A short introduction to Archaeometry of Ceramics

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Abstract

A short review on the archaeometry of ceramics is presented with the goal of introducing contemporary trends in this area. The methods used in identifying ceramics finds are briefly discussed. The typological and technological classification is described showing the respective advantages. The principal experimental techniques used in the archaeometric studies are discussed, such as the technique for dating ceramic.

Ceramics are the most frequently found objects in any excavation of any historical period from prehistory to modern times. Often, as with the Greek civilization, it is the most important witness to the artistry of a civilization; equally significant evidence of other forms of art such as painting has not been found. Archaeologists often specialize in typological ceramic analyses, to the point of being a decisive factor for the chronological placement of an excavation. The remarkable interest in archeometric research and in conservation for this type of material needs no explanation.
The most important research issues in archaeometry - dating, origin, cultural development, trade and relations between peoples - were addressed using investigative techniques which in some cases were based on their main use of ceramics (such as thermoluminescence dating).

In this speech, we will review the most commonly used themes and methods in relation to improvements in research on ceramics, and one that employs ceramics for better historical and artistic knowledge of a civilization. I will try to present the facts by providing elements to judge the level of development achieved by the various techniques and problems still open to discussion.

The starting point will be a brief discussion on ceramic production in the past and the basic elements of ceramics technology: raw materials, additives, firing process, glazing (or finishing) techniques, etc. Following is an outline of the main questions posed to archaeometrists and/or conservation experts and the methods followed to provide answers. At the end of the discussion on the problems will be a presentation of principal techniques used in studying ceramic artefacts: a) microscopy (optical microscopy, SEM, etc.), spectroscopic (XRF, XRD, FTIR, Raman, colorimetry, etc.), dating, imaging.

To conclude we will show examples of archaeometric research applied to the study of ancient ceramics.

Keywords: Ceramic, Archaeometry, Conservation, Typology

Introduction

Ceramics are the most frequently found objects in any excavation of any historical period from prehistory to modern times. Often, as with the Greek civilization, it is the most important witness to the artistry of a civilization; equally significant evidence of other forms of art such as painting has not been found. Ceramic fragments are frequently precious elements for archaeologists in order to date strata, find correlations (trade, relationships, etc.), qualify cultural context and technological development, thus archaeologists often specialize in typological analysis of ceramics [1]. The above justifies the remarkable interest shown by archeometric research, and that on conservation, for this type of material. In this short review, all themes and methods most commonly discussed in relation to improvement of research on ceramics, and the one that employs ceramics for better historical and artistic knowledge of a civilization will be covered. The text was arranged in order to provide elements to judge the level of development achieved by the various methods and techniques and problems still open to discussion.

Ceramic typology

Ceramic objects possess several elements that can be studied to identify their use, provenance and chronological placement. Looking at a section of a ceramic shard one can observe the bulk (or the body), the treated surface, sometimes finished with several layers of coating, all elements used in the technological characterisation of ceramics. Additional elements are the presence of inclusions in the bulk and surface glazing. These multiplicities of elements favour both the archaeologist and the archaeometrist in researching the attributes that are significant to identifying a find [2].

Ceramic-making has evolved over the centuries in quality (typology, use, value) as well as for production, decorating and coating techniques; it follows that ceramics need to be classified in order to organize the acquired knowledge and use it in research and applications. Archaeologists prefer a *typological classification*, in which artefacts are classified by ‘types’ and then the shards are artefacts are clustered for types. Underlying this approach is the assumption that artefacts were produced according to a shape or style, perhaps serially. This hypothesis holds true in the case of common ceramics that represent the majority of what is found in excavations. The concept itself of ‘type’ is difficult to rigorously define, there are, in fact, several theoretical and practical problems in the operative definition of a ‘type’. In order to overcome this obstacle an approach is followed based on *attribute (or feature) analysis,* in which artefacts are described according to a set of selected attributes, and which seeks to establish a direct correlation between one (or several) of these attributes and a style that can be attributed to a well-defined group in a period of time, in a particular region, showing a peculiar pattern. The main problem with this approach is how, among the myriad of attributes usually observed in a large assemblage of artefacts, it is possible find a subset that will allow an accurate identification of pieces of ceramics found in a context. Accurate means univocal, i.e. avoiding, as far as possible, that a ceramic fragment be erroneously attributed. In practice, most archaeologists use a pragmatic approach using types and attributes, depending on the problem at hand [3].

In both approaches, *shape* attributes are among the most fundamental properties by which artefacts are characterized and studied. These include the description of the general shape of the artefact, defined by its *contour* (the line which marks its boundary or cross section), as well as the description of particular shape properties, considered to be significant for specific archaeological issues. Traditional shape descriptions and classifications, however, rely on intuitive, often vague characterizations, which are hard to quantify. Terms such as ‘everted/inverted rim’, ‘squat body’, ‘high carination’, or even ‘elegant curves’, which do not have a unique interpretation, are commonly used. Many times archaeometry is asked to complete this frame giving more precision to the traditional ‘stylistic’ identification of ceramic artefacts and fragments.

In any case, the area of ceramic archaeometry faced the most important research issues, dating, origin, cultural development, trade and relations between peoples, using methods of investigation which in some cases found their main use for ceramic (such as thermoluminescence dating).

Ceramic materials can be identified and classified using their scientific properties. The chemical-physical properties of ceramic (raw materials and additives), firing techniques, and the characterisation of superficial coatings are probably the most important aspects to investigate. Also the colour and porosity of each part of the ceramic (body and surface) can be useful in this identification.

The most important physical properties of ceramic are:

- hardness

- resistance
- porosity
- density
- optical properties of the surface (colour, reflection, etc.)

Hardness and porosity can be measured with relatively simple instruments that are, therefore, sometimes used, also by archaeologists, to complete a simple characterisation of the ceramic without performing chemical analyses.

Chemical and mineralogical properties deal mostly with the raw material used to produce the artefact and its surface treatment. Clay is by far the most common material used to produce ceramic but, unfortunately, clays can be wildly different in chemical composition, microcrystalline structure and other important characteristics. Also the refining technique can significantly alter the final product; for example a good selection and cleaning of raw materials produces stoneware (a hard white paste) that is very different from a 'terracotta' (earthenware) characterised by coarse grains and, consequently, by great porosity. An important role in ceramic production is played by additives, such as degreasing, plant fibres, etc., that help obtain the optimal characteristics of the paste and in the firing. The additive can be identified by chemical analysis and microscopy. Moreover, the characterisation of the surface is fundamental to identifying a ceramic; the presence of a glass coating and the detection of its structure can be very important in an archaeometric study, as demonstrated recently by the research on the Lustro.

A technological classification can start with the simple observation of the ceramic body (porous/compact, white/coloured, with/without slip or glaze). Thus, the principal type of ceramic can be identified: pottery, earthenware, stoneware, porcelain, etc. Then, from the analysis, the classification can be refined, introducing new attributes, for example siliceous/calcareous ceramic. The firing temperature is another very important parameter; in fact some common ceramics are fired below 900° (brick, 'ad impasto' pottery, 'figulina' pottery, 'Red/black figures' with earth slip ('vernice'), *'bucchero'*), from 900° to 980° (Creamware, Terracotta, *Silicious Pottery ('Faience'), "Iznik Pottery"),* from 980° to 1100° (Stoneware, Earthenware, Porcelain); up to 1100° (kl inker, porcelain, Lithoceramic, fine stoneware, vitreous China). It is worth underline that firing processes and the cleaning of raw materials modify, sometimes to a large extent, the compositional profile of ceramic bulk, often making the research work of the archaeometrist more complex.

The large compositional variability of natural materials, often deriving from the properties of clay of a particular site, is the principal tool in the hands of the archaeometrist in order to accurately detect the provenance of a ceramic. The idea of replacing a typological with a classification based on scientific data cannot be very good, taking into account that the ultimate goal of classifying a ceramic is not to draw a picture of the product but rather to have a useful tool in the identification and attribution of 'finds'. It may be answered that parameters used are quantitative and allow a more accurate identification. However, there is the risk of fake groups, i.e. not having meaning for its use by the archaeologist. The prevalent attempt today is to integrate the two ways making a hybrid classification that is much more a tool for the identification than that to draw a general picture of the object, which can help to understand the meaning of the technological changes and their relation with the use and artistic expression.

Experimental technique in the archaeometry of ceramic

There are many simple experimental methods, as mentioned above, that can help to characterise ceramic. Macroscopic quantities, such as the percentage weight of the different ceramics found in a site, can be used by the archaeologist to demonstrate an assumption. The experimental techniques of material science can be very useful to characterise the ceramics; however only techniques that have demonstrated validity in assigning a ceramic to a particular 'type' are more frequently employed. The non-destructive (ND) techniques are placed in between the traditional analytical ones and those employed during the study make for their correct cataloguing. The real advantage of these techniques is, in fact, not only is the sample not destroyed, but it is also simpler and less expensive (transfer to the laboratory and sample preparation costs are cut). Unfortunately there are technical characteristics that cannot be detected in a ND way.

With chemical analysis, one can obtain a chemical profile of a sample that can be used in identifying the ceramic samples. Today the most common technique used in the determination of elemental profile is the X-Ray Fluorescence (XRF) that can be used in a laboratory with a sophisticated sample preparation that ensures a very good quality or in a ND manner with portable spectrometers that have, as mentioned above, several practical advantages [4]. Using the methodology set-up to analyse minerals, from the elemental profile, one can determine the mineralogical profile, substituting the elements with the compounds (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5). To complete the chemical analysis with a precise characterisation of the dispersed minerals, it is possible to use powder X-ray diffraction (XRD) that allows a qualitative, and sometimes semi-quantitative, analysis of the crystals. In mineralogical analysis a very powerful method is the observation of thin sections of ceramic with an optical microscope that allows the identification of single minerals (microcrystals) dispersed in the clay and their optical properties. Mineralogical characterisation leads, many times, to a good identification of the raw material used, the inclusions and in evaluating firing temperature. However, it is expensive and time-consuming and can be used only for a limited number of samples. Due to the heterogeneity of ceramic materials the microanalytical technique is essential to characterise the materials constituting the body as well as the coating. The scanning electron microscope is the most common microanalytical instrument used in the case of ceramics. This technique is very useful to analyse single crystals and to characterise the surface.

In archaeometric research trace elements play a very important role, overall in the determination of the provenance of raw materials [5]. The most employed technique is now the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) that is highly sensitive and capable of determining a range of metals and several non-metals at concentrations below part per trillion. Previously the Neutron Activation Analysis was used, that is a more expensive and complex technique. Detecting trace elements and using sophisticated methods of statistical data process it is sometimes possible to group the analyzed samples; this can be very important, comparing the results with those of archaeological studies of the same samples set, to determine the provenance of the materials constituting the ceramics found in the excavation. These studies are very important for prehistoric ceramic and in those cases in which the aim is to better define the cultural context and trading of a particular 'facies'.

There are many other techniques that are used to analyse the ceramic, such as Raman spectroscopy, multispectral analysis and PIXE, but the objective of this brief review is to provide a complete picture of experimental techniques, which in some cases have produced very significant results.

There are many techniques that allow you to view internal or external aspects of ceramic artefacts, the most common is the laser scanner for the construction of a tri-dimensional numerical model of the artefact or the radiography to control the interior of the object.

Dating ceramics

The presence of particular crystals (quartz and feldspars) in the clay is a formidable tool for dating ceramics and other material such as bricks and glass. Thermoluminescence dating (TL) is a technique that made it possible to obtain significant results in the study of archaeological ceramics; it is also very useful for authentication. TL was also used to date strata and reconstruct chronologies or to determine the different construction phases of a building. As in the case of Radiocarbon dating, today the TL is utilized in complex research to date strata and pinpoint the actual chronology.

Study the deterioration processes of ceramic

The durability of ceramics is evident from the fact that it is the most frequent find in an excavation. Ceramic is resistant to physical, chemical and biological aggression also due to its structure. The superficial qualification of the ceramic is performed to avoid the risk, well known also in ancient times, that the body, many times porous, can be attacked by environmental agents (mostly water). Unfortunately the superficial coating (glaze, slim) is the most precious part of a ceramic artefact, in many cases also with artistic value. The marked porosity of a ceramic body promotes, in fact, the absorption of dirt, conveyed by water and, even more so, by means of the fracture lines. This dirt, during the evaporation of the water, remains 'trapped' inside the abovementioned interface (as it is not able to migrate completely towards the surface due to the impermeable barrier of the glazing).

The superficial coating is interested, taking into account their different nature, by several degradation phenomena, the worst of which is the detachment of the coating. Other visible processes are decolouring and erosion, the first mostly due to chemical aggression mediated by water (soluble salts) and pollution.

The less porous ceramics, porcelain, stoneware, are more resistant to environmental action, but most fragile, because of their crystalline structure.

The techniques to study the processes of degradation are the same mentioned above on experimental techniques. The imaging techniques with the construction of a 3D numerical model of the object are even more used in the planning of restoration procedures.

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