

Invited paper

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Electroanalytical techniques in archaeological and art conservation

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Abstract: The application of electrochemical techniques for obtaining analytical information of interest in the fields of archaeometry, conservation and restoration of cultural heritage goods is reviewed. Focused on voltammetry of immobilised particles and electrochemical impedance spectroscopy techniques, electrochemical measurements offer valuable information for identifying and quantifying components, tracing provenances and manufacturing techniques and provide new tools for authentication and dating.

Keywords: analytical chemistry; archaeology; art conservation; ChemCultHerit; electrochemistry.

Introduction

Obtaining analytical information on the composition of works of art and archaeological objects is an essential demand for developing archaeometric and conservation/restoration studies. Among the wide variety of techniques used for this purpose, comprising from electron microscopy to diffraction, spectroscopy and isotope analysis, there is an increasingly growing use of electrochemical methods [1–3]. The aim of the current work is to provide an actualized view of studies dealing with the application of electroanalytical techniques in the fields of archaeology, conservation and restoration of cultural heritage. The focus will be made, rather than in the electrochemical techniques itself, in their implementation within the context of the the above disciplines in order to acquire information of specific interest for archaeologists and restorers.

Analysis of works of art and archaeological materials involves several important difficulties: the requirement of minimally invasive or non-destructive techniques and concomitantly, the disposal of minimal amounts of sample, the multicomponent nature of most of the involved samples and the heterogeneity of their distribution, frequently occurring as stratified systems. On the other hand, the environmental aggression, either mechanical, chemical and biological, adds new components which increase the complexity of the analytical procedure. Accordingly, the analytical methods are addressed not (or not only) to determine the ‘bulk’ composition of the object but also the distribution of components and the composition of the alteration products. Importantly, several information of archaeometric value involves the determination of the ‘textural’ properties (roughness, porosity) of surfaces and/or the microstructure of the materials. The paradigmatic case is the metallographic structure of metals, which provides information of the thermomechanical treatments employed in the fabrication of the artefacts [4, 5].

Electrochemical techniques were traditionally used in the field of cultural heritage conservation around corrosion studies and the stabilisation of metal objects, polarisation experiments and electrochemical impedance spectroscopy (EIS) being the reference techniques. The development of solid state electroanalytical

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techniques around of the voltammetry of immobilised particles (VIMP) methodology [6, 7] has prompted the introduction of new analytical procedures complementing those existing for analyzing cultural heritage objects. From the earlier applications of electrochemical techniques for analyzing works of art, focused on the identification of pigments in paint samples [8, 9], the scope of the materials and types of information accessible from electroanalytical data has increased significantly, covering a wide spectrum which includes authentication and dating [10–12].

Antecedents, conservative treatments

Although the earlier intersection between archaeology and electrochemistry is attributable to the work of Faraday and Davy [13], the modern application of electrochemical methodologies for treatment of metal artefacts can be considered as initiated by Rathgen in the 1920s [14, 15]. Potentiostatic methods for dechlorination and stabilisation of corroded metal objects were widely used as a result of the influential treatises of Plenderleith [16] and Organ [17], but the use of such techniques further decayed significantly [18]. Recent research is concerned with the diversification and optimization of methods for metal heritage treatment [19] including the proposal of different electrolytic methods [20–23]. The more recent approaches in this context paid attention to chloride removal [24, 25], rate control [26, 27] and ‘smooth’ stabilisation procedures [28, 29] and involve more or less extensive use of complementary spectroscopic, diffraction, etc. analytical techniques as well as general electrochemical techniques widely used the study of for metal corrosion: polarisation curves, open circuit potential measurements and electrochemical impedance spectroscopy [30]. Extensive literature in this field, not explicitly treating archaeological materials, will not be treated here.

Within the explicitly analytic domain, it has to be noted that, in general, samples from works of art are constituted by solid materials. Here, the electrography technique for mineral analysis developed by Fritz [31] and Glazunov [32] constituted the earlier antecedent for solid state electrochemical analysis (SSEA) [7, 33]. The invention of carbon paste electrodes, applied to the analysis of both organic and inorganic solids [34–36], prompted the development of the voltammetric analysis of solids in the late 20th century, mainly focused on mineral analysis [37–41]. Application of carbon paste-based methodologies in the field of cultural heritage is constrained, however, by the low disposable amount of sample. By this reason, the voltammetry of immobilised particles (VIMP) methodology developed by Scholz et al. [42–45] offered the possibility of expanding solid state voltammetry techniques to archaeometry, conservation and restoration [6, 7, 10–12].

Materials and techniques

The analysis of works of art and archaeological objects involves an enormous variety of elements, compounds and materials, from organic matter to minerals, metals and alloys and glass and ceramic materials. Electroanalytical techniques can be viewed within the scope of SSEA [7] and are mainly based on the VIMP. This technique is based in the mechanical attachment, via abrasive conditioning, of micro- or nanograms of a sparingly soluble solid to the surface of an inert electrode which is put in contact with a suitable electrolyte. Typically, paraffin-impregnated graphite electrodes are used in conventional three-electrode arrangements. Cyclic, differential pulse and square wave voltammetries have been the electrochemical techniques more extensively used, but chronoamperometric, chronopotentiometric, coulometric, etc. measurements have also been employed using the same electrode configuration, as described in several reviews [6, 7, 33, 46–48].

Voltammetric measurements based on VIMP have been combined with other spectroscopic, diffraction and microscopy techniques [6, 7]. In the specific field of cultural heritage, coupling of VIMP with atomic force microscopy (FM) [49–51] and scanning electrochemical microscopy (SECM) [52, 53] have been reported.

Electrochemical techniques have been applied intensively in corrosion studies on metals and the specific application for the conservation of metal artefacts has been reviewed [54]. Potentiostatic and potentiodynamic

polarisation curves and electrochemical impedance spectroscopy (EIS) have been traditionally used in studies on metal corrosion. Applications for diagnosis of the conservation state of metal artefacts [55, 56], compatibility between metals and sealing products [57], monitoring chloride removal procedures [58, 59] and characterization of organic coatings [60–63] have been reported.

Analytical information from electrochemical data

Identification and quantification of components

As previously noted, identification of pigments in pictorial samples was the first application of the voltammetry of immobilised particles methodology in the field of cultural heritage. Inorganic [8, 9, 50, 64] and organic [65–70] pigments were identified by their voltammetric signatures as well as metal alloys [71, 72] and corrosion products in metals [73–79], all based on VIMP signatures of sub-microsamples attached to paraffin-impregnated graphite electrodes in contact with different aqueous electrolytes. Characterization of metal alloys based on the measurement of the corrosion potential from open-circuit potential measurements has been also proposed accompanied by the preparation of an extensive database [80]. A data base for VIMP data for pigments and corrosion products has been also recently presented [81].

Figure 1 depicts an illustrative example of the application of VIMP into the archaeological domain. Here square wave voltammograms of samples from the corrosion patina of two leaded bronze sculptures of Roman age attached to graphite bars immersed into aqueous acetate buffer at pH 4.75 are depicted. In the negative-going potential scans, cathodic signals for the reduction of copper corrosion products (mainly cuprite and tenorite, C_{Cu1} and C_{Cu2} , respectively) are accompanied by overlapping signals for the reduction of lead corrosion products (PbO , $PbCO_3$ and $PbSO_4$, labelled as C_{pb}). In the positive-going potential scan voltammograms, anodic signals for the oxidative dissolution (stripping) of the metal deposits of lead (A_{pb}) and copper (A_{Cu}) formed as a result of the reduction of the respective corrosion products, can be clearly seen.

Quantification of the components of samples from works of art can be accessed using coulometric and voltammetric data described for mineral analysis [82, 83]. Since, in general, it is not possible to fix the amount

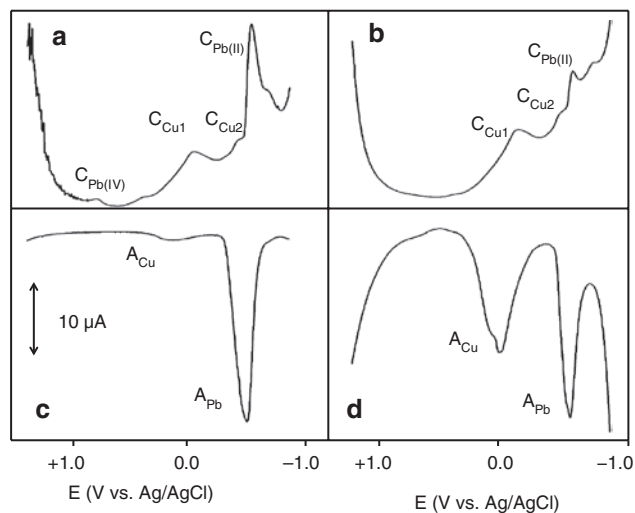


Fig. 1: Square wave voltammograms for sub-microsamples from the corrosion layers of two Roman leaded bronze sculptures attached to paraffin-impregnated graphite bars in contact with 0.25 M HAC/NaAc aqueous buffer at pH 4.75. Potential scan initiated at (a, b) +1.25 V vs. Ag/AgCl in the negative direction; (c, d) –1.05 V vs. Ag/AgCl in the positive direction. Potential step increment 4 mV, square wave amplitude 25 mV; frequency 5 Hz. C, cathodic signals; A, anodic signals.

of sample transferred onto the electrode, only relative quantitation is in principle accessible. Application to CdS [84] and metal ions in ceramic samples [85] have been reported.

The identification of different species in ceramics [86–88] and relative quantification permitted the speciation of Fe(III)/Fe(II) in ceramicware [89], Pb(IV)/Pb(II) in glasses [90] and different species in tin-opacified alkali glazes [91]. Peak current and peak areas are typically used when the species to be quantified display separated voltammetric peaks. In the case of components producing highly overlapping signals, as is the case of several copper pigments and corrosion products, identification of individual components [75] and quantification based on Tafel analysis at the foot [92] and middle region [93] of the common voltammetric peak have been described.

A particularly interesting example of speciation from electrochemistry was the Maya blue, a pigment which can be defined as an organic-inorganic hybrid material constituted by a mixture of palygorskite, a fibrous phyllosilicate clay, and indigo, an organic dye which can be extracted from *Indigofera suffruticosa* and other plants. The Maya blue, widely used in pre-Columbian times in Mesoamerica claimed attention by its remarkably stability, peculiar brightness and hue variability ranging from turquoise blue to green [94]. Since there is no disposal of historical sources describing the preparation procedure used by the ancient Mayas, the composition of the pigment was controversial until its recognition as a hybrid material [95]. There has remained, however, controversy about the reasons for the color stability and variability, the location of indigo molecules and the type of binding with the host inorganic framework [96]. The most extended view attributed the color of the pigment to bathochromic shift of the indigo absorption bands as a result of the association of the dye to the inorganic support [97] and assumed that indigo was the unique organic component of the pigment [98, 99].

A detailed analysis of VIMP data of a series of archaeological samples from different Mayan sites, suggested that dehydroindigo, one oxidised form of indigo, accompanies this dye as a minority organic component, the major or lower proportion of dehydroindigo (of yellow color) in the pigment, in turn depending on the conditions of preparation (temperature in particular) from a mixture of indigo and palygorskite, being determinant of the hue of the pigment [100]. Although additional electrochemical, spectroscopic and microscopy data were adduced supporting the presence of dehydroindigo and other minority organic components accompanying indigo were presented [101–104], this view was not unanimously accepted [98, 99]. The more recent voltammetric data coupled with chromatographic analysis of the extracts with organic solvents of synthetic Maya blue specimens support the presence of dehydroindigo, isatin and possibly other minor components accompanying indigo in the pigment [105, 106] and provided information on the kinetics of the Maya blue formation upon heating a mixture of indigo and palygorskite [107] as well as on the distribution of the dye molecules within the palygorskite matrix [108].

Figure 2 presents an example of VIMP speciation. In this figure, square wave voltammograms for two synthetic Maya blue-type specimens attached to paraffin-impregnated graphite bars in contact with aqueous acetate buffer at pH 4.75 are depicted. A series of specimens were prepared by crushing indigo (1% wt) plus palygorskite specimens and optionally heated in furnace above 100 °C. This last process is considered to be essential for preparing Maya blue replicants [94, 96]. The unheated specimen (Fig. 2a) shows two sharp peaks corresponding to the proton-assisted, solid state oxidation of indigo to dehydroindigo (IN_1) and the reduction of indigo to leucoindigo (IN_2) already described [100–104]. The heated specimen presented the above peaks accompanied by additional signals corresponding to other indigoid compounds, isatin (IS) in particular, clearly denoting that the heating process determines the appearance of new compounds. Interestingly, the relative height of signals IN_1 and IN_2 varies from one voltammogram to the other, a feature which is associated to the variation in the dehydroindigo/indigo proportion and can be used for relative quantitation [100–108].

Absolute quantification, however, is also possible from VIMP measurements upon adding a known amount of a reference compound which provides a voltammetric signal separated from those of the analytes [109]. In the case where the analytes display strongly overlapped voltammetric signals, application of the H-point standard additions method [110] permits to determine the absolute concentrations of the components providing that a suitable standard can be used. This method has been applied to quantify lead and tin in archaeological glazes [111] and pictorial dyes [112].

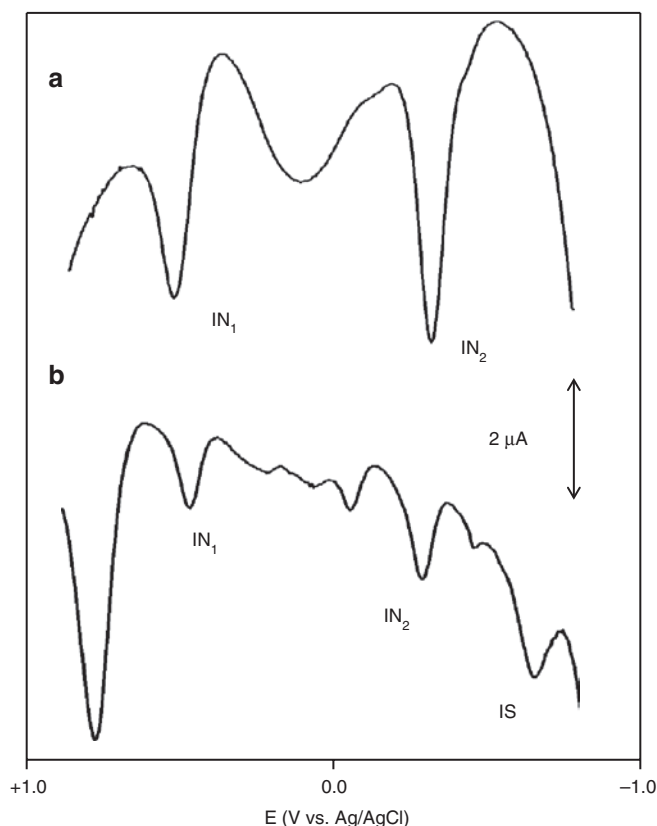


Fig. 2: Square wave voltammograms for sub-microsamples of two synthetic indigo plus palygorskite specimens (1 % wt indigo) attached to paraffin-impregnated graphite bars in contact with 0.25 M HAc/NaAc aqueous buffer at pH 4.75. Potential scan initiated at -0.75 V vs. Ag/AgCl in the positive direction. Potential step increment 4 mV, square wave amplitude 25 mV; frequency 5 Hz. (a) Unheated specimen; (b) Specimen heated at 130 °C in furnace during 2 h.

Application of voltammetric techniques, of course, has to be performed in synergistic combination with other analytical techniques. Multi-technique approaches combining voltammetry with scanning electron microscopy (SEM/EDX), Fourier-transform infrared spectroscopy (FT-IR) and gas chromatography (GC) for studying canvas paintings [113] and X-ray fluorescence (XRF), X-ray diffraction (XRD) and thermal analysis applied to ancient ceramics [114, 115] have been reported.

Monitoring conservation and local analysis

Electrochemical data have been applied to provide information relative to the conservation state and pathway of corrosion processes of metallic artefacts [56, 71–80] and archaeological glass [116]. Conversely, the study of the solid state electrochemistry of dyes [49, 51] provided information on theoretical modelling for the electrochemistry of ion-insertion solids [117–123].

The VIMP methodology permits not only the study, if necessary, of samples at the nanogram level extracted from the art object, but also performing ‘local’ analysis in regions of the surface of the objects by means of pencil electrode methodologies [124, 125]. This scheme can be applied to perform a layer-by-layer analysis of the composition of stratified corrosion layers in metals [126] and mapping corrosion products on the surface of archaeological pieces [127].

As recently reviewed [61], EIS has been also used in the archaeological domain for monitoring the conservation state of surfaces and the effect of protective coatings [55–63]. Using electrochemical cells adapted to low-size objects is accessible [59]. Recent applications for studying the corrosion of

iron objects [128] and *in situ* corrosion of bar chains in the Amiens Cathedral [129] have been reported. Current research is addressed to *in situ* measurements on sculptures and large size objects using gellified electrolytes [130–132].

Authentication, provenance and tracing

Authentication is an important analytical target in the context of cultural heritage and archaeology in general needing of a synergistic combination of formal-typological and physico-chemical analyses. Specific electrochemical tools complementing available methods have been proposed for lead artefacts on the basis of the appearance of VIMP signatures of Pb(IV)-oxide and different PbO forms in the voltammograms of samples from the corrosion layers of lead objects in contact with aqueous electrolytes [133, 134].

In several cases, authoring attribution and tracing the history of the samples can be derived from electrochemical data. In the case of wall paintings in the Sant Joan del Mercat church in Valencia (Spain), the local painter Vicente Guilló Barceló (1645–1698) was engaged by the Valencian *Cabildo* in 1695 for painting the central vault but his contract is cancelled and in 1697 and passed to Acisclo Antonio Palomino (1655–1726), working in Valencia until 1702. VIMP and Raman data permitted to discriminate the sections painted by Guilló, who used malachite as a green pigment, with those due to Palomino, who used mixtures of azurite and cobalt blue [92, 135].

These paintings suffered considerable damage during a fire produced in 1936 in the Spanish Civil War constituting an example of ‘extreme heritage’. Remarkably, the frescoes showed a chromatic shift consisting of a reddening of carnations and a blackening of blue and green robes and floral motifs. Voltammetric analysis of samples from carnations indicated that goethite ($\text{Fe}(\text{O}(\text{OH}))$) forming ochre pigments was partially dehydrated to hematite (Fe_2O_3) thus explaining the hue change from yellow to red and permitting the drawn of a temperature map of the vault during the firing event [136]. Similarly, the azurite and malachite green pigments were partially converted into black tenorite during the fire thus determining the corresponding blackening [92, 135].

The capability of electrochemical techniques for discriminating samples of different origins has been recently exploited for identifying the vegetal species in wood samples [137] and screening gildings in Valencian Altarpieces since 15th until 20th century [138] and permitted to detect the presence of Maya blue in wall paintings of the Substructure IIC in the archaeological site of Calakmul, dated in the Late Postclassical period [100, 139], thus anticipating significantly the date of use of the pigment with regard to the currently accepted period.

One of the crucial analytical demands for archaeological purposes is the elucidation of the provenance and preparation technique of the objects under investigation. When complete objects are available, typological analysis, elemental and isotope analyses can provide substantial information. These last analyses, however, in general require invasive protocols of operation making it unallowable so that, as in the case of metal analysis, obtaining analytical data from the corrosion layers is recommended [140–142]. In this context, VIMP records, combined with EIS and spectroscopic techniques can be used for characterising coins [143] and discriminating monetary emissions [144–146]. In the case of copper/bronze coins submitted to moderate corrosion, the screening is based on the record of characteristic voltammetric signatures of cuprite (Cu_2O) and tenorite (CuO) whose relative intensity varies with the ‘corrosion history’ of the object, the composition of the metal and its metallographic properties. Under moderate corrosion conditions, the above products dominate the composition of the corrosion patina, their proportion varying with depth. Then, operating at fixed electrochemical conditions and assuming a common ‘corrosion history’, the variation of the relative height of the VIMP signals for tenorite and cuprite with the intensity of the cuprite (which is the majority component) peak provides characteristic curves which can be modelled assuming a potential variation of those corrosion products with depth in the corrosion layers. These curves are highly sensitive to light variations in the metal composition and in its metallographic structure so that mint-characteristic curves have been obtained for different series of monetary emissions [147].

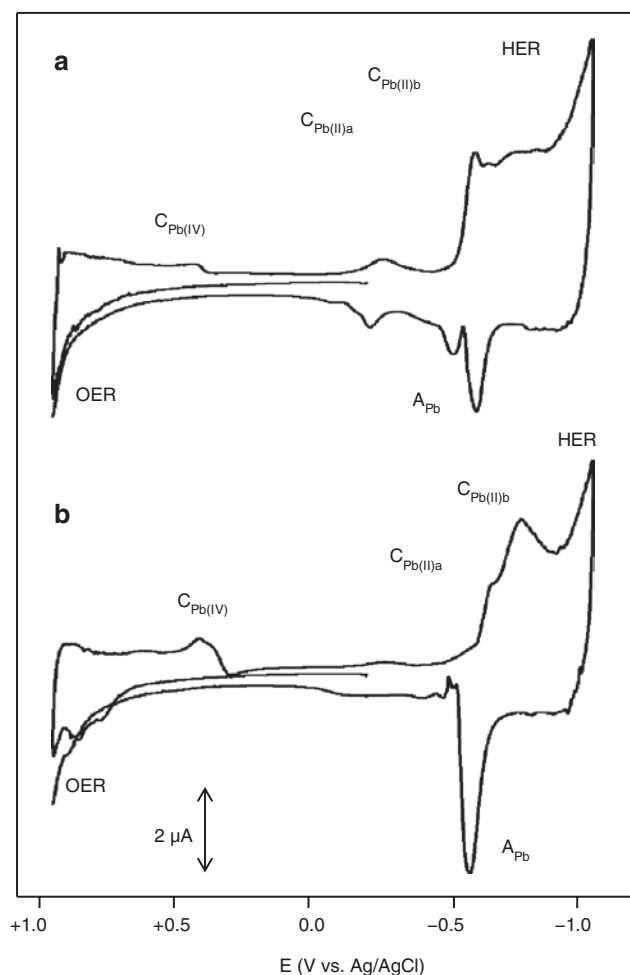


Fig. 3: Cyclic voltammogram, after semi-derivative convolution, of sub-microsamples extracted from archaeological (a) lead-soda-glass and (b) lead-potash glass attached to graphite electrodes in contact with 0.25 M HAc/NaAc aqueous buffer at pH 4.75. Potential scan rate 50 mV s^{-1} .

Similarly, voltammetric responses of sub-microsamples abrasively extracted from archaeological lead glasses displayed site-characteristic profiles [148]. The obtained voltammograms are dominated by lead-centered processes associated to the reduction of Pb(IV) centers (process $C_{\text{Pb(IV)}}$) and different Pb(II) (network-modifier Pb^{2+} and trigonal Pb_2O_4 chains) centers ($C_{\text{Pb(II)a}}$ and $C_{\text{Pb(II)b}}$ overlapping signals) [148]. Figure 3 compares the cyclic voltammograms for a lead-soda-glass and a lead-potash glass in contact with 0.25 M HAc/NaAc aqueous buffer where the above signals are clearly recorded accompanied by those for the stripping of lead (A_{Pb}), the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) at the extreme negative and positive potentials, respectively. Significantly different profiles were obtained for samples providing from different archaeological sites, as illustrated in Fig. 4, in which the two-dimensional diagram obtained from such voltammetric data representing the ratio between the peak current for the $C_{\text{Pb(II)a}}$ and $C_{\text{Pb(II)b}}$ processes ($i(C_{\text{Pb(II)a}})/i(C_{\text{Pb(II)b}})$) and the ratio between the A_{Pb} signal and the maximum current measured for the HER process ($i(A_{\text{Pb}})/i_{\text{HER}}$) is depicted for three different groups of samples of archaeological lead glasses from different Spanish sites.

Chronological correlations and dating

Establishing chronological correlations from electrochemical data is in principle accessible from VIMP analysis of series of coins [144–146]. A case of particular interest was again provided by the Maya blue for which the

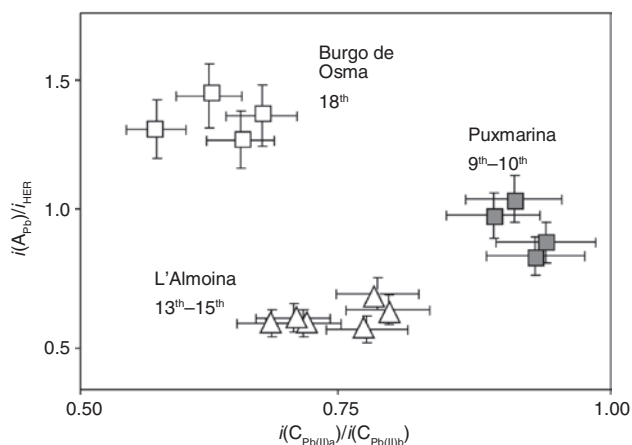


Fig. 4: Two-dimensional diagram from the voltammetric data such as in Fig. 3 representing the ratio between the peak currents for the $C_{Pb(II)a}$ and $C_{Pb(II)b}$ process ($i(C_{Pb(II)a})/i(C_{Pb(II)b})$) and the ratio between the A_{Pb} signal and the above ($i(A_{Pb})/i_{HER}$) for three different groups of samples of archaeological lead glasses. Experimental details in [148].

application to chemometric techniques to the VIMP signatures of a series of samples from different archaeological sites in Yucatán and Campeche (Mexico) suggested that the preparation procedure of Maya blue evolved along the Mayan times following a ramified scheme [100, 149–152]. It seems conceivable a view of the process in terms of a time evolution of a ‘Maya chemistry’ (to some extent anticipating several contemporary chemistry techniques such as hybrid inorganic-organic synthesis and thermal control of reactivity) [149, 153, 154]. Electrochemical monitoring of traditional indigo preparation procedures [102] and voltammetric analysis of samples from other Mayan materials [151, 155, 156] have supported a complex, evolutionary view of the Maya blue and related materials and the potential use of electrochemical data for revising the Maya chronology. Figure 5 shows a chronographic scheme for a set of archaeological Maya blue samples [100, 149]

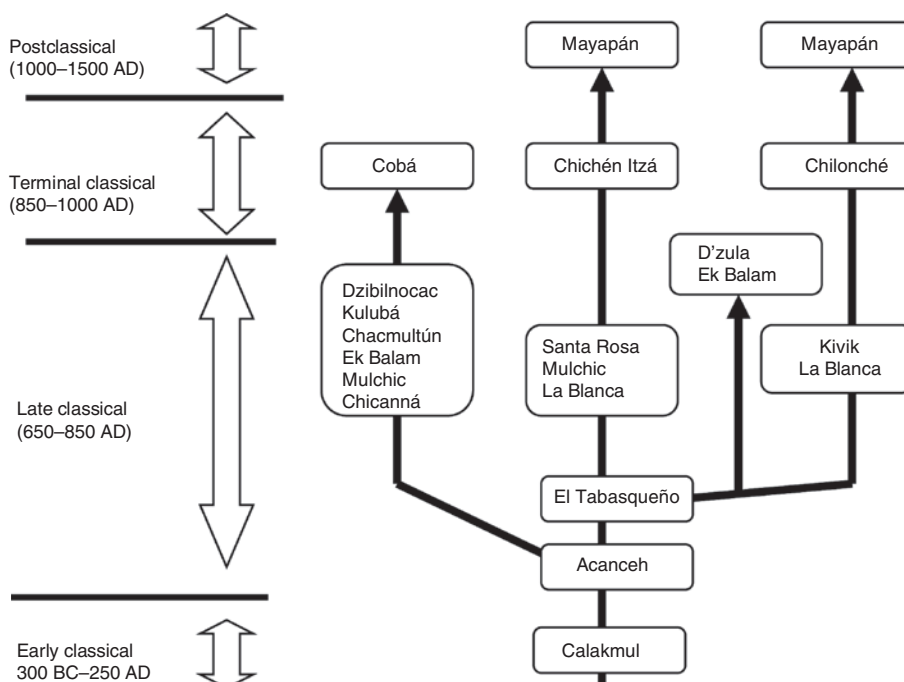


Fig. 5: Chronographic scheme for the archaeological Maya blue samples in refs. [100, 149] derived from the cluster analysis of electrochemical data crossed with spectral [150] and pyrolysis [152] data for archaeological sites in Yucatán and Campeche (México) and Guatemala.

derived from the hierarchical cluster analysis of electrochemical data [149] crossed with spectral [150] and pyrolysis/gas chromatography [152] data. In this diagram, each column corresponds to a given 'electrochemical type' (notice that in several sites, two different types appeared) and the hypothesised linkages derived from similarity relationships from cluster analysis is depicted.

Chemical methods of dating are focused on the monitoring of any phenomenon of chemical transformation which can be assumed to occur continuously with time under determined conditions. Amino acid racemization [157, 158] and obsidian hydration [159, 160] are well-known examples of chemical dating. In the context of archaeological metals, the relation between the Zn/Cu and Sn/Cu concentrations in the patina and the base metal for Cu-based alloys have been proposed as chronological indicators [161, 162]. Here, the driving processes are the decuprification, destannification and dezincation, widely extended phenomena in bronze and brass corrosion [163–166].

In this context, a first electrochemical method of dating of ceramic materials was proposed by Scholz, Brainina, Zakharchuk and coworkers based on monitoring the electrocatalytic effect exerted by the samples on the oxygen evolution reaction (OER) in aqueous alkaline media [167]. The supporting idea was that the number of defect sites created in the ceramics due to the action of cosmic radiation and other sources would increase with time. Since such defect sites act as catalytic centers for OER, the catalytic currents measured in VIMP experiments should permit, after calibration, the dating of the ceramic materials.

As occurring in physical dating methods such as radiocarbon [168, 169] or Meissner effect [170], the main difficulty for electrochemical dating is the superposition of different effects, in particular, those associated to environmental aggression which in turn can be quite sensitive to the composition of the sample and local conditions. Although these are factors particularly important for the case of metals, in some favourable cases, there is possibility of assuming reasonably that a common 'corrosion history' was experienced for different sets of samples. In fact, studies on long-term corrosion of metal surfaces [171–174], coincident with that derived from measurement of the Meissner effect on superconducting state of lead [170] appears to follow a common potential law.

In this context, recent proposals have been made for dating lead [175] and copper/bronze [176] objects from VIMP data for sub-microsamples attached to graphite electrodes immersed into aqueous electrolytes. In the first case, several methods, based on either the record of the relative height of voltammetric signatures for PbO_2 and PbO forms as well as on the measurement of electrocatalytic effects on for the hydrogen evolution reaction (HER) and OER in aqueous phosphate buffer permitted to construct consistent calibration curves covering since the 5th century BC to nowadays [175]. In the second case, calibration curves were obtained, covering a similar time interval, from averaged values of the ratio between the voltammetric signals for tenorite and cuprite [176]. Figure 6 depicts the calibration plots in double logarithmic scale for dating

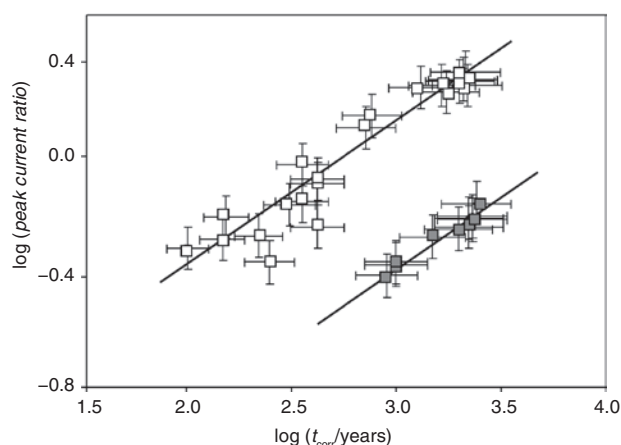


Fig. 6: Calibration graphs for dating lead (squares) and bronze/copper (solid squares) objects. Variation of the peak current ratios (see text and refs. [175, 176], respectively) with the nominal time of corrosion. In both cases, calibration data were extracted from square wave voltammograms of archaeological sub-microsamples attached to graphite bar in contact with aqueous acetate buffer. Continuous lines represent the linear fitting of data corresponding to potential rate laws.

lead and bronze/copper objects. In the first case, the peak current ratio between the signals for different PbO forms from square wave voltammograms of lead sub-microsamples attached to graphite bar in contact with aqueous acetate buffer at pH 4.85 was taken, whereas in the second the ration between the peak currents for tenorite and cuprite signals (C_{Cu_2} and C_{Cu_1} , respectively in Fig. 1) was taken. Continuous lines represent the linear fitting of $\log(\text{peak current ratio})$ vs. $\log(\text{corrosion time})$ representations. Remarkably, an essentially identical slope was obtained in both cases, corresponding to a potential variation of the respective peak current ratios, representative of the advance of the metal corrosion process with the corrosion time, assumed to be equivalent to the age of the objects. These features were consistent with the assumption that corrosion occurred under reasonably common and uniform conditions for all tested objects, following a potential rate law [170, 175, 176].

The time-dependent uncertainty of age determination was estimated as ± 150 years for the most ancient samples in the above studies, but obviously, it is strongly conditioned by the validity of the simplifying assumptions necessarily introduced, mainly the similarity in the composition of the base metal and the uniformity of the ‘corrosion history’ of the objects.

Under similar assumptions, the VIMP technique has been applied for dating leaded bronze [177] based on the increase of the proportion of lead corrosion products relative to copper corrosion products with the corrosion time, but here the calculations can be conditioned by the notable mutual influence in the respective voltammetric responses of those corrosion products [178]. The dating of porcine blood-based binding media used in Taiwanese architectural polychromies from voltammetric data based on haemoglobin-centered VIMP response has been also reported [179].

EIS methods have been tested for age estimates in the case of lead [180] and copper/bronze objects [181]. Using simply air-saturated mineral water as a non-aggressive electrolyte [80] and O_2 reduction as the redox probe [59], EIS permits testing the response of extensive regions of the archaeological objects. Here, the essential idea is that several EIS parameters will be dependent on ‘textural properties’ such as roughness and porosity of the corrosion layers which in turn will be dependent on the original composition of the metallic surface and the conditions and time of corrosion. At the current state of the art, however, EIS dating, although consistent with voltammetric dating, involves uncertainties larger than those from VIMP methods, as recently reviewed [182]. In this context, the use of catalytic effects on redox probes such as HER and OER processes, among others, is of interest for dating purposes [12, 167, 175, 182].

Electrochemical techniques can be seen as complementary analytical tools to be used in parallel to spectroscopic, diffraction, etc. techniques in synergistic way to develop analytical processes in the field of cultural heritage. It is pertinent to underline that electrochemical methods can provide information not only complementing that provided by other analytical techniques, but also information which cannot be accessed (or hardly accessed) through other techniques. This is the case of the determination of the oxidation state of electroactive species in ceramic materials and metal corrosion layers. Among other capabilities, the grouping of metallic samples by provenance with no need of sampling on the metal nucleus or the possibility of a reasonable direct dating of copper/bronze objects, are non-accessible to spectroscopy, diffraction, etc. techniques.

Future developments

Future developments involve the extension of electrochemical techniques to new methods of sample immobilization [183] and new materials used in works of art, for which only few studies have been reported, as is the case of textiles [67], paper, photographs, wooden objects [137], etc. On the other hand, the versatility of electrochemical techniques make it promising tools for studying more complex analytical problems such as the mutual influence of pigments, supporting materials [184] and binding media [50] and the effect of biodegradation in paint specimens [185, 186].

Apart from the inherent advances in voltammetric and EIS techniques, including their hybridization [187], another line of expansion would be the improvement of the implementation of nanoscale techniques (AFM, SECM and others) in their coupling with electrochemical measurements. In the immediate future, *in*

situ measurements with portable equipments, with special focus on EIS cells with gel electrolytes [130–132] should expand notably the analytical access to large-size objects.

Another aspect to be considered is the refined knowledge of the electrochemistry involved in solid state voltammetric measurements. Recent data support the idea that abrasive sampling provides information on the in depth variation of the composition of corrosion layers of metals, so that, via plausible modelling [146], refining of screening of provenances and dating [182] can be obtained.

Finally, it should be underlined that electrochemical methods have to be viewed as complementary to other existing microscopy, spectroscopy, diffraction, etc. techniques: the analytical information required by archaeologists, conservators and restorers can only be obtained through a synergistic combination of techniques. In this regard, a deeper intersection between electrochemical data and those from other techniques, as well as with the archaeological background, via application of chemometric techniques, constitutes a logical line of research.

Concluding remarks

The implementation of electrochemical methods in the fields of archaeometry, conservation and restoration of cultural heritage has experienced a significant growth in the last decades. In particular, the development of solid state techniques has prompted the acquisition of qualitative and quantitative information on the chemical composition of materials of interest but also the processing of such chemical information for achieving that of archaeological value, namely, tracing, authentication and dating.

In general, facing the analytical demands of archaeologists, conservators and restorers, requires the synergistic combination of different microscopy, diffraction, spectroscopy, etc. techniques. In this context, electrochemical techniques can be viewed as analytical tools allowing for providing relevant information in the field of cultural heritage.

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