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TERRACOTTA ARTEFACTS IS THERMOLUMINESCENCE ANALYSIS SUFFICIENT FOR AUTHENTICATION?

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ABSTRACT

In the last ten to twenty years, an increased number of ceramic objects regarded as ancient from the accompanying thermoluminescence analysis test certificates have come out of China and into the art market.

However, further testing has shown that in many cases they are recent products. The counterfeiting methods used are numerous, usually in the form of sculptures that consist of old and new parts, or that have been recently carved from an old, plain and worthless fired artefact are as frequently encountered as objects that have been made from a mixture of pulverized antique ceramics and modern binding agents. The paper describes methods for the uncovering of such fakes.

KEYWORDS: terracotta artefacts, authentication, counterfeiting methods, 3D-computer tomography, binding agent test, ceramic fingerprint

INTRODUCTION

Since the introduction of thermoluminescence analysis for the authentication of terracotta objects from the art market this has been the only method for the assessment of such objects. Fakers had taken advantage of this shortcoming and have developed several methods for counterfeiting antique terracotta objects that cannot be detected easily by thermoluminescence analysis.

For almost 3 decades now, thermoluminescence analysis has proved to be an indispensable tool for answering archeological questions. Dating can be achieved with a high reliability for objects with documented excavation records and known burial circumstances.

The method is also applied for authentication of antiques, however, detailed information about the finds is lacking in many cases. Therefore, an assumption of mean values for parameters influencing the calculation of the age from the measured dose is necessary which leads to a reduced accuracy of +/- 20 - 30%. Nevertheless the quality of such so called "Authenticity Tests" is principally sufficient for differentiation between genuine objects and fakes.

There are, however, several limitations and drawbacks to be kept in mind regarding authentication of terracotta antiques by thermoluminescence analysis. First, in many cases, the sampling possibilities are limited because of aesthetic reasons. Second, the method is, of course, restricted to dating of the objects' material only - irrespective of eventual later reworking. Finally, it is difficult to recognize material manipulations, e.g. the use of "artificial terracotta", a mixture of pulverized antique ceramic shards dating from the time period in question and modern organic or inorganic binding agents for the modeling of objects.

The common methods for counterfeiting antique terracotta objects are as follows:

1. Recent firing
2. Assembling of new and old parts - the latter being positioned in remote object areas favored for sampling ("pastiches") and leveling of the surface with a thin coating of "artificial terracotta" ("engobe")
3. Carving of sculptures from old, plain and worthless artefacts
4. Modeling of objects from „artificial terracotta"
5. Irradiation

Each of these fakes can be uncovered by appropriate analyses:

1. Thermoluminescence Analysis can easily differentiate between a clay fired in antiquity and a recent product
2. Modern X-ray technology and particularly 3D-Computer Tomography (CT) mean that pastiches can be quickly recognized: clearly varying grey tones of different materials, due to different absorption of the x-rays, straight cuts and glued areas as well as metal or plastic parts used for strengthening purposes are clear indications of manipulation and counterfeiting. For example see Fig. 1. During CT-analysis the object is x-rayed under rotation within the conical beam of an x-ray source from all sides. From the images the three-dimensional distribution of the x-ray diminishing coefficient is calculated by means of a mathematical algorithm. These data allow a layer by layer visualization of the object's volume in various plains.

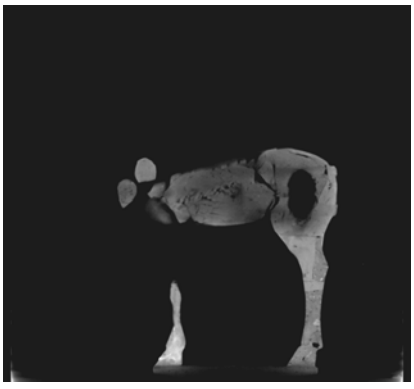

Fig. 1a

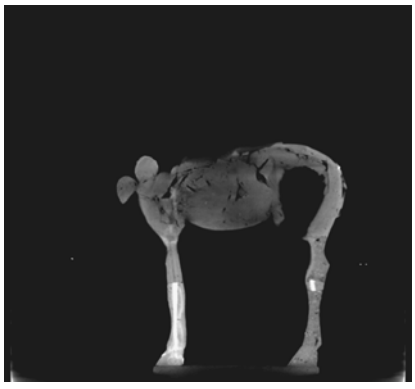

Fig. 1b

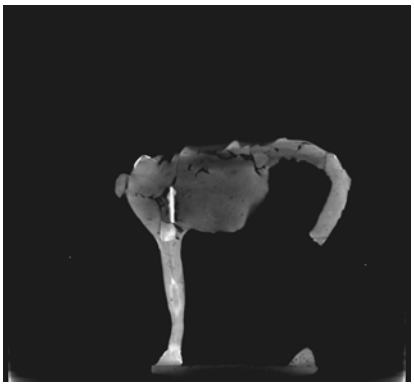

Fig. 1c

Fig. 1d **Fig. 1e** **Fig. 1f**

Fig. 1: 3D-CT of a terracotta horse attributed to the North Wei dynasty. Selected xy layers from left to right side of the object

3. Recently carved objects can be distinguished from objects modeled from unfired clay by careful microscopic examination of the surface.

4. The Binding Agent Test makes it possible to recognize products made from "artificial terracotta". The binding agents most commonly found in fakes are polyvinyl acetate (also known as a wood glue with the brand name "Ponal", Fig. 2) and cyano acrylate. These organic compounds can be clearly identified on the basis of their characteristic infrared spectra and can be distinguished with certainty from chemicals used for surface treatment.

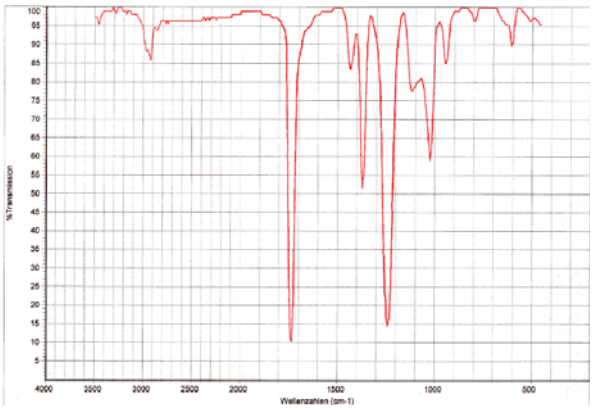

Fig. 2: FT-IR spectrum of polyvinyl acetate

The test is performed by extraction of a drilled sample of the object to be investigated with appropriate organic solvents and detection and identification of the modern constituents by chromatographic or spectroscopic analysis.

The presence of organic binding agents is not the only indication for manipulation of a material or the presence of „artificial terracotta": in order to be able to improve workability as well as to alter colour and morphology, it is often the case that filling agents such as sand, iron oxide or ground stone are added to the above mixtures. As a consequence, the proportions of the elements Si, Al, O, Fe, Ca, Mg, K, which vary within certain limits in natural clay, will obviously be found to be atypical upon chemical analysis of the composition of such an object's material.

Inorganic binding agents that are often used for the production of imitations (for example water glass or cement) can also be revealed by chemical analysis as a result of atypical alkali-silicon or calcium-silicon proportions.

Trace elements in the terracotta composition like P, S, Ba, Mn, Cr, Ni, Cu, Zn, Pb, Sr, Rb are characteristic for every clay-pit and their analysis can furthermore be used for determination of the clay's origin as well as for differentiation of material originally not belonging together upon performing a comparative chemical analysis, i.e. a "ceramic fingerprint" at various spots of an artefact.

Another good way of detecting unusual properties of terracotta objects which can indicate that they are not genuine is an examination of the material's morphology using electron microscopy.

When subjected to the appropriate magnification, fired ceramics are found to have a completely different appearance from "artificial terracotta" produced from ground fragments and binding agents: fired clay exhibits characteristics of a clinker (Fig. 3), whereas fakes produced

with bindings rather resemble a conglomerate (Fig. 4). However, this has to be considered as an auxiliary method which is not always leading to unequivocal results.

5. Using standard methods counterfeiting by irradiation can not be detected with certainty so far. However, a project for establishing appropriate means for uncovering also these fakes is under work.

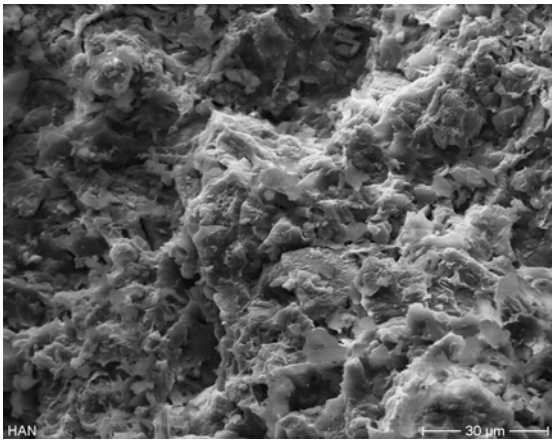

Fig. 3: SEM picture of a genuine terracotta

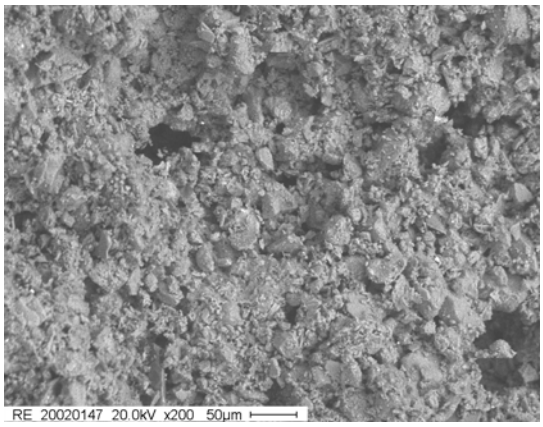

Fig. 4: SEM picture of an "artificial terracotta"

CONCLUSIONS

When assessing terracotta objects, the methods described in this paper indicate that it is possible to ensure a degree of certainty that cannot be guaranteed by thermoluminescence analysis alone. Thus, material analysis with (in the event of a positive result) subsequent determination of the age by means of thermoluminescence is the best way of ensuring a reliable assessment of such objects d'art.