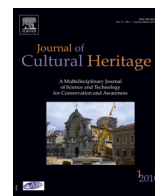




Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en



Short note

Provenancing of VI–VII century terra sigillata coming from Matera burial area by X-ray photoelectron spectroscopy



Simona Rella^a, Giuseppe Egidio De Benedetto^{b,*},
 Isabella Marchetta^c, Cosimino Malitesta^a

^a Laboratorio di Chimica Analitica – Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Di.S.Te.B.A., Università del Salento, via Monteroni, 73100 Lecce, Italy

^b Laboratorio di Spettrometria di Massa Analitica ed Isotopica, Dipartimento di Beni Culturali, Università del Salento, via Monteroni, 73100 Lecce, Italy

^c Archeologo collaboratore esterno della Soprintendenza per i Beni Archeologici della Basilicata (SBA BAS), Italy

ARTICLE INFO

Article history:

Received 6 October 2014

Accepted 17 April 2015

Available online 16 May 2015

Keywords:

X-ray photoelectron spectroscopy

XPS provenance studies

Terra Sigillata

Matera pottery

Apulian/Lucanian basin clays

ABSTRACT

One of the most important aspects of archaeometric investigations regards provenance. There are numerous studies on pottery in which the origin is investigated employing NAA, XRF or ICPMS. “Terra Sigillata” productions have been widely studied from the point of view of the composition as well. This work represents the first analytical application of the XPS technique in pottery provenancing and in particular of three Terra Sigillata wares exhibited in the Matera National Archaeological museum and dating back to the sixth-seventh century AD. XPS permitted to ascertain the samples were imported and among the different known ateliers the samples match the composition of Sigillata A/D, specifically the one produced in the factory of Henchir el-Guellal at Djilma, central Tunisia. The analyses also definitely excluded the possibility that a local production, imitating the shapes of African Terra Sigillata in accordance with the tendency of production typical of the sixth and seventh centuries AD, occurred.

© 2015 Elsevier Masson SAS. All rights reserved.

1. Introduction and research aims

Ceramics are durable material and are found in great amounts in the majority of archaeological sites dating from the Neolithic period onwards and for this reason they have been a major focus of archaeological sciences since their beginning. The physical sciences contribute to ceramic studies and help to reconstruct their life cycle from production through trade to use and provenance is one of the most significant inputs [1]. Provenancing on compositional bases has been conducted successfully for many archaeological, historical and artistic materials. The differences in element distribution from site to site, or, more frequently, the trace elements whose concentration level is geologically characteristic have been often used to drop an artifact to its origins. As it is not known a priori which elements are discriminating and provide useful information for locating the origin, many elements are generally determined, hoping the selection comprises those having definite discriminating power.

* Corresponding author.

E-mail addresses: giuseppe.debenedetto@unisalento.it, gedb67@gmail.com (G.E. De Benedetto).

In the present study, pottery samples are characterized as part of a large group of materials in graves, pertinent to small burial grounds located in the suburbs of Matera (Fig. 1S). Most of the burials are the result of occasional findings in the first half of the Twentieth century and were accompanied only by a few toponomastic notes and small descriptive indications. The general archaeological project, of which this paper introduces the first phase of archaeometric support, consists of the analysis of selected finds of the necropolises of Matera including also metal ornament and clothing, glassy and bronze furnishings [2–4]. Among the pottery finds, mostly made up of painted jugs and amphorae, three open forms (a plate, a bowl and a basin, Fig. 1 and Table 1S) of Terra Sigillata were investigated. The choice was driven by the difficulty of recognition of the productions since the identified typologies pointed out earlier datings compared to that of the entire group of artefacts referable to the VI–VII centuries. If for the context in the place Bridge St. Giuliano, where the presence of two “alla cappuccina” graves is described, the chronology of the stamped dish (inv. 13370) of the type H50B (EAA Atlas I.65, tav. XXVIII-14) confirmed the dating of the nucleus of objects (also not separately associable), discordant appeared the one of the bowl (inv. 13365) coming from the place Saint Lucy to the Bradano, of the type H18.1 (EAA, Atlas I.53, tav. XXIV-1) attested in the III century despite to the metallic ornament and clothing clearly referable to the VI–VII

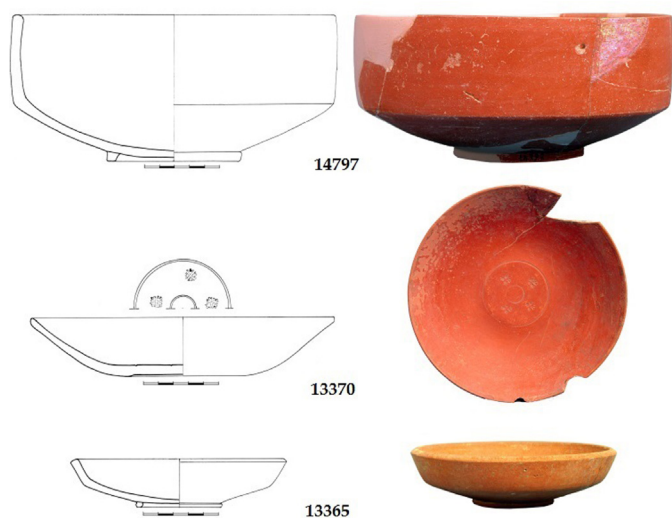


Fig. 1. Sample photographs of Terra Sigillata Wares analyzed in the present research.

century. Completely isolated appears the vessel (inv. 14797) coming from the Monte Igino di Timmari, with mat varnish to red brick, identified as Lamboglia 3b/H14B (EAA, Atlas I.33, tav. XVII-2) produced in A2 and dated to the half of the III century. The ability to define the specific productive circle could allow straight considerations on the consistence of the graves and on the possible associations with the other objects.

It is important to consider that the centuries V–VII are characterized by a progressive introduction of local productions that imitated the highly functional forms of Sigillata Africana [5]. These ateliers, initially linked to the crisis in the African market following the Vandal invasion, are now considered as protagonists of a real market parallel to “original” Africans products since the correspondence between the presence of imitations/absence of sigillate is not a rule in all sites.

In Basilicata, the presence of a furnace at Calle di Tricarico (MT) and one at Venosa (PZ), supported by the finding of material scraps, testifies the production of sigillata imitations between the IV and V century [6,7] and possibly points to define a local production. According to the above considerations, to obtain exhaustive and discriminating data, a comparison of samples coming from certain local production (Furnace of Tricarico) with the data available in the literature relating to clays of the hydrogeological basin of Matera [8–10], was carried out. Then, the unknown Terra Sigillata samples were compared with both these local samples and different African productions, whose data are available from various studies [11–13], in order to locate the connected ateliers and then the chronology of the chosen objects.

X-ray photoelectron spectroscopy (XPS), a multi-elemental and non-destructive analytical technique, was the selected analytical tool. It probes surfaces, however it can give bulk information by analyzing the cross-sections or pulverizing the sample. This technique has been widely used to analyze archaeological and artistic materials since the seventies, generally in the characterization of coatings or patinas [14–19]. XPS, despite the lower sensitivity respect to established analytical techniques such as NAA or ICPMS, shows distinctive characteristics as it permits the analysis of all elements but hydrogen and helium, the speciation, i.e. the determination of the oxidation state of the elements; also sample sputtering permits the study of concentration profiles of a given species, along the thickness.

The main aim of the present study was to determine whether samples could be local or imported products. XPS, for the first time

to our knowledge, was used in a provenance study of Terra Sigillata wares and demonstrated effective and of great help for the correct interpretation of the archaeological records.

2. Experimental

XPS analysis was carried out using a Leybold LHS10 spectrometer equipped with an unmonochromatized AlK α source (1486.6 eV) operating at 10 kV and 17 mA and a SPECS multi-channel detector. The base pressure in the instrument was 10⁻⁹ mbar. Samples of appropriate size for the housing of the sample holder of the instrument were obtained by museum conservators. The fragments were anchored by the use of copper adhesive tape to the bar of the unit sample holder and then were introduced into the analysis chamber through a rail system. For some samples, those belonging to Calle of Tricarico furnace, it was also possible to pulverize part of the sample. The obtained powder was adhered on the copper adhesive tape properly shaped. For each sample a wide-scan spectrum (WS) was acquired in the energy range 0–1400 eV, by adopting the FRR mode (fixed retarding ratio), while high-resolution (HR) regions were acquired in fixed analyzer transmission mode (FAT). HR spectra relevant to C1s, K2p, Si2p, O1s, Al2p, Ca2p, Fe2p, Mg1s, and Na1s were recorded. Data analysis and peak deconvolution were performed by means of SpecsLab software that allows satellites and background correction (in this case Shirley background subtraction) as well as curve-fitting of photoelectronic peaks. Surface charging was calculated considering C1s (BE = 284.8 eV – signal of aliphatic carbon) to estimate correct binding energy (BE) for each signal. Few additional measurements have been performed by an Axis ULTRA DLD Spectrometer (Kratos Analytical, UK).

Quantitative analysis was performed by determining atomic ratios (mol/mol), employing relative sensitivity factors [20] measured using pure solid standards and reported in fundamental literature [21]. Validation of selected factors to be applied to our samples was performed by analysing a proper certified material (Brick Clay, SRM 679, NBS) by the same apparatus in the same experimental conditions.

3. Results and discussion

It is well known the XPS capability to give both surface and bulk analysis by simply probing ceramic surfaces or powders. Powder analysis is generally preferred because less prone to surface contamination. Also data relevant to African Terra Sigillata reported in literature are obtained generally from powders [11–13]. Two fragments from Furnace of Calle of Tricarico, Tr1s and Tr2s, and the relevant powders, Tr1p and Tr2p, were analyzed by XPS using the same experimental setup as described in the experimental section. The resulting data are reported in Table 1 and show a substantial homogeneity between bulk and surface of the samples for the main elements, as both the differences are not statistically significant at a confidence level of 95% (paired *t*-test, *n* = 5, *P* = 0.05). This test permitted to neglect the difference between the two sampling mode (powder and bulk) for the main elements as due simply to random

Table 1

Atomic ratios of main elements to silicon for both surface and powder of two Sigillata samples from Calle of Tricarico furnace (means of three measurements; the errors reported represent $\pm 1 \times$ standard deviation).

| | Al/Si | Fe/Si | Mg/Si | Ca/Si |
|-------------|-----------------|-------------------|-------------------|-----------------|
| Tr1-powder | 0.31 \pm 0.03 | 0.096 \pm 0.014 | 0.091 \pm 0.003 | 0.35 \pm 0.03 |
| Tr1-surface | 0.32 \pm 0.03 | 0.063 \pm 0.012 | 0.084 \pm 0.005 | 0.40 \pm 0.05 |
| Tr2-powder | 0.33 \pm 0.02 | 0.034 \pm 0.004 | 0.063 \pm 0.006 | 0.38 \pm 0.03 |
| Tr2-surface | 0.33 \pm 0.04 | 0.067 \pm 0.009 | 0.077 \pm 0.009 | 0.34 \pm 0.04 |

Download English Version:

<https://daneshyari.com/en/article/1037856>

Download Persian Version:

<https://daneshyari.com/article/1037856>

[Daneshyari.com](https://daneshyari.com)