

MetalEspaña 2020/2021

III Congreso de Conservación y Restauración del Patrimonio Metálico

Joaquín Barrio Martín
Milagros Buendía Ortuño (eds.)

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Anejos nº 6 | 2022

Departamento de Prehistoria y Arqueología
Facultad de Filosofía y Letras,
Vicerrectorado de Investigación
Universidad Autónoma de Madrid

**Cuadernos
de Prehistoria
y Arqueología**
de la Universidad Autónoma de Madrid

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Electrochemical techniques for dating metallic heritage

Técnicas electroquímicas para la datación del patrimonio metálico

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Abstract

In the last years a series of electrochemical methods aimed to date metal artifacts have been devised. These are based on the voltammetry of immobilized particles methodology, a solid state electrochemical technique that permits the use of samples from the metal patina of few nanograms. The state of the art is revised summarizing the dating methods proposed for lead, copper/bronze, leaded bronze and gold.

Key words: Electrochemistry, Metal heritage, Dating

Resumen

En los últimos años se han ideado una serie de métodos electroquímicos destinados a fechar artefactos metálicos. Estos se basan en la metodología de voltamperometría de partículas inmovilizadas, una técnica electroquímica de estado sólido que permite el uso de muestras de la pátina metálica de pocos nanogramos. Se revisa el estado de la técnica resumiendo los métodos de datación propuestos para plomo, cobre/bronce, bronce con plomo y oro.

Palabras clave: electroquímica, patrimonio metálico, datación

1. Introduction

Dating archaeological objects can be considered as an essential part of their scientific examination. In general, physicochemical techniques of dating require the disposal of any physical or chemical property that varies in a well-defined (“universal”) way with time and that was accessible to its experimental determination. Additionally, but importantly, it is required that the technique was non — or minimally — destructive.

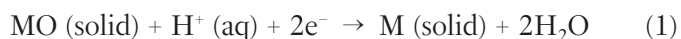
Dating metallic heritage is in principle favored by the existence of generalized corrosion processes. However, the high sensitivity of such processes to the composition, manufacturing techniques, and local environmental conditions made difficult the development of corrosion-based dating methods. Currently, precise dating of metallic artifacts is only possible when they are associated to organic matter to be dated by means of radiocarbon technique, or ceramic materials to be dated by means of thermoluminescence or obsidian hydration techniques (Doménech-Carbó, 2015). In fact, with except qualitative indications on the dezincification and destannification processes (Doménech-Carbó, 2017), proposed methods are limited to lead dating based on superconducting measurements (Reich et al., 2003) and gold dating based on the determination of He, U, and Th (Eugster, 1996; Eugster et al., 2009). These methods, however, suffer from the need of sample amounts at the milligram level.

In this context, we have proposed electrochemical methods for dating metallic heritage based on the voltammetry of immobilized particles methodology (VIMP), a technique developed by Scholz and coworkers (Scholz and Meyer, 1998; Scholz et al., 2014) that permits the analysis of solid samples at the nanogram level. This has prompted the use of the technique in the fields of archaeometry, conservation and restoration (Doménech-Carbó et al., 2009, 2018). Here, it is presented a review of the essential characteristics and current status of electrochemical dating techniques.

2. Characteristics of the VIMP

The VIMP is based on the abrasive attachment of a solid material to the surface of an inert electrode, generally paraffin-impregnated graphite, which is subsequently put in contact with a suitable electrolyte where the solid is insoluble or scarcely soluble. Then, the voltammetric response is obtained upon application of a variable difference of potential between the working electrode containing the solid sample and a reference electrode, typically Ag/AgCl or saturated calomel electrodes. The voltammograms consist of a current/potential graph in which the processes of electrochemical oxidation or reduction appear as peaked currents at different potentials.

The most interesting electrochemical processes detected by means of the VIMP are those corresponding to the reduction of metallic oxides and salts to their corresponding metals. In these processes, the deposit of a metal oxide adhered to the graphite electrode is converted into a deposit of the corresponding metal on that electrode. For the case of a metal oxide MO in contact with an acidic electrolyte (aqueous solutions of HCl, H₂SO₄, acetic/acetate buffer, etc.) this process can be represented as:



Two important characteristics have to be underlined: i) the process defines a voltammetric peak at a potential characteristic of the metal compound; ii) the peak current is in principle proportional to the net amount of solid MO deposited onto the electrode surface.

Accordingly, the voltammogram can be used to identify the solid material but also for quantification. This second issue, however, offers a problem: since the exact amount of solid sample transferred by abrasion onto the graphite electrode cannot be controlled, the peak currents are not reproduced in replicate experiments on the same solid sample. When there are no restrictions in the disposable amount of sample, the addition of solid internal standards can provide “absolute” quantifications. In the case of works of art and archaeological artifacts, however, only relative quantifications are in general available. For dating purposes, this implies that at least two different voltammetric signals should be balanced for age estimates (Doménech-Carbó et al., 2013).

Given these VIMP characteristics, the dating methods involve sampling on the external patina of the metal object removing net amounts of few nanograms of sample. This permits the maintenance of the macroscopic integrity of the object but limits the information to the surface region. Accordingly, the VIMP-based metal dating methods are based on the voltammetric monitoring of the advance of the metal alteration process assumed to occur under uniform conditions (Doménech-Carbó and Scholz, 2019). There are two difficulties to be accounted for: i) the composition and textural properties (crystallinity, porosity, compaction...) of such layers depend on the composition of the base metal, its metallographic structure and the “corrosion history” of the object and these can be highly variable; ii) these properties will vary in general with the depth and also can be different in different regions of the object.

As a result, electrochemical dating is limited to series of artifacts having similar composition and metallographic structure and having a reasonably common — and uniform — history. Despite these difficulties, there are a significant set of cases where these simplifying assumptions can be applied.

3. Electrochemical metal dating

3.1. Lead dating

Lead objects corroded under burial conditions exhibit in general a primary patina mainly composed of dense, “impermeable” litharge (PbO) which subsequently forms a secondary patina of permeable, porous PbO. In contact with acetic/acetate buffer, these two PbO forms are reduced at different potentials to Pb metal giving rise to two separate voltammetric signals at potentials between -0.5 and -0.9 V vs. Ag/AgCl. The ratio between the peak currents can be used as an age marker facilitating the built of a satisfactory calibration graph (Doménech-Carbó et al., 2011).

A second age marker can be obtained taking the ratio between the peak currents for the reduction of minority PbO₂ forms, appearing as peaks at highly positive potentials vs. Ag/AgCl, and the peak currents of PbO reduction (Doménech-Carbó et al., 2011). This procedure is based on the fact that, under aerobic conditions, the oxidation of PbO to PbO₂ is thermodynamically favored. Then, although very slowly, PbO patinas will progressively form PbO₂ and the electrochemical monitoring of the PbO₂/PbO ratio can be taken as a quantitative age marker.

3.2. Copper and bronze dating

Copper and bronze VIMP dating was based on the measurement of the quotient between the peak currents corresponding to the reduction of tenorite (CuO) and cuprite (Cu₂O) to Cu metal using acetic/acetate buffer at pH 4.75 as electrolyte (Doménech-Carbó et al., 2014). In these conditions cuprite is reduced to Cu metal at ca. -0.1 V vs. Ag/AgCl whereas tenorite is reduced at ca. -0.4 V. Here, the

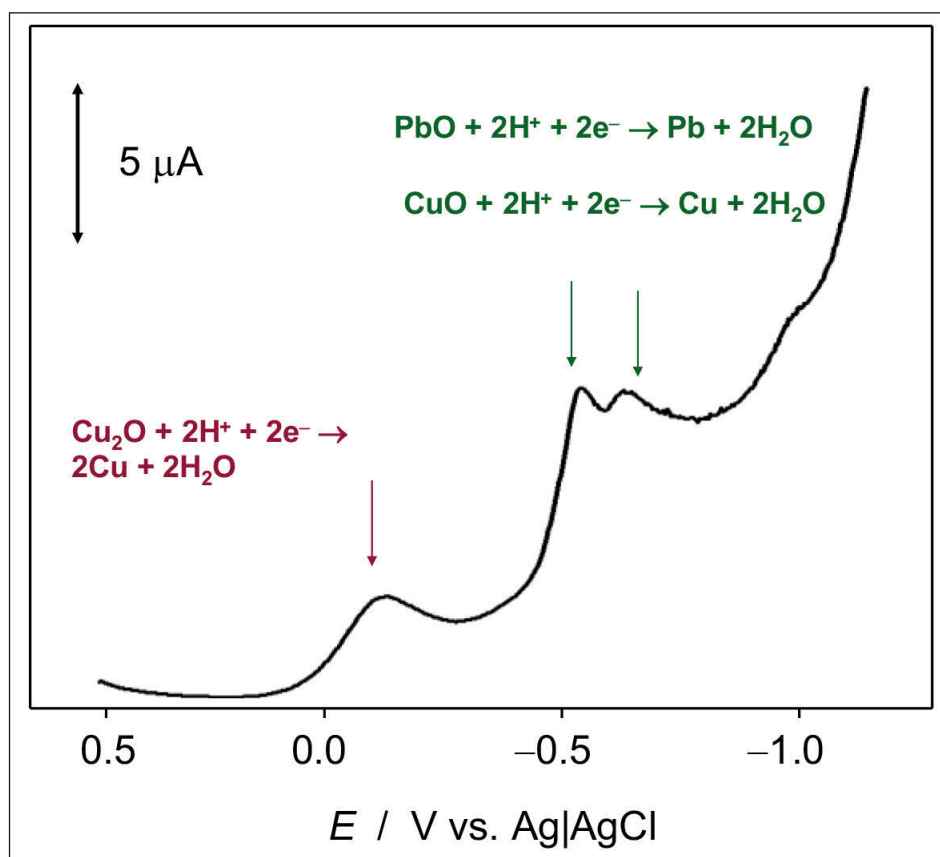


Figure 1. Square wave voltammogram for a nanosample extracted from an Iberian coin showing the cathodic signals corresponding to the reduction of cuprite, tenorite and litharge. Electrolyte, 0.25 M HAc/NaAc, pH 4.75. Potential scan initiated at 0.55 V vs. Ag/AgCl in the negative direction; potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz

Figura 1. Voltamperograma de onda cuadrada para una nanomuestra extraída de una moneda ibérica que muestra las señales catódicas correspondientes a la reducción de cuprita, tenorita y litargirio. Electrolito, 0,25 M HAc/NaAc, pH 4,75. voltamperograma a 0,55 V vs. Ag/AgCl en sentido negativo; altura de los impulsos de potencial 4 mV; amplitud de onda cuadrada 25 mV; frecuencia 5 Hz

situation is similar to that described for lead. The aerobic oxidation of cuprite to tenorite is thermodynamically favored so that this process will advance with the age of the object. Figure 1 shows a typical voltammogram for an Iberian coin showing the signals for the reduction of cuprite, tenorite and litharge.

The method, however, is applicable to moderately corroded objects. In these, the corrosion determines the formation of a primary patina of “impermeable”, defective cuprite that subsequently yields a secondary patina where less crystalline and compact cuprite is accompanied by tenorite and eventually other corrosion products depending on the corrosive environment (Robbiola and Hurtel, 1997).

3.3. Lead bronze

Lead bronze was frequently used, among other contexts, in Roman statuary. Lead acts as a protective physical barrier but also as a sacrificial component because the electrochemical corrosion of this metal occurs preferentially to that of copper. Since corrosion occurs in general via formation of local electrochemical cells where the metal oxidation is coupled to oxygen reduction, bronze exposed regions yield copper corrosion products. In most cases, the voltammetric response of samples extracted from the patina of lead bronze sculptures consists of separate peaks for cuprite reduction and litharge reduction. Now, thermochemical

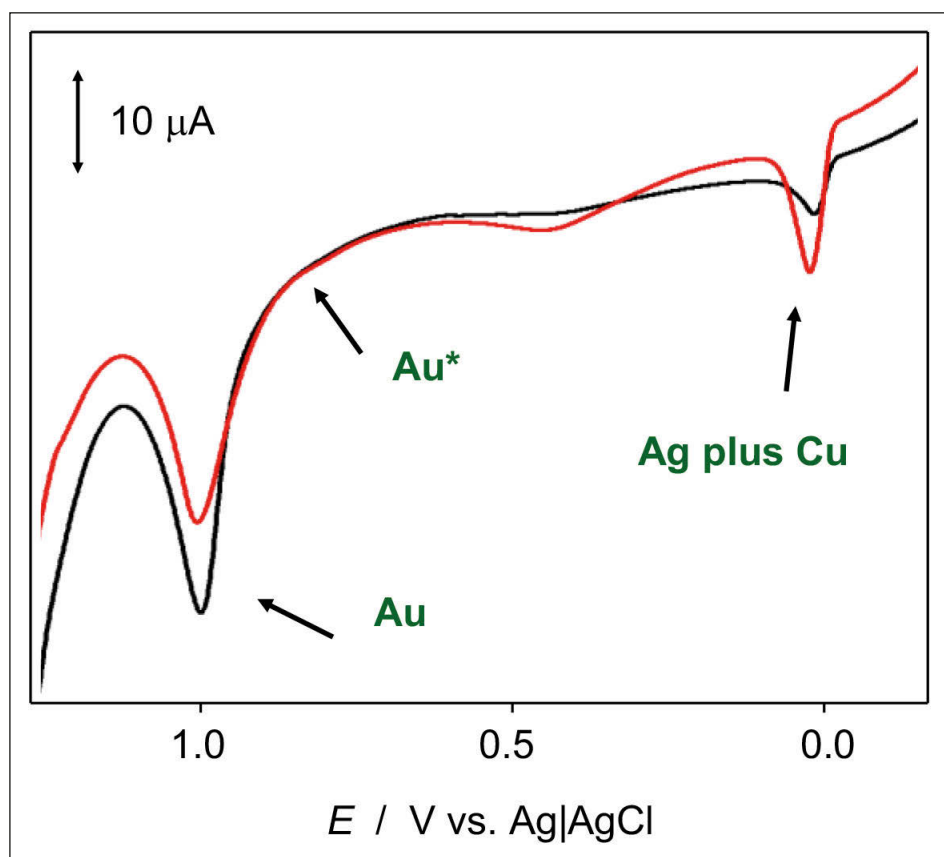


Figure 2. Linear potential scan voltammogram for a nanosample extracted from a Roman coin showing the anodic signals corresponding to the oxidation of bulk gold (Au), gold active sites (Au^*) and Ag plus Cu. Electrolyte, 0.10 M HCl. Potential scan initiated at -0.15 V vs. Ag/AgCl in the positive direction; potential scan rate 50 mV s^{-1} . The first (black) and 2nd (red) scans are superimposed

Figura 2. Voltamperograma de barrido de potencial lineal para una nanomuestra extraída de una moneda romana que muestra las señales anódicas correspondientes a la oxidación ordinaria de oro (Au), sitios activos de oro (Au^*) y Ag más Cu. Electrolito, 0,10 M HCl. La exploración potencial se inició a $-0,15$ V vs. a Ag/AgCl en la dirección positiva; velocidad de barrido 50 mV s^{-1} . Se superponen el primer (negro) y segundo (rojo) barridos de potencial

calculations predict that the ratio between the net amounts of copper corrosion products and lead corrosion products must increase with the age of the object. Accordingly, the cuprite reduction to litharge reduction peak current ratio must increase with the corrosion time defining a new age marker. Experimental data from the Roman archaeological site of Valeria and other provenances agreed with this prediction and permitted to construct a satisfactory calibration graph (Doménech-Carbó et al., 2018a), recently confirmed upon studying a collection of coffin portraits of the Krakow museum (Doménech-Carbó et al., 2021a).

3.4. Gold dating

Gold, due to its noble chemical nature, is particularly interesting for dating. Its reluctance to be chemically oxidized in an aerobic environment implies that gold aging is much less sensitive to local conditions of degradation than other metals. Gold aging can be associated to three processes: i) the “ordinary” corrosion of silver and copper, usually present as minority — but even majority — components in gold objects; ii) the adsorption of oxygen functionalities forming different adsorbates in the external surface subsequently suffering place exchange with subsurface atoms; iii) the generation of defect sites in the external surface layers incremented by the above processes.

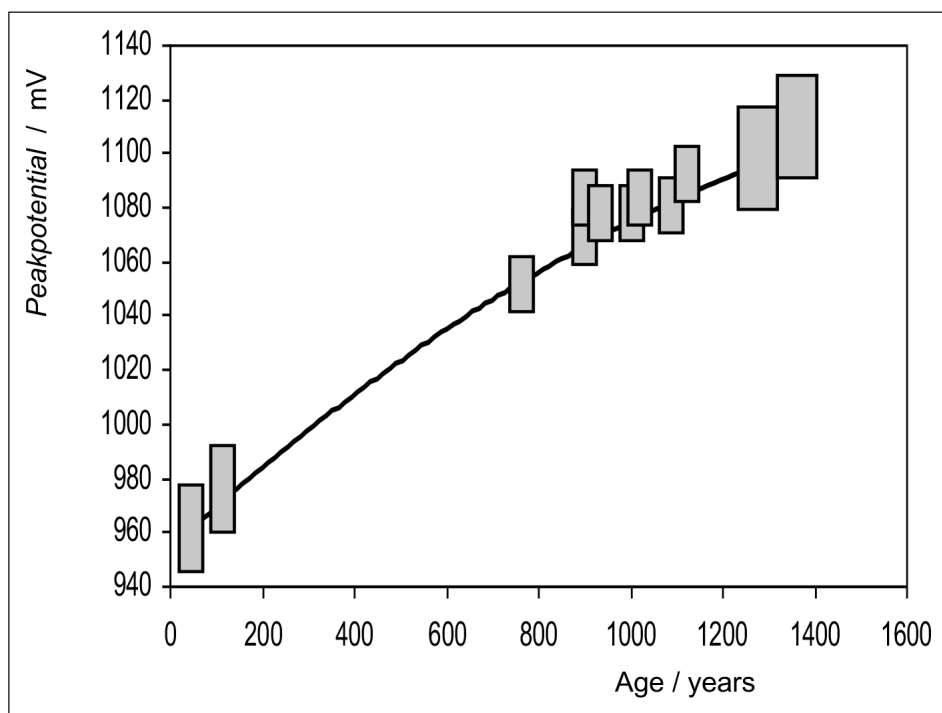


Figure 3. Calibration curve for archaeological gold using the shift in the peak potential of the main oxidation signal (Au in figure 2) after correcting deviations from reversibility

Figura 3. Curva de calibración para oro arqueológico utilizando el cambio en el potencial pico de la señal de oxidación principal (Au en la figura 2) después de corregir las desviaciones de la reversibilidad

The relevant point to emphasize is that these processes can be studied by VIMP. HCl aqueous solutions are particularly useful because in contact with these electrolytes gold is oxidatively dissolved to form Au(III)-chloride complexes in solution:



For bulk Au atoms this process occurs at ca. 1.0 V vs. Ag/AgCl in 0.10 M HCl where is clearly separated from the oxidation of active, coordinatively unsaturated, gold sites which occurs at ca. 0.8 V as well as the oxidation of Ag and Cu to the corresponding — low soluble — chloride salts ca. 0.0 V. These processes can be clearly seen in the voltammogram depicted in figure 2.

The ratio between the signals for the oxidation of active gold sites and bulk gold can be used as a quantitative age marker (Doménech-Carbó et al., 2018b). This method can be refined from the detailed analysis of the voltammetric parameters via Tafel-type analysis and corrections of the non-reversible character of the voltammetric waves, resulting in satisfactory calibration graphs using currents and peak potentials (Doménech-Carbó et al., 2020). Figure 3 depicts a calibration curve based the shift in the peak potential of the main oxidation signal (Au in figure 2) after correcting deviations from reversibility.

3.5. Multi-scan approaches

Sampling with graphite bars on the surface of metal artifacts determines in general the transference of a set of laminas of micrometer size of the metal patina (Doménech-Carbó et al., 2018b; 2021b). The application of electrochemical inputs to these laminas resulting in the reduction of metal oxides to

metal deposits (or, in the case of gold, the oxidative dissolution of the metal) determines the progressive delamination of the sheets attached to the electrode. Then, the application of successive potential scans obtains slightly different voltammetric responses representative of the composition, crystallinity, etc. of increasingly deeper regions of the patina.

This in-depth voltammetric analysis can be used for dating purposes. In the case of copper/bronze objects submitted to smooth atmospheric corrosion, the voltammetric response is sensitive to changes in the compaction, porosity, crystallinity, etc. properties of the cuprite patina. The variation of the peak current with the scan number is representative of the gradient of these textural properties through the patina. This gradient should vary with the age of the object, our data revealing the suitability of this multi-scan voltammetric technique to construct age calibration curves (Doménech-Carbó et al., 2021b). This methodology can easily be extended to gold in order to monitor the gradient of silver plus copper concentration in the subsurface zone with satisfactory results in publication.

4. Final considerations

Electrochemical techniques based on the VIMP methodology can be used to date different archaeological metals, namely, lead, copper/bronze, leaded bronze, and gold. In the current state of the art, these techniques can be applied with a reasonable precision in favorable cases where the simplifying hypotheses (uniform composition and metallography, uniform corrosion) can be applied.

Future developments will include the extension to other metals such as tin, zinc, and silver, the refinement of the sampling and data analysis techniques and the improvement of the knowledge of the aging processes and the mechanisms of the involved electrochemical processes. Despite the current limitations of the methods of electrochemical metal dating, they offer a valuable tool for archaeologists, conservators and restorers complementing available conventional dating techniques.

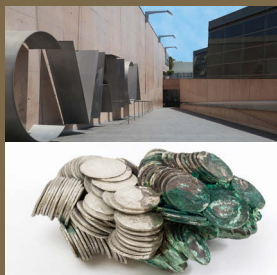
Acknowledgments

The work was carried out within the framework of project PID2020-113022GB-I00 which was financially supported by *Ministerio de Ciencia e Innovación* and *Agencia Estatal de Investigación* (AEI) of the Spanish government.

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MetalEspaña 2020/2021

III Congreso de Conservación y Restauración del Patrimonio Metálico

Joaquín Barrio Martín
Milagros Buendía Ortuño (eds.)

El volumen 6 de la Serie Anejos a CuPAUAM recoge la publicación de las Actas del III Congreso de Conservación y Restauración del Patrimonio Metálico, *MetalEspaña 2020/2021*. Esta monografía es el resultado de las actividades científicas llevadas a cabo en los tres días de sesiones. En sus páginas se integran, de una manera muy equilibrada entre investigación e intervención, trabajos con unos contenidos multidisciplinares en su carácter analítico, deontológico y técnico. Con ello se demuestra que la combinación de Ciencia, Tecnología Aplicada y Conservación-Restauración es la mejor manera de abordar la recuperación y cuidado de los objetos que componen el Patrimonio Metálico.

Las Actas que se editan en esta monografía han sido posibles gracias a la implicación y al trabajo conjunto de las tres instituciones organizadoras de *MetalEspaña 2020/2021*: Universidad Autónoma de Madrid (SECYR), la Subdirección General de los Museos Estatales (Museo Nacional de Arqueología Subacuática ARQVA) y la Fábrica Nacional de Moneda y Timbre (Museo Casa de la Moneda).