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Authentication and characterisation of pottery sherds from Apricena (FG)

C. Miliani[a,*], N. Forini[b], A. Morresi[a], A. Romani[a], S. Spigarelli[c]

[a] *Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy*
[b] *Servizio di Fisica Sanitaria, Università di Perugia, c/o Ospedale Policlinico, 06100, Perugia, Italy*
[c] *Dipartimento di Scienze della Terra, Università di Perugia, Piazza dell' Università, 06100, Perugia, Italy*

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Abstract

This paper presents the preliminary results of an investigation on medieval ceramics from Apricena using thermoluminescence (TL), optical microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray microanalysis (EDS). The combination of physical and chemical–mineralogical analyses has lead to an authentication and an initial characterisation of the ceramic sherds. © 1998 Elsevier Science B.V.

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1. Introduction

Ceramics have always been denoted as the main index fossil in archaeological excavations. They are one of the most important means for dating strata and reconstructing past events concerning trades and technologies [1–3]. Studies using, thermoluminescence for age authentication, optical microscopy and scanning electron microscopy (SEM) for an accurate observation of the morphology and energy dispersive X-ray microanalysis (EDS) for the qualitative and semi-quantitative determination of the chemical elements present, provide information for the most complete characterisation of artefacts. This kind of information enhances the archaeological information obtained by stylistic observation.

The present paper deals with the preliminary study of 32 pottery sherds from excavations in Apricena (Foggia, southern Italy), directed by Dr. F.P. Maulucci, of the ‘‘Soprintendenza Archeologica della Puglia-Centro Operativo per l'Archeologia della Daunia.'' The sherds, along with other heterogeneous fill material, were found in moats surrounding the remains of the medieval castle, the hunting residence of Federico II of Svevia.

The first step was to date the sherds, in order to get information about the method of filling the moats. For this, a thermoluminescence analysis was conducted to authenticate all the fragments.

The second problem was that for most of the ceramic fragments, the characteristics of the original object were not known. Moreover, the fragments were so heterogeneous, even macroscopically, that an accurate characterisation was necessary. Therefore, the coating techniques of the sherds were examined for

*Corresponding author. Tel.: +39-75-5855590; fax: +39-75-5855598, e-mail: fotochim@unipg.it

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all the samples, and the ceramic bodies were characterised.

2. Archaeological samples

Based on macroscopic observation, nine achromatic, uncoated sherds and 23 decorated samples, with transparent glazed slip, were distinguished (ranging in glaze thickness from 0.01 to 0.2 mm). Among the glazed fragments, six were monochrome sherds, (three green, two ochre-yellow and one white), and 17 were polychrome fragments. The recurrent pigments are sparkly green, dark brown, and different shades of ochre ranging from yellow to dark red.

3. Analytical techniques and sample treatment

3.1. Thermoluminescence

The TL measurements were performed with a special Harshaw 2000 A+B analyser which permitted the temperature range to be extended up to 500°C with a power supply. The samples were prepared by taking about 10 mg of fine powder from the pottery, without any previous chemical or mineralogical characterisation. Each sample was divided into two equal parts and one part was irradiated by a Stabilipan Siemens X-ray irradiator with a beam of 130 keV energy at an exposure of 400 R for 10 min. The thermoluminescence curves were obtained by heating the samples at a linear rate of 10° C/s up to about 400°C without preheating. Nitrogen gas was used through the heating process at a pressure just below atmospheric pressure.

3.2. Optical microscopy

Observation of polished cross-sections of the sherds was performed using a polarising petrographic microscope working at middle magnitude.

3.3. Scanning electron microscopy and energy dispersive X-ray microanalysis

SEM examinations and EDS semi-quantitative analyses were performed on a Philips XL30 SEM fitted with a LaB_6 electron gun and an EDAX/DX4 analyser.

Samples were prepared by micro-cutting or by simply cracking the sherd and observed either in polished cross-section or in fresh fractures. All samples were coated with a thin carbon layer in order to obtain a conductive surface.

4. Results and discussion

4.1. Thermoluminescence

A varying number of liberated electrons may become trapped in imperfections in the lattice when several dielectric solids, (indicated as phosphors) are exposed to ionising radiation. These 'electron traps' are holes of potential energy. If the thermal stimulation is sufficient, the electrons escape and return to the ground state, releasing a small fraction of energy as visible light. This effect is called thermoluminescence (TL) [4].

If different traps are involved in the process, the light intensity as a function of temperature, at constant heating rate, results in a multipeak curve, called a glow curve. The light intensity or the area under the peak, can be considered proportional to the radiation dose (the so-called dosimetric property).

Thermoluminescence has been used, for several years, to date archaeological materials, particularly pottery. The basic steps for determining age are:

1. measuring the TL signal of the sample, i.e., the intensity at a temperature, normally higher than 300°C. This quantity is called natural TL (NTL);
2. determining the TL-sensitivity (S) of the samples as the ratio of TL-output due to an irradiation with an artificial dose radiation (ATL) and actual dose (D) used:

$$S = \frac{\mathrm{ATL}}{D}$$

3. measuring the annual dose (D_a), assumed to be constant.

Therefore, the age-formula is:

$$T(\mathrm{years}) = \frac{(\mathrm{NTL} \cdot S)}{D_a}$$

where T is the interval between the last firing and the measurement.

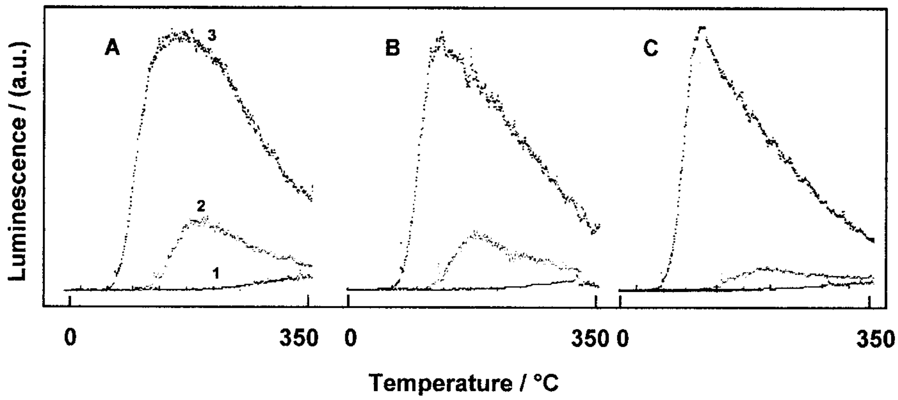

Fig. 1. Thermoluminescence curves from three different aged sherds; pottery A and C are about 200 years older and younger than B, respectively. Curves 1–3 are instrumental background, natural dose and artificial dose, respectively.

The annual dose (D_a) can be measured by setting a dosimeter in the exact place where the archaeological findings are recovered. Often, as in our case, accurate data on environment and modality of excavation are not known; moreover we have not any representative sample of the soil around each pottery sherd. We authenticated the samples, with a relative dating, by assuming a constant value for D_a.

In order to create a relative age scale for the analysed ceramic sherds, the mean environmental exposition rate D_a was assumed to be 0.4 R/year [5]. This relative dating procedure was tested by measuring about 500 samples of known age which were supplied by The Archaelogical Institute of the University of Perugia. The error was about 25% [6].

The experimental results indicate that the archaeological findings can be divided into three age groups, each group separated from the other by about 200 years (Fig. 1):

1. Group A: the oldest one, (three sherds).
2. Group C: the youngest one, (11 sherds).
3. Group B: (11 sherds).

Seven sherds were insensitive to TL analysis.

4.2. Optical microscopy observations

Using polished cross sections of the sherds, optical microscopy was used to obtain data on the texture and mineralogy of the paste, in order to obtain information regarding to the origin of the raw materials, ceramic technique, firing and burial conditions [7]. The sherds under study showed an extreme heterogeneity of the clayey matrix, with respect to both the texture and the mineralogical composition. All sherds had secondary products (mostly carbonates and phosphates) overlaying the external surface which are probably the result of mineralogical changes which occurred during burial.

4.3. Scanning electron microscopy and energy dispersive X-ray microanalysis

SEM was coupled with EDS detection to study all the fragments from Apricena.

A complete chemical-mineralogical characterisation of the sherds (coating and body), obtained from the information extracted from the SEM/EDS examination, in conjunction with X-ray diffraction data, X-ray fluorescence and electron microprobe analysis, is forthcoming.

The SEM images taken on fresh fractures and polished cross sections of the sherds provided information on the morphological and compositional features of the body and slip surface. The images produced by back-scattered electrons (BSE) were used to distinguish the different compounds on the basis of the different atomic numbers, which gave high spatial resolution. Moreover, examination of the fresh fracture surface and polished section provided some technological information on the structural and mineralogical changes of the interval morphology, which occurred during firing [8,9].

Table 1
Analytical results obtained by SEM/EDS; the sample QH2 19B is an example of sherd with carbonate–silicate matrix; QA2 35B is an example of sherd with silicate matrix

Sample	Na	Mg	Al	Si	P	S	Pb	Cl	K	Ca	Ti	Mn	Fe	Zn	As	Total
QH2 19B	2.82	4.44	10.17	44.13	0.60	0.53	0.93	0.24	1.53	29.79	0.45	0.00	3.88	0.24	0.26	100
QA2 35B	2.72	5.32	12.52	60.24	0.51	0.00	0.18	0.00	2.15	6.76	0.65	8.97	0.00	0.00	0.00	100

The EDS analyses were performed on different areas of the polished cross sections. Sometimes BSE contrast, due to heterogeneous composition, clearly showed a compositional gradient, which was confirmed by elemental X-ray analysis.

Semi quantitative analysis of the paste showed two main groups: (a) sherds with silicate matrix; and (b) sherds with carbonate–silicate matrix. The composition of these matrices is related to the use of Ca-poor and Ca-rich clays (marbly clays) as raw materials (Table 1).

The SEM/EDS examination of the sherds with coating (glaze and paint glaze) confirmed a silicon–lead composition of the glaze for all the fragments. A possible classification could be made using the PbO/SiO_2 ratio, an index of the relative variation in the coating mixture. In addition, the analytical data revealed a wide variability in composition within a single glaze showing a high heterogeneity of the pastes used and the possibility that the main components underwent diffusion and differentiation phenomena with partial de-mixing during firing. Changes in the amount of lead at the body/glaze interface with an opposite variation of SiO_2 and Al_2O_3 were observed. In some samples, Sn was detected along with Pb. This sometime occurs in some minerals which can be used as raw materials in lead-producing processes but it could also be due to early attempts to obtain a new kind of pottery called 'protomaioliche' [10]. These artifacts were characterised by a coating layer of white SnO_2.

The analytical data from the polished sections supplement the information from the optical microscopy observations about the pigment identification in the body/glaze interface. Some of the painted sherds with dark brown and sparkly green colours were characterised by the presence of the Mn and Cu pigments, and most of the fragments had sharp contact lines between the glaze and body.

Moreover, in the pores of the coating, secondary phase crystallisation can be seen which was probably formed during the firing process.

The sherds underwent some mineralogical changes during burial which included crystallisation of secondary products, mostly carbonates and phosphates.

5. Conclusions

The preliminary investigation on medieval ceramics from Apricena had lead to authentication of the samples and initial characterisation.

The results obtained on the glaze coating are in agreement with the results from the analysis on the medieval ceramics of Castello di Salerno (12th–15th century) [11]. Future investigations on the production site of the ceramics and on raw clays of local origin will be carried out in order to obtain information about the origin of the raw materials.

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