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Analytical Chemistry

Dating Archaeological Copper/Bronze Artifacts by Using the Voltammetry of Microparticles**

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Abstract: *A method for dating copper/bronze archaeological objects aged in atmospheric environments is proposed based on the specific signals for cuprite and tenorite corrosion products measured through the voltammtry of microparticles method. The tenorite/cuprite ratio increased with the corrosion time and fitted to a potential law that yielded a calibration curve usable for dating purposes.*

Absolute dating is an important target in archaeometric studies. For much materials, radioactive series and luminescence analysis can be used for this purpose.[1,2] It is, however, particularly difficult in the case of metallic artifacts, where the ^{14}C radiocarbon method can occasionally only be performed when traces of organic matter appear.[3] For this reason, several dating procedures have been proposed based on the analysis of the extent of ageing processes on archaeological artifacts, pioneered by the obsidian method developed by Friedman and Smith for dating ceramics.[4] This philosophy was applied by Reich et al.[3] to date archaeological lead by using measurements of the Meissner effect.

In this context, Scholz, Brainina, Zakharchuk et al.,[5] proposed an electrochemical method for dating ceramic materials based on the electrochemical monitoring of the generation of point defects in such materials and the concomitant increase of their electrocatalytic effect on selected electrochemical processes. Here, the voltammetry of microparticles (VMPs), a solid-state electrochemical method developed by Scholz et al.,[6] was used.

In previous reports, we described the application of this method for dating archaeological lead[7] and other applications in the field of archaeometry, conservation, and restoration.[8] This method involves a series of simplifying assumptions: a) the composition of the samples and the conditions of conservation/aging can be considered to be similar; b) the corrosion proceeded uniformly during the entire lifetime of the artifact. Assuming that these conditions hold, a calibration graph can be constructed from a set of well-documented samples and subsequently used to date unknown pieces.

Here, we report an application of the VMP method for dating archaeological copper-based artifacts that is based on determining the tenorite/cuprite ratio by exploiting the production of well-differentiated voltammetric responses by such compounds. The proposed method is based on the fact, that upon contact with air, a natural cuprite (Cu_2O) film is formed on copper, which subsequently yields different corrosion products, depending on the nature of the environment,[9] and is particularly sensitive to the presence of chloride ions.[10] Under conditions of ageing in an atmospheric environment with no intensive corrosion in contact with soils or marine aerogels, one can assume that a layer of tenorite (CuO) is continuously formed over the primary patina of cuprite.[11] The aerobic oxidation of cuprite into tenorite ($2\,Cu_2O + O_2 \rightarrow 4\,CuO$) is a thermodynamically spontaneous process ($\Delta G^\circ_f(Cu_2O) = -146\ \mathrm{kJ\,mol^{-1}}$; $\Delta G^\circ_f(CuO) = -130\ \mathrm{kJ\,mol^{-1}}$)[12] favored by the prolonged contact of the artifacts with a CO_2-rich atmosphere as well as with calcareous materials.[13] Such conditions hold for samples of coins, thus making these pieces favorable candidates for building a calibration graph. Accordingly, three series of coin samples from different collections (Museum of Prehistory of Valencia (MPV), Museum of Archaeology of Xàtiva (MAX), and Antonio Doménech-Francés private collection (ADF); see the Supporting Information) were studied. Prerequisite were the absence of any type of previous restoration/cleaning treatment and the absence of intensive mineralization of the coin surface. VMP measurements, complemented by conventional scanning electrochemical microscopy coupled to an energy-dispersive X-ray microanalysis system (SEM-EDX), Fourier-transform infrared spectroscopy (ATR-FTIR), and

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light microscopy examination techniques were used. The VMP measurement was performed using the 'one-touch' sampling procedure[14] based on the graphite pencil method[15] with commercial graphite pens. To test the suitability for field analysis using portable equipment, aqueous acetate buffer at pH 4.75 was used as the electrolyte with no previous degasification. Blank experiments in deaerated solutions do not produce significant differences in the copper-localized voltammetric response, while the electrochemical reduction of dissolved oxygen occurred at potentials more negative than those used for dating purposes (see below). Figure 1 compares the voltammetric response of samples from "fresh" and "aged" Eurocent coins and two archeological coins coined in 1890 and 1700.

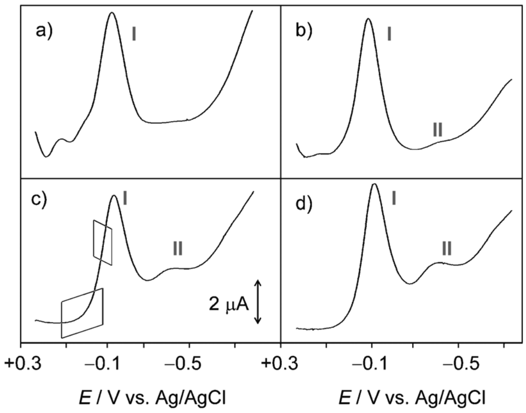

Figure 1. Square-wave voltammograms (SWVs) for one-touch samples from coins: a) fresh Eurocent; b) aged Eurocent; c) ADF19 (coined 1890); d) ADF16 (coined 1709) immersed in air-saturated 0.25 M aqueous Hac/NaAc, pH 4.75. Potential scan initiated at +0.25 V in the negative direction; potential step increment 4 mV; square-wave amplitude 25 mV; frequency 5 Hz. Tafel regions (see text) are marked in (c).

The "fresh" copper coin exhibits a cathodic peak at −0.10 V versus Ag/AgCl (I) which can be attributed, on the basis of previous studies on the VMP of copper-based pigments and corrosion products,[16] to the reduction of cuprite (Cu_2O) to copper metal. This peak is accompanied in aged coins by a second peak at −0.40 V (II), which can be attributed to the reduction of tenorite[16] (CuO), the corresponding processes being described by Equations (1) and (2):

$$Cu_2O_{(solid)} + 2\,H^+{}_{(aq)} + 2\,e^- \rightarrow 2\,Cu_{(solid)} + H_2O \tag{1}$$

$$CuO_{(solid)} + 2\,H^+{}_{(aq)} + 2\,e^- \rightarrow Cu_{(solid)} + H_2O \tag{2}$$

This voltammetry can be interpreted on the basis of extensive literature on copper corrosion,[9–13] and kinetic studies on long-term metal corrosion,[11,17] on the assumption that, under ordinary atmospheric corroding conditions, the copper/bronze surface is covered by a layer of cuprite that forms a primary patina. It is known that, under exposure to a corrosive environment, a secondary patina (or even tertiary, associated with pedological processes) develops, with azurite, malachite, brochantite, etc. minerals now being formed, depending on the environment.[9] The presence of cuprite and tenorite in the coins was confirmed by SEM/EDX data from the appearance of infrared bands at 620 and 583 cm^{-1}, respectively.[18]

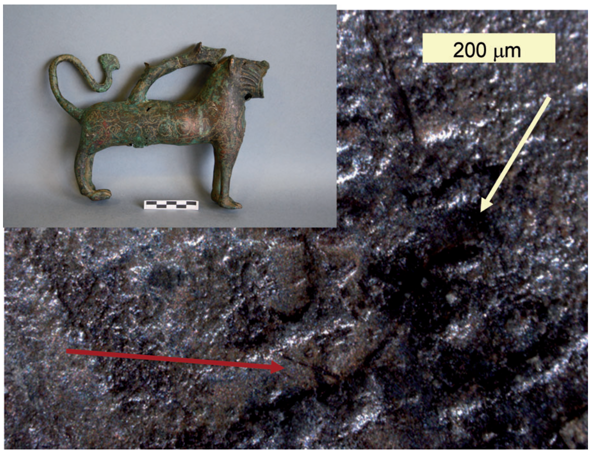

Figure 2. Light microscopy image (40×) of a Spanish coin dated in 1770. The red and yellow arrows mark regions where cuprite and tenorite appear, respectively. Inset: water pitcher of the Caliphal period from Valencia (Spain), dated to 950 AD.

The hypothesis that tenorite was continuously formed from cuprite during the ageing process is directly supported by the ubiquitous presence of tenorite in copper coins. Figure 2 shows a light microscopy image of coin ADF14, dated in 1770, where one can see a general reddish area covered by black aggregates. SEM/EDX analysis (Figure 3) of spots in such regions confirmed their composition as cuprite and tenorite, respectively. The corresponding analysis of relatively large regions of the coin, however, provided O/Cu ratios between those of cuprite and tenorite, exceptionally different from this ratio in cases where pedological deposits of silicates partially covered the coin. Remarkably, the O/Cu

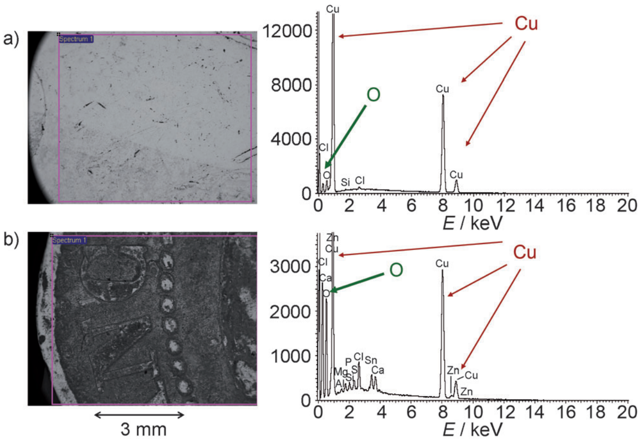

Figure 3. Back-scattered electron images (left) and EDX spectra (right) of: a) a fresh Eurocent coin (2007) and b) coin ADF07, coined in 1864.

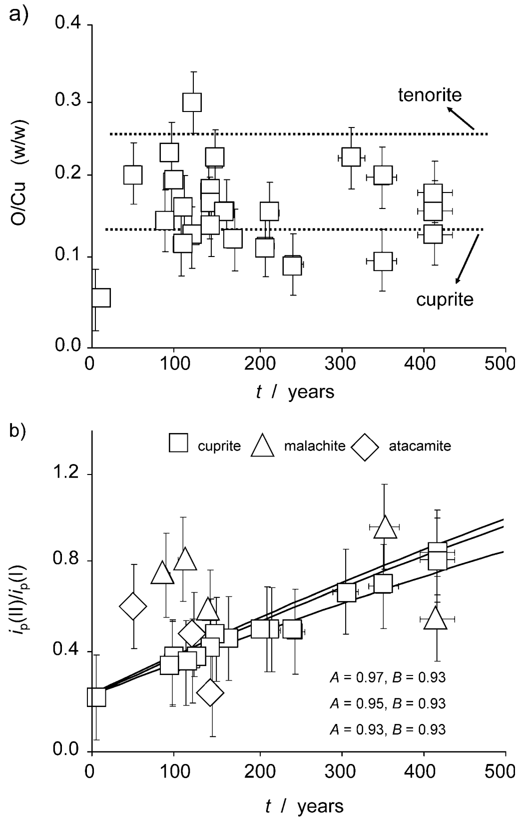

Figure 4. Variation with the corrosion time of the apparent (tenorite)/(cuprite) ratio calculated for coins from the ADF collection as: a) the average O/Cu (w/w) ratio determined from SEM/EDX analysis and b) $i_p(\mathrm{II})/i_p(\mathrm{I})$ determined from voltammograms such as in Figure 1 labeled on the basis of the main component determined from Tafel analysis. Continuous lines in Figure 4 b correspond to theoretical variations from Equation (3) using the indicated values of *A* and *B*.

ratios exhibited a high degree of variability, with no apparent systematic variation with the corrosion time (Figure 4 a). This can be attributed to the inhomogeneities in the distribution of the minerals in the surface of the coin as well as to the presence of other copper corrosion products and other accompanying minerals.

In contrast, plots of the ratio between the peak currents for the reduction of tenorite and cuprite ($i_p(\mathrm{II})/i_p(\mathrm{I})$) showed a monotonical increase on increasing the corrosion time. For dating purposes, the essential idea is that, in agreement with the voltammograms in Figure 1, the height of the tenorite peak II relative to the cuprite peak I increases as the age of the coin increases (Figure 4 b). The relatively large dispersion of the data could be attributed (see below) to the different amount of the corrosion products other than tenorite in the secondary patina, confirmed by specific voltammetric signatures, SEM/EDX, and ATR/FTIR spectra.[16]

Although an accurate description of the corrosion process requires the consideration of a variety of factors, such as porosity, resistivity of metal and corrosion layer phases, contact resistivity at the interfaces, oxygen diffusivity, etc.,[19] one can propose an approximate description of such processes based on several simplifying assumptions.[20] In this formulation, the long-term corrosion process was described in terms of simultaneous interfacial reactions occurring at the metal/primary patina (M/PP) and primary patina/secondary patina (PP/SP) boundaries. It was assumed that:[20] a) kinetic laws can be expressed in terms of the variation with time (t) of the amount (mass, mole number) of component (cuprite, tenorite) by surface unit (x) formed during the prolonged corrosion process at the j-interface; b) potential rate laws of the form $\mathrm{d}x/\mathrm{d}t = K_j x^{-\delta}$ apply in all cases, where K_j represents the rate constant of that process. Assuming that only cuprite and tenorite exist as corrosion products, the net rate of formation of the primary (cuprite) patina would be $\mathrm{d}y/\mathrm{d}t = K_1 y^{-\alpha} - K_2 y^{-\beta}$, while the rate of formation of the secondary tenorite patina would be $\mathrm{d}z/\mathrm{d}t = 2K_2 y^{-\alpha}$. Voltammetric measurements under fixed conditions (electrolyte, potential interval, scan rate, etc.) provide signals I and II whose intensity (peak current, peak area) can be considered as proportional to the amount of the corresponding depolarizer.

Assuming that the formation of tenorite starts when a certain amount of primary patina (y_o) has been formed, integration of the above equations between $t = 0$ and t leads to a relationship between the peak current ratio ($i_p(\mathrm{II})/i_p(\mathrm{I})$; see Figure 1), and the corrosion time of the type shown in Equation (3):

$$\frac{i_p(\mathrm{II})}{i_p(\mathrm{I})} = G + \frac{G_H[2(1+\alpha)K_2 t]^{\frac{1}{1+\alpha}}}{G_1\left[y_o^{1+\beta} + (1+\beta)(K_1 - K_2)t\right]^{\frac{1}{1+\beta}}} = G + \frac{At^a}{B + t^b} \qquad (3)$$

where G_I and G_II (or A and B) are electrochemical constants that characterize the type of electrochemical process and conditions (square wave amplitude, frequency, etc.), but are independent of the amount of sample transferred to the working electrode, and G is a constant that is representative of the base line correction for peak II.

The presence of corrosion products other than cuprite and tenorite, however, could influence the voltammetric response of archaeological samples. As previously described,[16,20] the reduction of cuprite occurs at potentials close to that of basic copper carbonates and hydroxychlorides, so that peak I can be taken as representative of the total amount of such products in the secondary patina. To determine the composition of the corrosion layers, the modified Tafel representations (see the Supporting Information), based on linear plots of $\log[(i_p - i)/i_p]$ versus $\log(E - E_p)$ recorded in the central region of the peak I, were used. As already described,[14,16,20] the values of the slope (SL) and the ordinate at the origin of such plots (OO) are characteristic of the composition of the corrosion layer. Accordingly, two-dimensional plots of the slope versus the origin can be used to characterize corrosion products and estimate their relative amounts in binary mixtures.

The application of the modified Tafel analysis of voltammetric curves to samples from the studied coins is illustrated in Figure 5. Data points are concentrated around the cuprite region, but several coins are shifted towards the malachite or the atacamite zones. Comparison of such data with those in Figure 4 b reveals that the data points for coins where the patina is dominated by cuprite can be fitted to theoretical

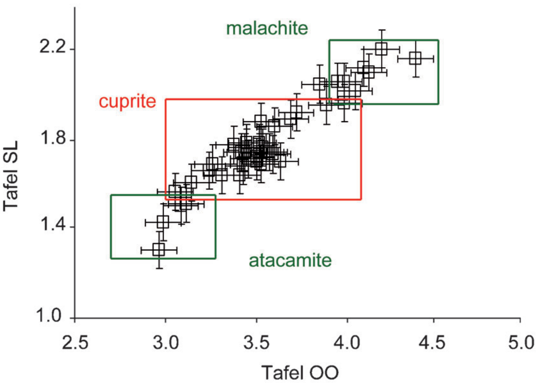

Figure 5. Plots of the modified Tafel slope versus the modified Tafel ordinate at the origin derived from plots of $\log[(i_p - i)/i_p]$ versus $\log(E - E_p)$ using data in the central region of the voltammetric peak I in voltammograms such as in Figure 1.

lines from Equation (3), whereas data points for coins whose position in the modified Tafel diagram in Figure 5 falls within the malachite and atacamite regions exhibit large dispersion.

Calibration data for the studied coins using the values of the i_p(II)/i_p(I) ratio fit well with the predictions from Equation (3). Figure 4b compares the values of the i_p(II)/i_p(I) ratio with theoretical curves from Equation (3) using $G = 0.06$, $A = 1.0$, and $B = 1000$.

The calibration curves from SWV data using the coins whose corrosion products were mainly copper oxides (36 from a total of 46 tested coins) are shown in Figure 6. Data correspond to peak current measurements from the horizontal base line without and with background subtraction. Examination of data in Figure 6 indicates that the time range over which the proposed method is relevant is 0–1500 years. It is pertinent to underline that the suitability of the proposed method of dating is clearly limited by the confidence level of the used simplifying assumptions concerning the uniformity of the corrosion conditions. The relative uncertainty in the time estimate ($\Delta t/t$) was calculated using the conventional theory of error propagation through Equation (4):

$$\frac{\Delta t}{t} = \left(\frac{\Delta i_p}{i_p}\right)\left[2+\frac{At^a}{B+t^b}+\frac{B+t^b}{At^a}\right]\left[\frac{B+t^b}{aB+(a-b)t^b}\right] \qquad (4)$$

where $\Delta i_p/i_p$ represents the uncertainty in the measurement of peak currents. Figure 6 shows theoretical lines taking $A = 2.3$, $B = 1000$, $\alpha = 0.03$, $\beta = 0.07$. Interestingly, the values of α and β were close to those corresponding to Pb ageing determined by independent methods.[3,7]

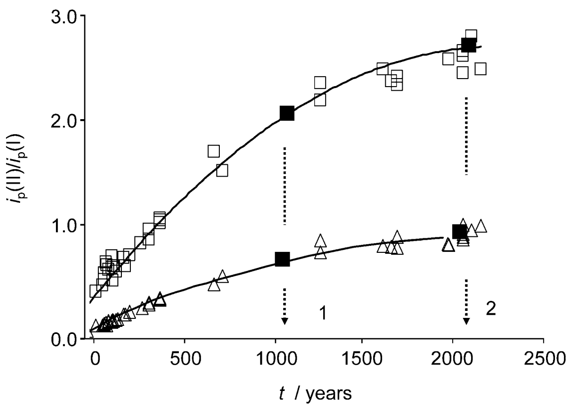

Figure 6. Calibration plot from voltammetric data (conditions such as in Figure 1) for all coins in this study without (squares) and with (triangles) background current subtraction. Data points for a Montefortino helmet of Roman age (1) and a water pitcher (2) from the Caliphal period (see text) are marked as solid squares.

To illustrate the applicability of the proposed method, analogous "one-touch" sampling was applied to a water pitcher from the Caliphal period (see Figure 2) and a Montefortino helmet of Roman age found in the Cañete street site in Valencia (Spain). Insertion of the corresponding data points into the calibration curve provides corrosion times of 1050 ± 80 and 2150 ± 150 years, respectively, in agreement with dating derived from the analysis of the archaeological context (accompanying ceramics, etc.).

In summary, the application of the VMP technique to nanosamples extracted from copper and bronze archaeological artifacts yields specific signatures for cuprite and tenorite which can be used for dating purposes. The peak current ratio between such signals increases monotonically with the corrosion time, thereby providing a calibration curve which can be used for dating archaeological pieces submitted to moderate or light corrosion in an atmospheric environment.

Experimental Section

Electrochemical experiments were performed at 298 K in a low-volume three-electrode cell. The reagents and portable equipment are described in the Supporting Information. VMP experiments were performed at graphite electrodes (Staedtler Mars 200 HB, 2.0 mm diameter) upon mechanically transferring a few nanograms of sample by means of the 'one touch' method already described.[7] Importantly, a blank voltammogram at the unmodified electrode was obtained for each sample using the corresponding graphite bar. LM, SEM-EDX, and ATR-FTIR analyses of the coins were performed using the instrumentation described in the Supporting Information.

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