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Electrochemical discrimination of manufacturing types of pottery from *Magna Mater* Temple and Fora of *Nerva* and *Caesar* (Rome, Italy)

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ABSTRACT

The voltammetry of immobilized microparticles (VIMP) methodology is applied to a series of pottery samples from the Roman sites of *Nerva's Forum* (second half of 9th-early 11th A.D), *Caesar's Forum* (second half of 9th-early 11th A.D) and *Magna Mater* Temple (III century). The VIMP sampling applied to voltammetric and electrochemical impedance spectroscopy (EIS) measurements was applied by the first time to acquire archaeometric information on archaeological pottery. VIMP measurements using pressed sample pellets on gold electrodes in contact with air-saturated 0.10 M H_2SO_4 have permitted to detect voltammetric signals for the reduction/oxidation of Fe and Mn minerals as well as catalytic effects the mineral components on gold oxidation and oxygen reduction reaction. A consistent sample grouping was obtained using independent EIS measurements performed on microparticulate deposits of pottery samples on graphite electrodes in the same electrolyte.

1. Introduction

Ceramic materials are of great importance in the archaeological science as far as each population, over the centuries, has developed specific production technology depending on the knowledge and sources of raw materials (Towe, 1999). Archeologists usually discriminate potteries according to the morphology, style and the decoration of the pottery (Aruga et al., 1993) while the characterization of the materials had helped the knowledge about production technologies, raw materials used and provenance (Gomez et al., 2002; Rathossi et al., 2004; Chatfield, 2010; Andaloro et al., 2011; Kramar et al., 2012). Moreover, ceramics can be considered as chronological indicators carrying out information about the archaeological context (Medeghini et al., 2014). Accordingly, the discrimination between different pottery types is of archaeometric interest, but this aim is frequently made difficult by the fragmentation of the objects and their appearance in ill-defined archaeological contexts.

There are several factors that influence the production of pottery in the ancient times: temperature, reducing or oxidant atmosphere in the furnace, duration of the firing, crystallization of neoformed minerals as well as the skills of the artisan (De Benedetto et al., 2002). Pottery is usually characterized by means of elemental analysis, accompanied by thermal analysis, X-ray diffraction, Raman spectroscopy, SEM-EDS, FTIR, (Mangueira et al., 2013, 2016), as well as neutron and synchrotron radiation-based techniques (Bennington, 2004; Botti et al., 2006; Barone et al., 2011), usually combined in multi-technique approaches (Maltoni et al., 2012; Grifa et al., 2013;De Vito et al., 2014; Medeghini et al., 2014). Several of available techniques, however, involve the use of interdepartmental equipments, thus limiting their practical use for routine analysis when large number of objects is recovered from the archaeological sites, a common demand of archeologists, conservators and restorers.

In the current report, we present a methodology aimed to complement the existing techniques for pottery grouping of application in routine analysis and even for in-field analysis. This is based on the voltammetry of microparticles (VIMP), a technique developed by Scholz et al. (2014), which needs a minimally invasive sampling (Doménech-Carbó et al., 2009, 2013). The VIMP technique, previously used for characterizing different iron and manganese compounds in ceramic materials (Doménech-Carbó et al.,2001 & 2002; Sánchez-Ramos et al., 2002) and for discriminating the production centers of archaeological lead silicate glasses (Doménech-Carbó et al., 2016), has been used here for the first time to discriminate pottery samples. In order to validate the proposed electrochemical methodology, the study was applied to a series of samples coming from the *Caesar's Forum* in Rome (second half of 9th-early 11th A.D.) which were previously

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divided into three groups on the basis of petrographic analysis, microstructure, mineralogical and chemical composition (De Luca, 2006; Coletti, 2012; De Vito et al., 2018). The proposed methodology is extended here to samples of potteries extracted from other two different archaeological sites in Rome, namely, *Magna Mater* Temple and *Nerva's Forum*, dating back to the III century and the second half of 9th-early 11th A.D., respectively, which have not been previously described.

In order to enhance the sensitivity, a gold electrode was used for replacing graphite electrodes as a sample substrate. This methodology, new in the VIMP frame, is directed to characterize the ceramic materials on the basis of the direct reduction/oxidation of solid electroactive components (mainly Fe and Mn minerals) and their possible catalytic effects on gold-centered processes (Hasse et al., 2013; Doyle and Lyons, 2014) and the catalytic effects on the oxygen evolution reaction (OER) and the reduction of dissolved oxygen (Jeyabharathi et al., 2014).

VIMP measurements were performed in aqueous acidic media (0.10 M H_2SO_4) and were complemented by ATR-FTIR and electrochemical impedance spectroscopy (EIS). This last is an electrochemical technique which has been also used in the study of cultural heritage (Cano et al., 2010; Redondo-Marugán et al., 2017).

2. Experimental

2.1. Instrumentation and methods

Voltammetry of Microparticles was performed at 298 K in a three-electrode cell using a CH I660C device (Cambria Scientific, Llwynhendy, Llanelli UK) using air-saturated aqueous 0.1 M H_2SO_4 solution (Panreac) as a supporting electrolyte. A BAS MF 2012 gold electrode was used as a working electrode, the three-electrode arrangement being completed by a platinum wire auxiliary electrode and an Ag/AgCl (3 M NaCl) reference electrode. The analysis of ceramic bodies was carried out by extracting, with the help of a scalpel, 2–5 μg of sample from the section of the ceramic fragment, and powdering it with an agate mortar and pestle. The material was extended and grouped forming a fine disk of ca. 5 mm diameter on the plane face of the mortar and then the gold electrode was pressed on it forming a pressed pellet.

EIS experiments were performed by powdering 2–5 μg of sample into an agate mortar and pestle. The powder was subsequently transferred by abrasion to the surface of the gold electrode and dipped into the electrochemical cell so that only the lower end of the electrode was in contact with the electrolyte (air-saturated aqueous 0.1 M H_2SO_4). Spectra were recorded in the 0.1 and 100.000 Hz frequency range with amplitude of 5 mV at a bias potential of 0.0 V or −0.4 V. Three different experiments were done for each sample.

Complementary IR spectra in the ATR mode were obtained accumulating 16 scans at a resolution of 4 cm^{-1} using Vertex 70 (Bruker Optik GmbH, Germany) Fourier-transform infrared spectrometer equipped with an FR-DTGS (fast recovery deuterated triglycine sulphate) temperature-stabilized coated detector and a MKII Golden Gate Attenuated Total Reflectance (ATR) accessory. The spectra were processed using the OPUS 5.0/IR software (Bruker Optik GmbH, Germany).

2.2. Archaeological context and samples

The ceramic objects here studied cover a vast period of time (III and IX-XI A.D. centuries) and consist of glazed ceramic fragments. In particular the ceramics from *Magna Mater* temple, dating back to III century A.D., were found in some rooms of the two sectors in the southwestern area of the Sanctuary, consisting of *tabernae* and *fullonicae*, and in part from *tabernae* and a *latrinae* of the *Domus Tiberiana* (De Luca, 2006; Coletti, 2012; De Vito et al., 2018). The ceramic samples from the *Nerva's Forum*, coming from *domus* porticata of high Roman aristocracy, dated between the mid IX^{th} and the mid X^{th} centuries (De Luca, 2006) and those from *Caesar's Forum* in two *domus terrinae* of low social groups, dating back to the X^{th} and beginning of the XI^{th} century.

In details, 7 fragments from the *Magna Mater* Temple (TMM18, TMM86, TMM87, TMM98_RZ, TMM98_RZ58, TMM99, and TMM5653), 5 fragments from the *Nerva's Forum* (US1425, US1428, US1445, US1445_5, and US1458) and 6 fragments from *Caesar's Forum* (Ces8, US1490, US1495_4, US1495, US3180, and US3180foc) were studied.

3. Results and discussion

3.1. Mineralogical and microstructural properties

Previous XRPD, SEM-EDS and EMPA analysis of samples (De Vito et al., 2018) revealed the presence of quartz, both plagioclase (from albite to Ca-rich albite) and alkali feldspar (sanidine), and hematite as ubiquitous components although with different abundances, often accompanied by biotite, pyroxene (augite), rare olivine (fayalite) and calcite (primary and secondary). The absence of clay minerals and the presence of mica suggested a firing temperature from 900 °C to 1050 °C. The presence of hematite suggested that the potteries were fired under oxidizing conditions and the low presence of primary carbonate and/or neoformed minerals indicated the use of non- or moderately calcareous clayey materials, consistently with ATR-FTIR spectra (see Supplementary information, Fig. S.1).

3.2. Voltammetric pattern

Voltammetric measurements consist of the record of the current passing through an electrochemical cell when a (difference of) potential varying with time is applied between a working electrode and a reference electrode. In VIMP, the pottery sample is attached to the working graphite electrode and the voltammogram reflects the chemical changes occurring in the solid material associated to the transfer of electrons through the system. Fig. 1 shows the square wave voltammograms of samples (a,b) US1445 and (c,d) US1425 from *Nerva's Forum* deposited on gold electrodes immersed into air-saturated aqueous 0.1 M H_2SO_4 aqueous solution. In the negative-going potential scan voltammograms (Figs. 1a, c), cathodic signals at +0.85 V (C_{Au}) and −0.15 V vs. Ag/AgCl (C_{ORR}) appear accompanied by a series of more or less intense signals between +0.65 and −0.45 V. These signals are limited by the rising currents associated to the evolution of oxygen (oxygen evolution reaction, OER) and hydrogen (hydrogen evolution reaction, HER) at the positive and negative extremes of applied potential. The signal at −0.15 V (C_{ORR}) corresponds to the reduction of dissolved oxygen (Doyle and Lyons, 2014) whereas the peaks +0.65 and −0.45 V can be associated to the reduction of Fe(III) minerals, typically hematite (Fe_2O_3) and goethite (FeO(OH)) (Grygar, 1997;Doménech-Carbó et al., 2002). The peaks appearing in the same region of potentials in positive-going potential scans (Figs. 1b,d) can be attributed to the oxidation of Fe(II) ones, typically, augite ($Ca_{0.61}Mg_{0.76}Fe_{0.49}(SiO_3)$, falayite ($Fe_2SiO_4$), gehlenite ($Ca_2(Al,Fe, Mg)(Si,Al)_2O_4$) and chrisolite ($(Mg,Fe)_2SiO_4$. Such signals are accompanied by a prominent oxidation wave at +1.20 V (A_{AuM}) which corresponds to the oxidation of the base gold electrode to gold oxide forms (Doyle and Lyons, 2014) catalyzed by the ceramic materials, the gold oxide being reduced (peak C_{Au}) in positive-going potential scans.

In several cases, such as in that of sample US1425 from *Nerva's Forum* (see Figs. 1c,d), additional cathodic and anodic peaks at ca. −0.50 V (C_{Pb}, A_{Pb}) appear. These signals can be attributed to the presence of Pb(II) species (Doménech-Carbó et al., 2016) released from white lead used in the decoration of the pieces.

3.3. VIMP grouping

For our purposes, the relevant point to emphasize is that the chemical and mineralogical composition of the ceramic sample will