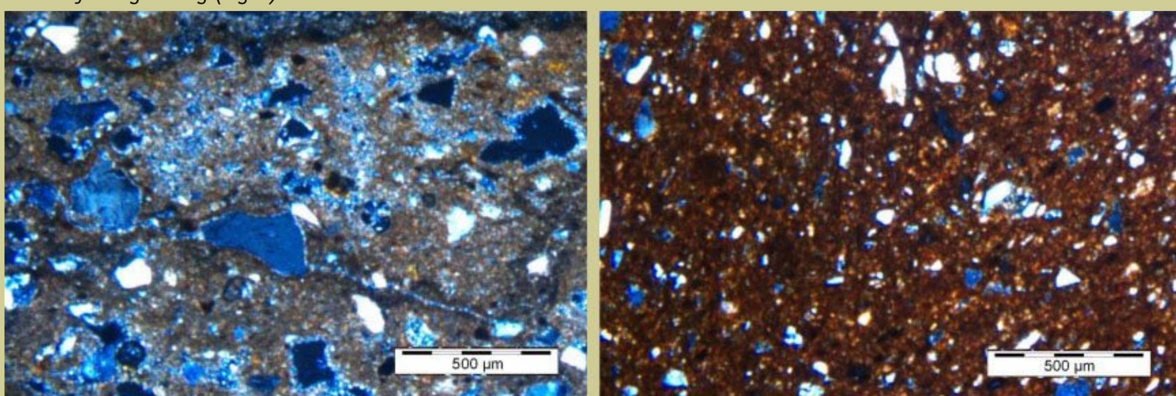
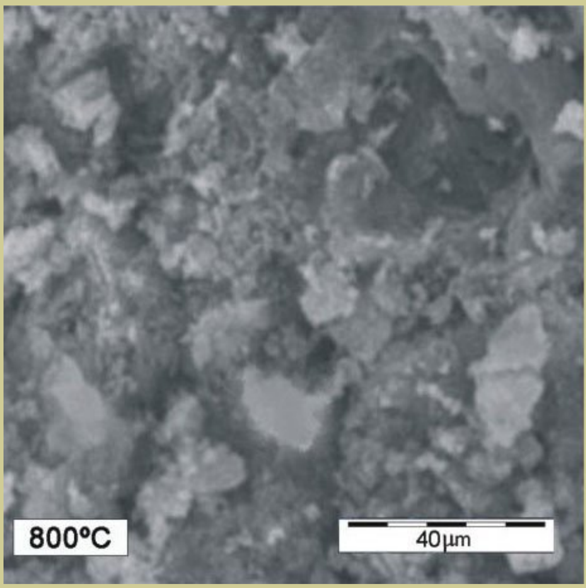


Figure 3 (below). Detail of an image taken by POM of different processing techniques on terracotta; traditionally treated (left) and artificial grinding (right).





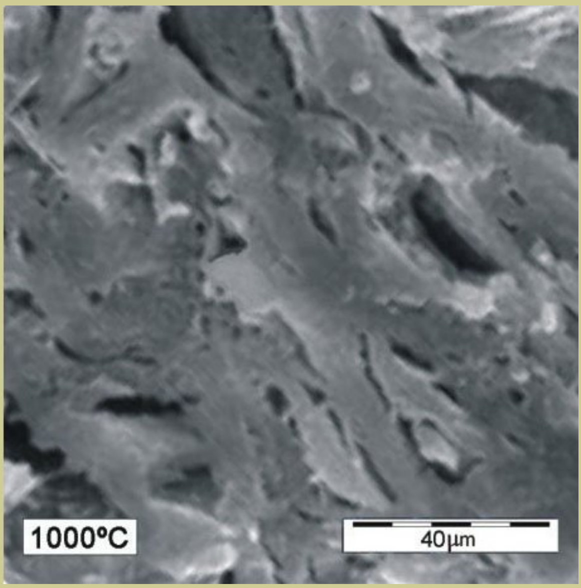


Figure 4. Detail of an image obtained by SEM of two clay samples in two firing degrees, in which we can found differences in the fusion degree of the components.

This information provides us with clues about the techniques used in the creation of the clayey mass such as the grinding or screening to get a more or less heterogeneous granulometry (which directly affects the terracotta porosimetry), the degree of fusion of certain elements due to the degree of firing, the presence and the quantity of micro-fractures, the crystal orientation (which indicates a machine-treated clay), the degree of hetero-geneity in the arrangement of the components (the result of a better or worse kneading), etc.

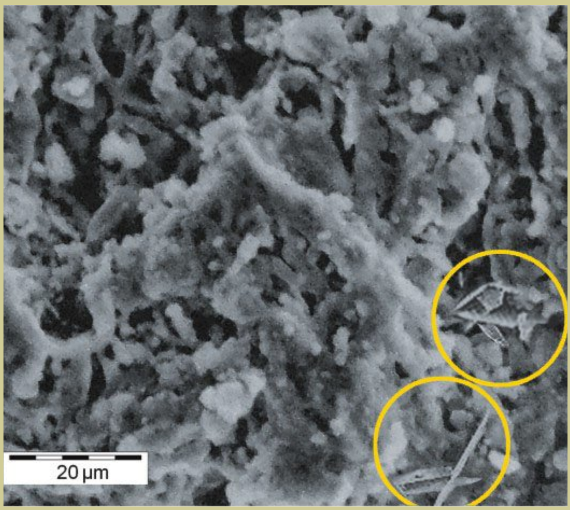


Figure 5. Detail of a image obtained by SEM of a terracotta with traces of calcium sulfate crystallization.

Figures 4 and 5 illustrate these technical differences. For example, in figure 4 it can be observed that the raw material has been roughly screened and does not appear to have been milled, whereas in figure 5 the grain is more homogeneous suggesting a more advanced preparation process and possibly mechanical grinding or greater natural disintegration of the clayey material.

This data is useful for the conservation of terracotta sculptures, as it provides information at a structural level about both the techniques used in their creation and their current condition, and offer insights into their future behaviour and potential weaknesses or sources of decay.

Scanning Electron Microscopy

The high-resolution images provided by Scanning Electron Microscopy (SEM) and the possibility of elemental analysis by energy dispersive X-ray micro-analysis (EDX) to verify the nature/composition of specific elements, provide important complementary information to that obtained by optical microscopy concerning the origin of the clay, the techniques used in its creation, the state of conservation and the effectiveness of the different conservation interventions.

Knowledge about the creation technology

The identification of the components of the mass, the observation of the homogeneity of their distribution in the paste and the texture, and the chemical analysis of the major elements will allow us to study the physical material at a deeper level than using just optical microscopy. Its porosity and microtexture can be observed more clearly (in 3D and at higher resolution), as well as the degree of vitrification of the mineral phases and the homogeneity of their distribution in the matrix. These results provide useful insights into the technology used in the creation of the pieces such as screening, kneading and firing temperature.

Identification of external elements and their effects

SEM also allows us to identify foreign materials such as salts, pollutants, or deposits. Although salt efflorescence, stains and deposits are often clearly visible on the surface of a piece, detailed microscope observation enables us to find out more about the nature of these minerals and the way they interact with the components of the terracotta. These are key steps to help us defining exactly what work is required to clean, protect or restore and to indicate the degree of damage suffered by the work in the past and that may occur in the future. By ascertaining the specific solubility of salts in the terracotta, thanks to the reliable identification of salt mineral species and their current status (dehydration or recrystallization), then the film or the corrosive effect of non-original components such as adhesives or binders and the oxidation caused by metallic elements, etc. can be measured and analyzed in depth, and treated according to the specific needs.

Physical state of the material

Another important point is that the observation of the terracotta pores characteristics and the interrelationships between the components, and more importantly, the analysis of any morphological variation that may have occurred over the years will reveal the degree of compaction and strength of the material. This is due to the presence of microcracks - either intercrystalline or intracrystalline -, the presence of new porosity or an increase in the specific surface of certain particles. SEM observation offers us a detailed image of the interrelationship between crystals, and helps locating problems with peeling, cracking or powdering and their possible causes. The sources of such damage (lime blowing, low degree of vitrification of the matrix, disintegration of a component due to chemical dissolution, etc.) can also be located precisely.

All this data is very important in terms of conservation as it refers to specific factors that directly affect the strength and the physical and chemical behaviour of the material, and can provide effective guidelines for preventive conservation and restoration treatments. If we can identify errors due to the creation technology, it will be possible to foresee, for example, that the physical resistance of the object itself is very limited due to an obvious defect in firing; that any changes in humidity could cause salt crystallization because of an erroneous pre-wash of the clay that has led to excessive amounts of soluble salts; or that with any weakening in the support material, peeling and flaking will occur due to a lack of homogeneity in the paste mixing.

With this technique we can also measure the damage that the work has suffered since it was made, such as the deposit of external corrosive elements and physical degradation caused by aggressive cleaning methods, or changes in porosity due to the use of insulation products such as consolidants, unsuitable adhesives or protective films.

All this information will provide us with both historically valuable technical information and physical data necessary for the treatment or restoration of the sculpture.

Conclusion

As we have seen in this review, scientific methods of analysis used in other fields can also be applied to terracotta sculpture and the information obtained may be of great value. These methods are particularly useful in fields as diverse as art history and conservation-restoration, as they provide the necessary scientific reliability and a clear starting point for further technological and conservation studies.

Being able to date accurately the creation of a sculpture in terracotta, to locate geographically the source of the original clayey material, to find out more about the techniques used in its creation, and the direct consequences of these processes and those resulting from the environmental conditions in which the artwork has been kept, is necessary and beneficial in all its aspects. The means to achieve this are readily available and have proved to be highly reliable.

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