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AUTHENTICATION OF ROMAN CORRODED LEAD ARTEFACTS FROM ARCHAEOLOGICAL SITES IN CALCAREOUS ENVIRONMENT IN JORDAN BY ELECTROCHEMICAL ANALYSIS

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ABSTRACT

The process of authentication involves a wide variety of steps that are intimately linked and completely interdependent. In this research voltammetry of micro-particles (VMP) is used to date and authenticate a five late Roman lead balance weights. The chronology of the archaeological finds together with lead balance weights was estimated to be 4th century AD. A set of independent experiments: square wave voltammetry and electrochemical impedance spectroscopy (EIS) with the corresponding calibration curves obtained from several archaeological samples, which have been done in our laboratory. The collected sample were corroded under burial conditions in calcareous soils, are consistent with an attribution of the age of both studied lead samples. The ratio of PbO₂ and the porous PbO which formed during the process of lead corrosion in the calcareous environment reflects the date of corrosion. These attribution, however, must be taken with caution because of the differences in the aging process for the studied samples and the lead materials used for calibration purposes corresponding to the reduction of the PbO 'continuous' patina formed under the ordinary exposure of the lead piece to the atmospheric environment. The ratio between peaks resulted from the corrosion process of Ancient lead and reference one revealed the date of corrosion. Assuming the 4th century AD chronology of the lead samples erection to be correct, it was found that the applied method provide the same result which is consistent with archaeological estimations.

KEYWORDS: Authenticity, Dating, Corrosion, Voltammetry, Weight lead, Impedance Spectroscopy

1. INTRODUCTION

Authenticity is a vital process in archaeology and is extremely important to the archaeological context especially for the less developed techniques for metals (Ali & Abd-Allah, 2015; Holtorf & Schadla-Hall, 1999; Miller, Sayre, & Keisch, 1970; Nambi, 1981; Odegaard & Cassman, 2014; Cruz et al., 2015; Liritzis 2006). The more that is known about the artifacts and its relation to the surrounding environment the more that can be interpreted on boarder issues. A methodology for dating archeological lead artifacts based on the voltammetry of microparticles is described. This methodology is based on the comparison of the height of specific voltammetric features from PbO_2 and PbO corrosion products formed under long-term alteration conditions (Brusic, Dimilia, & MacInnes, 1991). Two basic requests must be met for the electrochemical instrumental technique when it is applied in conservation of cultural heritage research: sensitivity, for attaining significant data from very small quantity of nano, micro or milligramscale; and specificity, for definitely identifying compounds and quantifying the analytes from the complex combinations of substances that form the materials present in the monument, sarcophagus or other artifacts (Rocca, Mirambet, & Steinmetz, 2004; Taylor, 1993). Other requirements are also required for analytical method when it is applied to archaeological objects. Electrochemical voltammetry of microparticles technique were used for the authenticity of lead samples. This methodology is based on the comparison of the height of specific voltammetric peaks from PbO_2 and PbO corrosion products formed (Doménech, 2011). This attribution, however, must be taken with caution because of the differences in the aging process for the studied samples and the lead materials used for calibration purposes corresponding to the reduction of the PbO 'continuous' patina formed under the ordinary exposure of the lead piece to the atmospheric environment. The proposed electrochemical technique enables the dating of lead artifacts with a time-dependent (Antonio Doménech-Carbó, Doménech-Carbó, & Costa, 2009; A Doménech-Carbó et al., 2017; Lahanier, 1991).

According to Lahanier et al. (1991) the electrochemical techniques are non-intrusive, non-destructive, fast, allowing the analysis of single arti-

facts as well as large collections of them. This method are able to deal with various shapes and sizes as well as providing information on both average or bulk composition of the artifact. Another advantage of this multi-element analysis, it's capability of allowing qualitative information on multiple elements or compounds present in the artifact by means of a single measurement (Lahanier,1991).

Materials authentication could help in our understanding not only to their functions but about other matters, such as trade and economy (Burtenshaw, 2013). In fact, the material remains of the past that conform to contemporary aesthetics are often the most valuable. It gives artifacts their legal authenticity and archaeological significance (Lovata, 2016).

Qasr Al-rabah temple is located in Al-Qasr town, approximately 5 km to the north of Al-rabah town, about 5 km to the north of Karak city and 18 km to south of Wadi Al-Mujib (Fig.1). During the Roman period, Qasr Al -rabah was one of the important cites of the ancient world. It was first excavated in 1993 by Al-Shiyab followed in the period 1995-2002. Early excavation which was conducted by Al-Shiyab, (1993), revealed that the site was extensively settled during the Roman and Byzantine periods. This site comprises a collection of ruins of various buildings and structural remains (Fig. 2). Considerable collections of glass, lead-based scale weights were uncovered, together with plenty of ceramic sherds from different structures (A. Al-Shiyab, 1993). Archaeological studies at the site were very rare and limited. Waterhouse (1998) studied the construction style of the tombs (Waterhouse, 1998). Abu-Baker et al. (Abu-Baker et al., 2014) studied the composition and corrosion behaviour of five archaeological lead scale weights. In a study conducted by Al-Shorman and Shiyab (2015) several ceramic sherds have been chemically and mineralogical analyzed to see the effect of function on selecting raw materials and technology.

The current article describes the analytical studies performed on five lead samples, one of the samples correspond to a fragment of a lead sarcophagus and the second weight sample from roman period. The data estimated from archaeological context was late Roman period (al-Āmmah, 1997; Al-Shiyab, 1993; Al-Shorman & Shiyab, 2015).

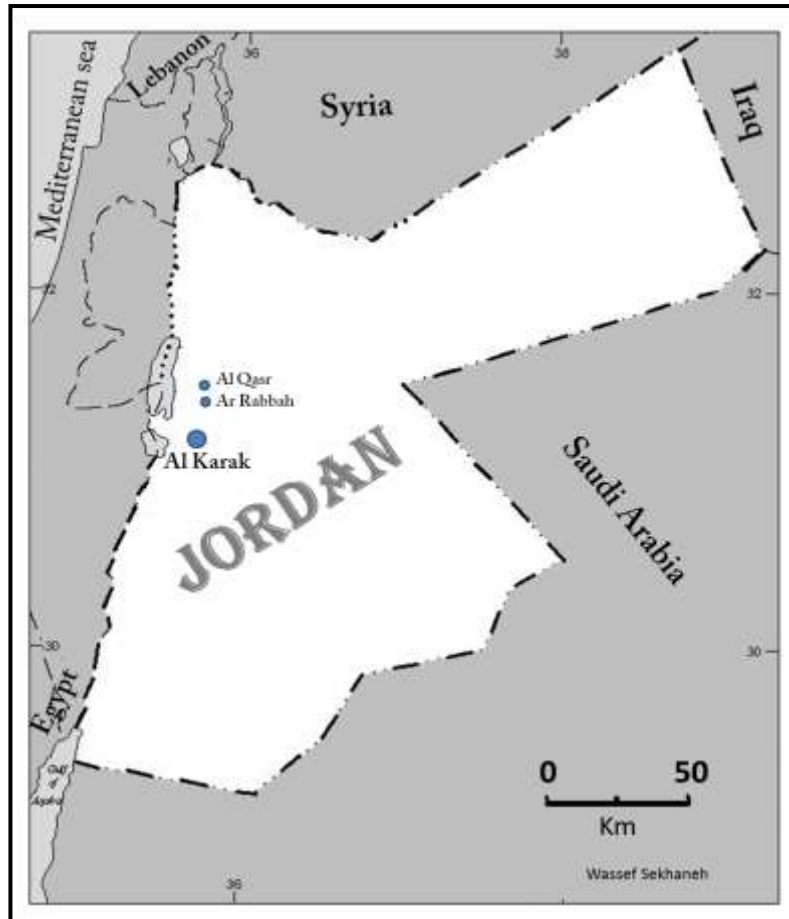


Figure 1. The location of archaeological site of Qsar Al -rabah



Figure 2. Temple remains in the study area

The study is primarily aimed to authenticate and to date the samples (Fig. 3). For this purpose, a series of electrochemical methods developed in our laboratory at Valencia university (Antonio Doménech-Carbó, Doménech-Carbó, & Peiró-Ronda, 2011; Antonio Doménech-Carbó, Doménech-Carbó, Peiró-Ronda, Martínez-Lázaro, & Barrio-Martín, 2012; Antonio Doménech-Carbó et al., 2016; Antonio Doménech-Carbó, Doménech-Carbó, Capelo, Pasies, & Martínez-Lázaro, 2014) have been used. These methods, based in the voltammetry of microparticles method-

ology for analyzing solid materials developed by Scholz et al. (Scholz, Schröder, & Gulaboski, 2005), involve non-destructive sampling and permits to obtain relevant information for archaeometry, conservation and restoration (Antonio Doménech-Carbó, 2010; Antonio Doménech-Carbó, et al., 2009; Antonio Doménech-Carbó, et al., 2016), in particular, for authentication (Antonio Doménech-Carbó, Doménech-Carbó, Peiró-Ronda, & Osete-Cortina, 2011; Doménech, 2011).




Samples weights and dimensions of the lead-balance weights		
1. unshaped lead weight		Weight: 39.28g Max.Length: 34.90mm Max. width: 26.30mm Max. thickness: 10.30 mm
2. Square lead weight		Weight: 27.58g Length: 26.91mm Width: 26.45mm Thickness: 4.28mm
3. Perforated square lead weight		Weight: 6.62g Length: 16.98mm Width: 16.27mm Thickness: 3.24mm
4. Cubic lead weight		Weight: 11.68g Cubic: 10.93x10.88x10.44mm
5. Cylindrical lead weight		Weight: 5.34g Length: 11.16mm Width: 9.74mm Thickness: 6.29mm

Figure 3. The studied lead samples from the temple of Qasr Al-rabah

It should be noted, however, that dating is obtained upon comparison of electrochemical data for samples with those for reference archaeological lead

of known age which has been aged under identical calcareous environmental of burials conditions Table 1.

Table 1. reference lead samples After Doménech-Carbó (A Doménech-Carbó, et al., 2017)

Sample	Description of the Artifacts	Provenance
MP-1-1 to MP-1-3	Votive figurine; dark green surface, apparently homogeneous with greenish localized regions in corners	Iberian site (Despeñaperros, Jaén), fourth to second century BC
MP-2-1 to MP-2-3	Buckle, black surfaces with high homogeneity but with several localized greenish pits	San Cristóbal church (Picassent), 18th–19th century AD
UPV-1	Gades, la danza, dark grey surface apparently homogeneous	Sculpture by Antonio Miró, 2001
UPV-2	Crónica del viento, dark grey surface apparently homogeneous	Sculpture by Martín Chirino, 1991
UPV-3	Unidad yunta, dark grey surface apparently homogeneous	Sculpture by Pablo Serrano, 1970
V-122-1 to V-122-3	Fragment 1 of sculpture, dark grey surface with greenish localized regions	Valeria site, second half of the first century AD
V-390-1 to V-390-3	Fragment 2 of sculpture, dark grey surface with greenish localized regions	Valeria site, second half of the first century AD
VI-1-1 and VI-1-2	Fibulae, dark green surface, apparently homogeneous, with greenish pitting and localized regions in corners	El Viveret site, first to second century AD
G-1-1 to G-1-4	Pieces 1–4 of a set of weights, black surfaces with high homogeneity	Gadara site, fourth century AD
X-1	Fragment of spur (Caliphal period), dark green surface with greenish localized regions in corners	Xàtiva (Valencia), AD 950

The study is based on disposable data for calibration corresponding to samples corroded under burial conditions in calcareous soils all from the Mediterranean region of Spain Doménech-Carbó, A., et al., (2017).

2. MATERIALS

Sampling was performed by means of the one-touch technique already described (Doménech-Carbó et al. 2011) using 0.1 mm diameter graphite bars (Staedtler HB). One touch method means: the minimum amount (im microe or nano scale) of corrosion products that one could get once electrode touch the materials. Sample 1 consisted of a lead plate ca. 1.5 × 1.5 × 0.3 cm. Fig. 4 shows an apparently recent cut in one of its corners and one circular hole (ca. 1 mm diameter) in the vicinity of other of the corners. Except in the cut region, the piece is covered by a gross, continuous white-grey patina. Sampling was performed in the center of the piece and in the cut region (labeled in the following as S1corr and S1cut). Sample 2 consisted of an irregular lead plate covered by a gross white crust (see Fig. 4). Sampling was performed in two regions where the patinated lead appeared exposed with grey (S2grey) and reddish (S2red) hues. As a control, a lead sample from the buildings at the University of Valencia (30 years old) was used. Architect used these lead nails in the construction of the building, and they used it as decoration features. The lead nails were the same age of the construction and uses as reference to measure the time of corrosion process. This consist-

ed of a grey button 1 cm diameter with no traces of gross corrosion processes.

Table 1. Description of the studied samples in this study.

Sample	Piece	Description
S1corr	Piece 1	Corroded zone of white-grey hue
S1cut	Piece 1	Cut region, dark grey hue
S2grey	Piece 2	Grey region exposed under the white crust
S2red	Piece 2	Reddish region exposed under the white crust

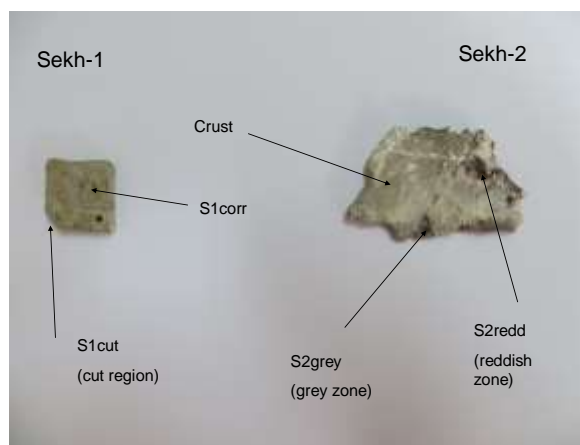


Figure 4. Image of the lead fragments in this study with indication of regions where the sampling was carried out.

3. METHODS AND EXPERIEMENTS

The advantage of using the electrochemical method are non-intrusive, non-destructive, fast and allowing the analysis of single artifacts as well as large collections of them. This method could use various shapes and sizes to provide information on both av-

erage or bulk composition of the artifact and the exact and localized composition of areas. Multielement analysis capability, allowing qualitative information on multiple elements or compounds present in the artifact by means of a single measurement. Electrochemical experiments were performed using a CH I660C potentiostat according to the manufacturing product. Measurements were performed in 0.25 M acetic acid/sodium acetate Buffer (Panreac), pH 4.75, in a thermostated three-electrode cell under argon atmosphere using a AgCl (3M NaCl)/Ag as reference electrode and a platinum-wire auxiliary electrode. Voltammetry of micro-particles (VMP) experiments were performed at sample-modified at paraffin impregnated graphite electrodes (PIGEs).

Five independent measurements were performed for each sample; reported numerical values for the different electrochemical parameters involved in this study correspond to average values from each series of measurements. Electrochemical impedance spectroscopy (EIS) was carried out using a ± 10 mV perturbation signal within a frequency range from 100 kHz to 0.10 Hz at different potentials. Sampling for electrochemical measurements was performed by means of the 'one-touch' procedure by pressing the edge of the graphite electrode on the desired point of the lead sample as described in literature (Antonio Doménech-Carbó, et al., 2012; Scholz, et al., 2005). Sampling was performed on two of the fragments whose surfaces appeared as no submitted to recent scratching. Sample S1cut, immersed into 0.25 M HAc/NaAc, pH 4.75. Potential scan initiated at +1.25

V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

4. RESULTS AND DISCUSSION

The authenticity result compares the square wave voltammograms recorded for for : a) recent lead fragment (30 years old); b) sample S1cut, immersed into 0.25 M HAc/ NaAc, pH 4.75. Potential scan initiated at +1.25 V in the negative direction. Potential step increments 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

The authenticity tests measurements (VMP) for (30 years old) lead piece shows no sign of detectable corrosion layer and very low intensity peak, which is related to the short time span of the sample S1cut in contact with aqueous acetate buffer (Fig 5a,b). The voltammogram of the S1cut sample shows the characteristic features of archaeological lead. As you can see from the figure and if compared with Fig.5a one defines the define and the sharp cathodic peaks at +0.80 V, assigned to the reduction of PbO_2 -type species, and -1.00 V, which correspond to the reduction of 'porous' layers of PbO formed on the metal surface. Such peaks accompany the ubiquitous peak at -0.70 V corresponding to the reduction of the PbO 'continuous' patina formed under the ordinary exposure of the lead piece to the atmospheric environment (A Doménech-Carbó, et al., 2017) .

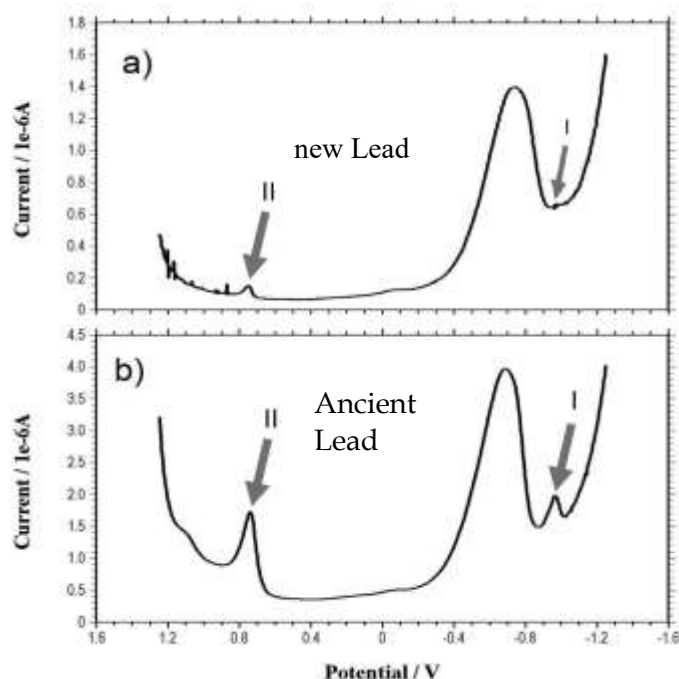


Figure 5. Square wave voltammograms for graphite electrodes modified by means of 'one-touch' methodology

As can be seen in Fig. 6 the cyclic voltametric responses recorded at graphite electrodes modified by means of 'one-touch' methodology for: a) modern lead fragment (30 years old), b) sample S1corr, c) sample S2grey; d) sample S2red. The samples exhibit the profiles characteristic of aged lead, with enhanced cathodic signals at ca. -1.0 V (marked by arrows) and oxidative dissolutions signals at ca. -0.50 V (dotted arrows). These last signals correspond to

the oxidation of lead metal previously generated in the reduction of lead corrosion products at more negative potentials. Pb metal is oxidized to Pb^{2+} (aq) ions in solution giving rise to characteristic tall (stripping) peaks. As seen in figure 5 the voltammetry measurements: a) recent lead fragment (30 years old), b) sample S1corr, c) sample S2grey; d) sample S2red, immersed into 0.25 M HAc/NaAc, pH 4.75. Potential scan rate 50 mV/s.

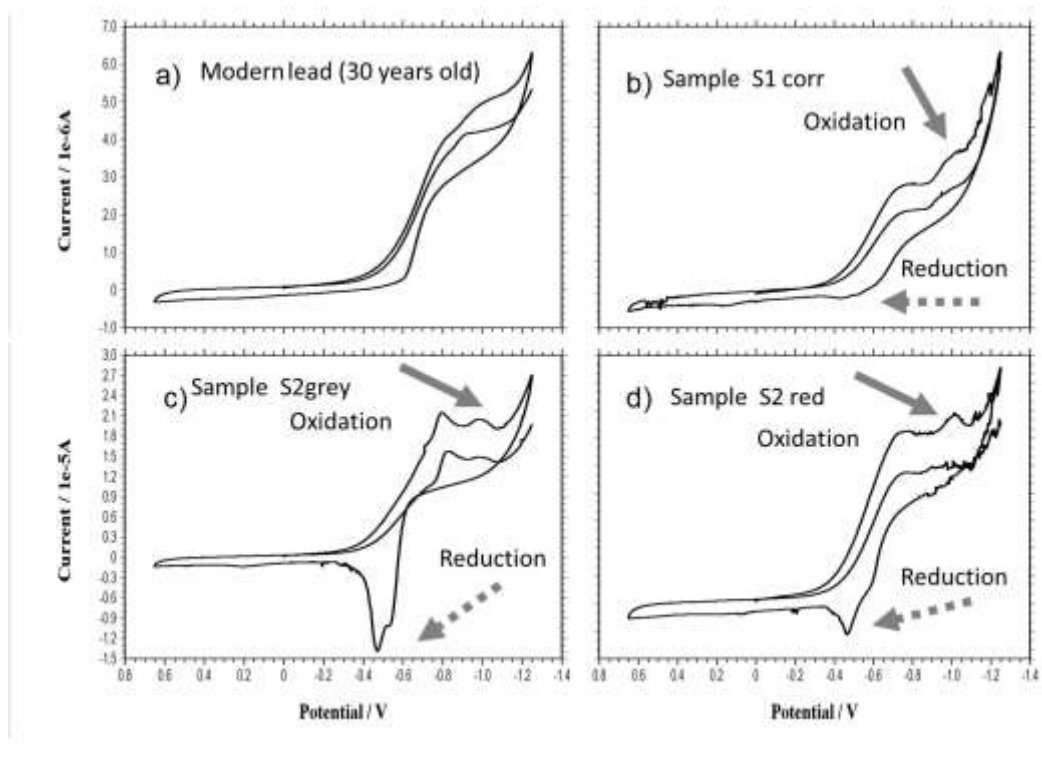


Figure 6. Cyclic voltammetry measurements for graphite electrodes (Oxidation-Reduction) modified by means of 'one-touch' method for the lead samples

Such stripping peaks can be clearly seen in square wave voltammograms obtained upon scanning the potential in the positive direction, as can be seen in Fig. 4. Here, the lead stripping signals at ca. -0.50 V are accompanied by minor signals attributable to copper (oxidative dissolution peak at ca. 0 V). Other weak signals could denote the presence of antimony (ca. -0.20 V) and arsenic (ca. +0.20 V).

In order to confirm the result in Fig. 4, and for double checking that our result is consistent with the estimation, the square wave stripping method was used. Through this method stripping peaks can be clearly seen in square wave voltammograms ob-

tained upon scanning the potential in the positive direction, as can be seen in Fig. 7. Here, the lead stripping signals at ca. -0.50 V are accompanied by minor signals attributable to copper (oxidative dissolution peak at ca. 0 V). Other weak signals could denote the presence of antimony (ca. -0.20 V) and arsenic (ca. +0.20 V) as a minority accompanying elements. The presence of minor components accompanying lead can be considered as demonstrating of the 'ancient' origin of the metallic material, as far as the signals of minority components are absent in 'modern' and contemporary lead (Antonio Doménech-Carbó, et al., 2011; Doménech, 2011).

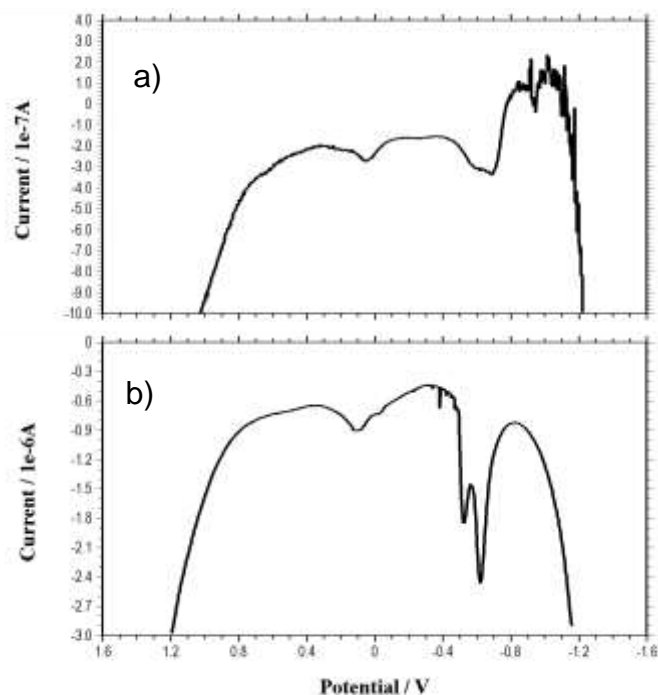


Figure 7. Square wave voltammograms for graphite electrodes modified by means of 'one-touch' methodology for samples a) S1corr and b) S2grey immersed into 0.25 M

The dating method of the studied samples was performed using the procedures described in detail in (Antonio Doménech-Carbó, et al., 2009; Antonio Doménech-Carbó, et al., 2012; Scholz, et al., 2005), as described in the following.

The method is based on the determination of the peak ratio for signals corresponding to the reduction of continuous and porous PbO layers recorded, as recommended in (Scholz, et al., 2005), in voltammograms such as in Fig.7. The peak current ($i_p(\text{II})/i_p(\text{I})$) and peak area ($A(\text{II})/A(\text{I})$) ratios for the studied samples (see Table 1) was compared with the calibration curve obtained for Spanish archaeological samples. This comparison can be seen in Fig. 6, where the variation of the peak area ratio vs. the estimated age is depicted. In this figure, $A(\text{II})/A(\text{I})$ is plotted against $(\text{age})^{0.935}$, a representation resulting

from the fit of calibration data to a potential law as previously described (Antonio Doménech-Carbó, et al., 2009; Scholz, et al., 2005). As can be seen in Fig. 7 that data points for samples S1corr, S2grey and S2red are located close, but separated, from the calibration line, whereas sample S1cut falls clearly separated from the calibration line. These data suggest that both samples S1 and S2 are contemporary and their age can be estimated within a time range of ca. 1500 ± 150 years. Sample S1cut separates clearly from the above, but this separation can be attributed to the different time in which this region was probably submitted to corrosion. Squares correspond to calibration data from Spanish samples Purple squares denote the measured samples in this study, which have an age of 1600 years BP (Fig. 9).

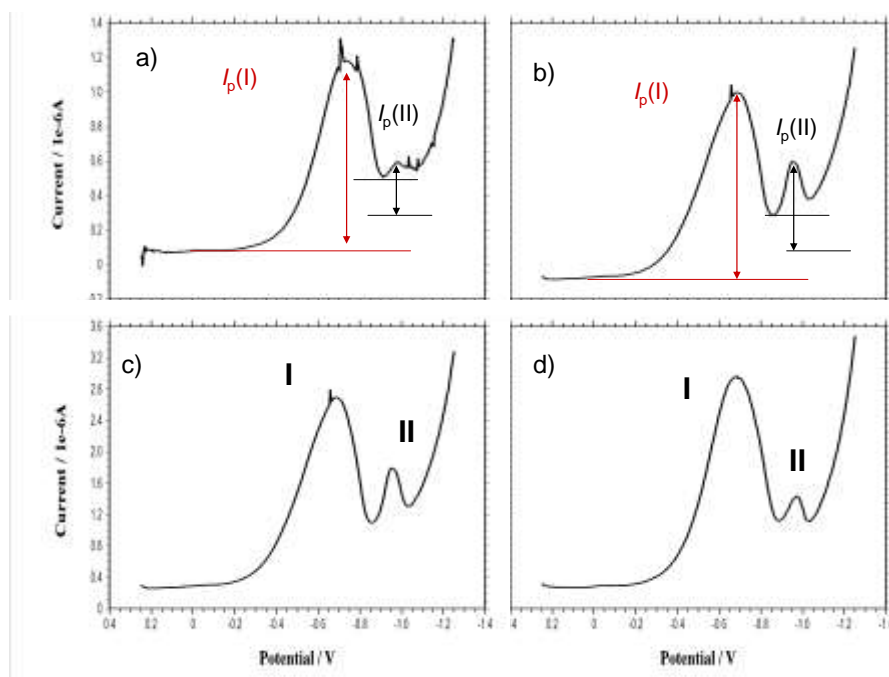


Figure 8. Square wave voltamograms for graphite electrodes modified by means of 'one-touch' methodology.

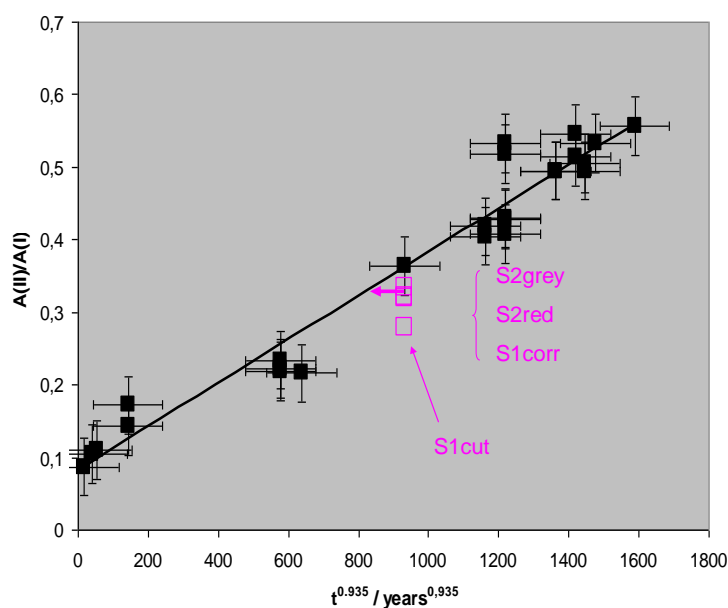


Figure 9. Peak area ratio vs. estimated age representation for archaeological lead.

As previously described, the Litharge PbO to Plattnerite PbO₂ ratio, expected from the intensity of peak current ratio between the signals(II) and (I), $i_p(\text{II})/i_p(\text{I})$, is used to calculate the age of a lead artifacts. Figure 8 shows the position of the ancient samples in our study, corrosion products were extracted from lead weight balances from the site of Qasr Al-rabaha (4th century AC, Jordan) (see Fig. 3), in the calibration curve constructed from already reported table 1.

Using Electrochemical impedance spectroscopy measurements (EIS) to confirm the authenticity by

comparing the series of samples in Table 1 with our measured samples. EIS experiments produced results comparable to those reported in Doménech-Carbó, A., et al., (2017). The Fig. 10 compares the (phase angle) vs. $\log(\text{frequency})$ plots for recent lead and S2grey sample, both in contact with aqueous acetate buffer. Here the high frequency region for both samples is similar while the phase angle clearly differs in the low frequency region. This feature can be attributed to the different charge transfer properties associated to the different thickness of the corrosion layers. Comparison of the measured phase an-

gles at a frequency of 0.10 Hz, taken as age-representative quantity (Antonio Doménech-Carbó, et al., 2012; Scholz, et al., 2005), permits a calibration plot depicted in Fig. 10. As can be seen in this figure, here once again data for the studied samples are consistent with the attribution to an aging time of ca.

1600 years. Bode (phase angle) vs. log(frequency) plots for a recent lead fragment (30 years old, black data points), and sample S2grey (red data points), immersed into 0.25 M HAc/NaAc, pH 4.75, aqueous solution. Bias potential -0.95 V.

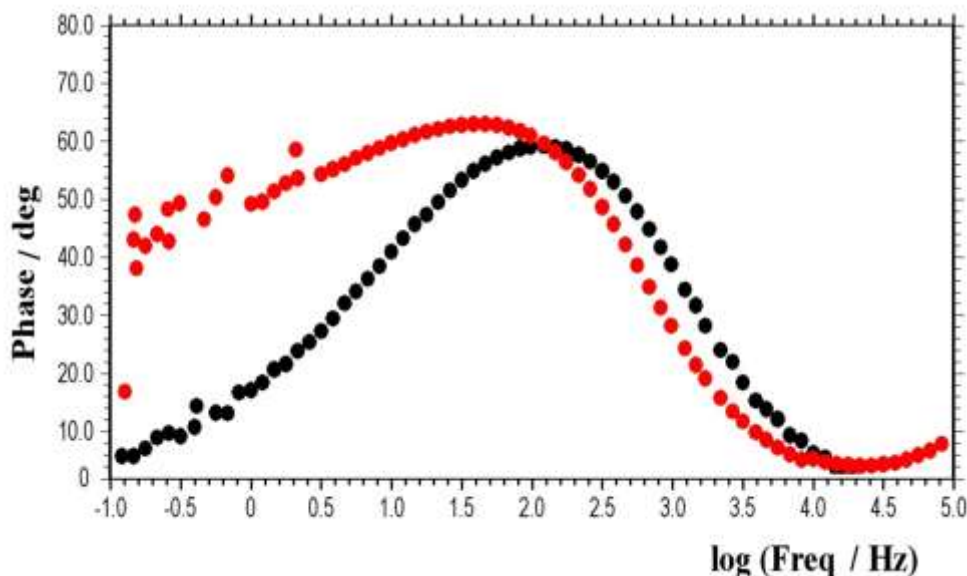


Figure 10. Bode (phase angle) vs. log(frequency) plots for a recent lead fragment (30 years old, black data points), and sample S2grey (red data points), immersed into 0.25 M HAc/NaAc, pH 4.75, aqueous solution. Bias potential -0.95 V.

EIS experiments are achieved in this study for samples that were used different bias potentials and electrolyte media, including 0.25 M aqueous of acetic acid / sodium acetate buffer at pH 4.75. After equilibration for 10 min, the EIS curves showed excellent good repeatability for replicate experiments performed for a fixed set of conditions. However, experiments varying the level of the immersion and the

location of the connected clamp, although maintaining the profile of Bode plots and Nyquist, produced major variations in the numerical values of the impedance variables. These features can be seen in Fig. 9, where the Bode plots and the Nyquist of repeated experiments for a sample in two different immersion plus clamp configurations are shown.

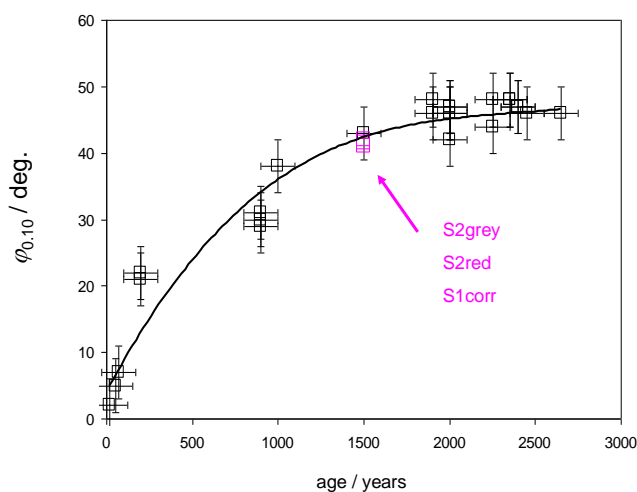


Figure 11. Calibration plots showing the variation of phase angle at a frequency of 0.10 Hz, $\phi_{0.10}$, with the corrosion time for samples in this study. Data from EIS experiments for sample-modified graphite electrodes immersed into 0.25 M HAc/NaAc. Bias potential -0.95 V.

As can be seen in Fig. 8, insertion of data points for S1corr, S2grey and S2red samples in this study falls in the calibration curve obtained from a set of archaeological lead samples from Spain (Doménech-Carbó et al. 2009, 2012) for an age of 1500 ± 100 years, thus agreeing square wave voltammetric data from independent experiments. Fig.11 shows the variation of the maximum phase angle at intermediate frequencies with the nominal age of several artifacts in the study. From five replicate EIS measurements for each sample that were immersed in mineral water. The continuous curve corresponds to the fit of the data to a potential equation. In calibration plots resulted (Fig.11), the variation of the phase angle φ frequencies with respect to the age of several samples is shown.

5. CONCLUSION

Assuming the 5th century AD chronology of the lead samples erection to be correct, it was found that the applied method provide the same result which is consistent with archaeological estimations. The voltammetry of microparticle-nanoparticle is an excellent non-destructive method, used in authenticity and dating archaeological materials.

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The electrochemical methods which have been used in this study are easy, cheap and convenient. VMP could help in a absolute chronology for archaeological metals.

At the expense of a re-calibration using additional archaeological samples, the electrochemical analysis performed on samples in this study permits to conclude:

1) The studied samples exhibit the voltammetric features characteristic of lead of archaeological origin, namely, stripping peaks for minority components accompanying lead and well-developed signals for PbO₂ and porous PbO patinas.

2) Comparison of electrochemical parameters using two sets of independent experiments: square wave voltammetry and electrochemical impedance spectroscopy with the corresponding calibration curves obtained from Spanish archaeological samples corroded under burial conditions in calcareous soils, are consistent with an attribution of the age of both studied lead samples to 1450 ± 150 years. This attribution, however, must be taken with caution because of the differences in the aging process for the studied samples and the lead materials used for calibration purposes.

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