

Voltammetric methods applied to identification, speciation, and quantification of analytes from works of art: an overview

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Abstract Voltammetry of microparticles, an electrochemical methodology based on the record of the voltammetric response of sparingly soluble solids mechanically transferred to the surface of inert electrodes in contact with suitable electrolytes, is able to provide significant analytical information in the fields of conservation and restoration of cultural goods. Using this methodology, identification, speciation, and relative and absolute quantification of analytes from works of art samples can be achieved. Applications to the analysis of organic and inorganic pigments in paints, fibbers, ceramic materials as well as alteration compounds in paintings and metallic artifacts are reviewed.

Keywords Voltammetry of microparticles · Works of art · Identification · Speciation · Quantification · Chemometrics

Introduction

Scientific examination of works of art is an essential task for archaeometry, conservation, and restoration of cultural heritage. A great variety of pieces providing from archaeological or historical sites to contemporary art can be considered as cultural goods whose study and preservation is the aim of conservation science [1]. This involves a variety of analytical demands, from dating to characterization of the artistic techniques and technologies of production of materials and pieces, from authentication to assessing the state of conservation, monitoring degradation, and/or detection of prior conservative treatments.

Analysis of works of art, however, offers special difficulties. First of all, non-destructive methods are desirable or, if not possible, the use of a minimal amount of sample as possible is needed. Secondly, multiple analytical information is demanded by conservators and restorers. For instance, analysis of a painting involves colorimetric analysis, microscopy data for discerning the several layers and chemical/mineralogical analysis for determining the composition of the preparative layer(s), binder, pigments, protective layers, and eventually alteration products and/or re-paints. Additionally, the presence of (or residuals from) biological agents and/or monitoring the effect of environmental attack has to be determined. A wide variety of analytical techniques, each one providing partial information, have to be combined for satisfying analytical demands. Electrochemical methods can be used, complementing microscopy, spectroscopy, etc. techniques, for obtaining chemical, mineralogical, textural, etc. composition of the samples from works of art and archaeological artifacts.

Most of the analyses involved in conservation science are made difficult by the high dilution of several components in the sample (pigments, for instance), their distribution in different layers, the presence of interfering compounds, alteration products, and matrix effects. Accordingly, a judicious combination of analytical techniques must in general be employed for obtaining the desired information. Available techniques comprise, among others, from optical microscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry, and transmission electron microscopy to X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy, and X-ray fluorescence [1].

In the last years, voltammetric methods have been added to disposable techniques for analyzing cultural goods. This

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is based in the so-called voltammetry of microparticles approach (VMP), a general methodology for analyzing solids developed by Scholz et al. [2, 3]. This is based on the mechanical attachment of micro- or nanograms of a sparingly soluble solid to the surface of an inert electrode, typically, paraffin-impregnated graphite electrode (PIGE) whose voltammetric response in contact with suitable electrolytes is recorded. Improving the analytical performance of approaches involving carbon paste electrodes [4–9], VMP is of particular interest for the analysis of works of art because of the small amount of sample required, its inherently high sensitivity, and by the fact that it provides direct information of the mineralogical composition and oxidation state of the electroactive species. Application of VMP to mineral, organic, semiconductor, etc. analysis can be seen in recent reviews [10–13] and texts [14, 15].

In this context, VMP was applied for identification of inorganic [16–22] and organic [23–30] pigments, ceramic materials [31–34], metals [35], and alteration products [18, 36–38], and for mineral and oxidation state [39, 40], speciation, and evaluation of the impact of environmental conditions on the conservation of metal objects [41–44]. Relative quantitation [45–48] and absolute quantitation [49–51] procedures applied to the above or related materials have been also reported. In the current report, a review of the capabilities of VMP for providing analytical information in the fields of archaeometry, conservation, and restoration is presented. This approach is able to provide identification of original materials and techniques used by the artists, determination of dosages, identification of alteration products, and evaluation of protecting layers and environmental aggressions so that information relevant for authentication, school characterization, dating, etc. can be derived from analytical data. A summary of such applications is depicted in Fig. 1.

Electrochemical processes

It should be emphasized that VMP involves different types of electrochemical processes, all having in common the existence of a solid (or mixture of solids) material attached to an inert electrode. In most cases, a solid-state redox process occurs consisting of the transformation of the parent solid into a second solid material. This process involves the coupled transport of electrons and charge-balancing electrolyte ions in the solid material and can be described in terms of the model due to Lovric, Scholz, Oldham, and co-workers [52–56]. In this formulation, the electrochemical reaction initiates at the electrolyte/electrode/particle three-phase boundary and expands through the solid particle via electron hopping between immobile redox centers in the solid coupled with ion transport across the solid. The diffusion equations for electron and ion transport can be solved for reversible electron transfer with no phase changes in the solid [52–56]. This situation is operative for the electrochemistry of Prussian blue [12–14] and probably for many organic dyes [22–29, 57, 58] in contact with aqueous electrolytes although in several cases, however, the electrochemical process involves the formation of new solid phases and the appearance of miscibility gaps [59].

A situation of particular interest is provided by the reduction of metal oxides and salts to the corresponding metal. In the case of lead oxide, the formation of lead metal phase occurs via epitaxial growth of a metallic layer from the oxide/electrode interface, as suggested by in situ XRD and AFM data [60, 61], but, in general, intermediate species in solution phase could be involved in the reduction of metal salts to metals depending on the experimental conditions [10–15].

Finally, oxidative or reductive dissolution processes can occur. Here, the original solid is reductively or oxidatively

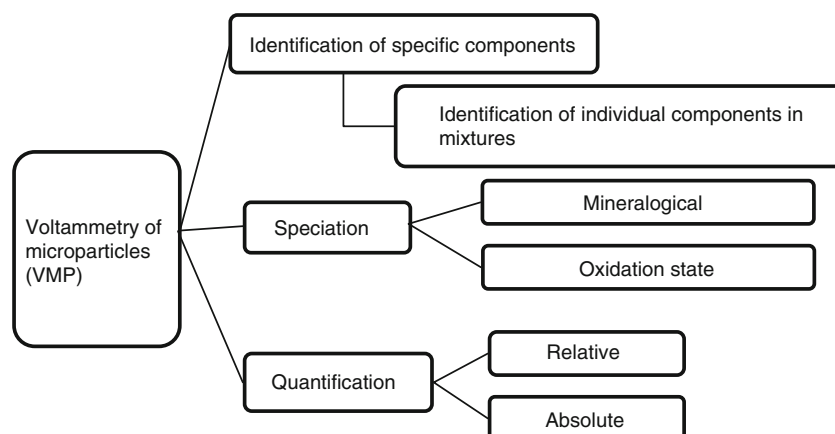


Fig. 1 Schematics for the application of VMP to archaeometry, conservation, and restoration sciences

passed to species in solution. The typical case is that of well-known stripping peaks for the oxidative dissolution of metals like cadmium, copper, lead, mercury, tin, or zinc, a process extensively used for determining trace metals in solution [62, 63]. A second group of processes is formed by the reductive dissolution (or oxidative dissolution) of metal oxides and salts, typically represented by iron oxides and related materials. The electrochemistry of iron(III) oxides and hydroxy-oxides has received significant attention [19, 20, 64–74] so that several phenomenological descriptions, based on solid-state reaction kinetics have been provided [68, 69, 71]. In the case of iron oxides, the rate of reductive dissolution is driven by the detachment, via ion diffusion or complexation reaction of metal centers from the reduced metal sites in the surface of the solid particles. As a result, the position and shape (roughly, peak width) of the voltammetric peaks depend on the average particle size and the homogeneity of the particle size distribution [20].

Direct identification of species

As previously noted, VMP can be used to identify metals, inorganic pigments, organic colorants, and pigmenting species in ceramic materials, as well as their alteration products. In the most favorable situation, only one or few electroactive species exists and, in this second case, the different species display electrochemical responses at well separated potentials. In these circumstances, peak potentials and shape-dependent voltammetric parameters can be used for characterizing the different species.

Typical cases of clearly discernible voltammetries are inorganic pigments of different metals. A typical example can be seen in Fig. 2, where the cyclic voltammograms of vermilion and minium, two red pigments widely used in medieval paintings, in contact with aqueous acetate buffer are shown. Here, not only cathodic signals can be separated, but also anodic stripping peaks recorded after application of a reductive step allow for identifying pigments. Thus, cadmium-, cobalt-, copper-, lead-, tin-, zinc- and zirconium-based pigments, among others, can be clearly discerned from the peak potential of oxidative dissolution peaks recorded for the corresponding metal deposits upon application of stripping techniques [18, 27, 32].

The identification of the specific metallic pigment, however, should be made from the cathodic signal corresponding to the metal salt to metal reduction. Although the electrochemical response varies slightly on the granulometry of the material and the type of support electrode, inter-laboratory trials indicate that most species can unambiguously be determined from voltammetric data [20]. In general, however, the identification of a particular pigment within the same family cannot be achieved merely

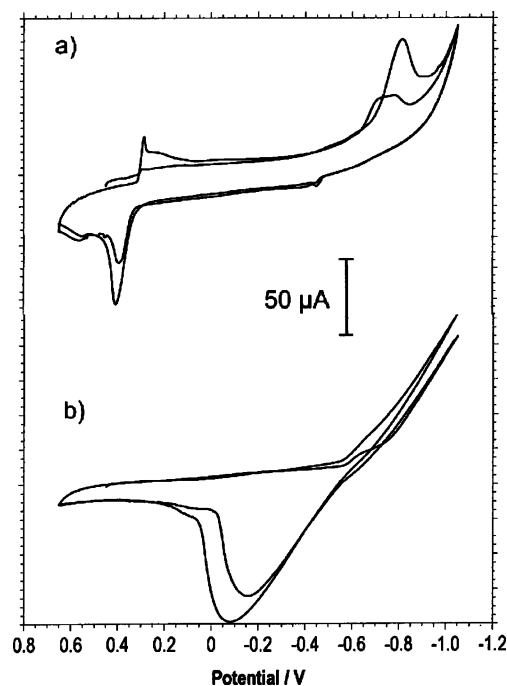


Fig. 2 Cyclic voltammograms for: *a* vermilion and *b* minium, attached to PIGEs and immersed into 0.50 M sodium acetate buffer, pH 4.75. Potential scan rate 50 mV/s. In this and in all subsequent figures, potentials are referred to the AgCl (3 M NaCl)/Ag reference electrode

by inspection of the corresponding peak potential. Then, the use multiparametric pattern recognition criteria, introducing half-width potentials, onset potentials, etc., illustrated in Fig. 3, is recommendable [22, 75]. In fact, using a given support electrode and a given electrolyte, repeatability tests show satisfactory results. This can be seen in Fig. 4, where the square wave voltammograms for four different commercial azurite pigments attached to PIGEs in contact with aqueous potassium phosphate buffer at pH 7.0 are shown. The voltammetric profiles for the different azurites were essentially identical, thus allowing for a clear distinction between azurite and other copper pigments using shape-dependent parameters [75, 76].

The case of, for instance, typical lead pigments, namely, lead white, minium, litharge, massicot, Naples yellow, chrome yellow, and tin-lead yellow, is illustrated in Fig. 5. Here, the voltammetric responses of such materials in contact with aqueous electrolytes are close, so that the distinction between different pigments requires an accurate treatment of shape-dependent parameters [22].

An additional complication arises in several paint samples because of the presence of binding media accompanying pigment particles. Interestingly, voltammetric profiles are sensitive to the presence of other materials in the sample, binding media in particular. As it is well-known, pigments are accompanied in such samples by bindings and other materials, namely, proteinaceous materi-

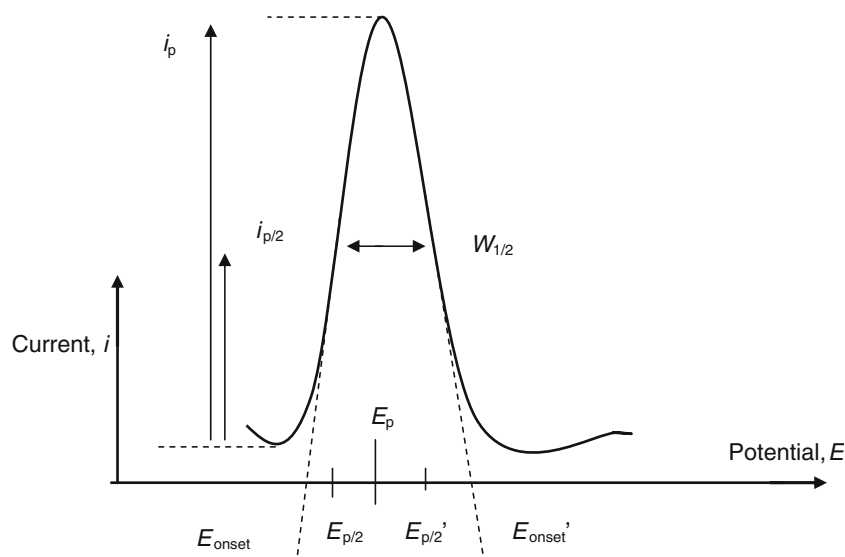


Fig. 3 Schematics for parameters able to be used for pattern recognition in voltammetric peaks

als and drying oils, either alone or mixed together. Proteinaceous tempera (milk or casein, egg, and animal glue) have been used since antiquity, whereas drying oils began to be used in Europe some time before the thirteenth century. *Tempera grassa* emulsions of oil and egg and, less frequently, oil and casein or gelatin, have been used for obtaining particular chromatic effects. Proteinaceous materials undergo hydrolysis reactions followed by oxidation, crosslinking, condensation, and dehydration of amino acids, while oil paint films undergo crosslinking reactions, oxidation of unsaturated acids, and hydrolysis of glyceride bonds [77].

Although proteins are rather stable and undergo little chemical change under normal conditions of temperature and humidity, their moisture produces slow hydrolysis of

the peptide linkages and eventually permits the action of fungi and bacteria. Aging yields possibly some changes in protein structure [78], while exposure to light, particularly ultraviolet, can produce the breaking of crystalline and peptide linkages. Apart from the above processes, proteins and amino acids can form complex species with metal cations. In fact, complexation interferes seriously the chromatographic determination of binders in pictorial samples [79–81].

Following Erhardt et al. [77], hydrolysis has been recognized as the main chemical reaction in oil paint films at all time scales. Hydrolysis may yield saturated fatty acids (which lack the functional groups that react during the crosslink process), unsaturated fatty acids, and short-chain fatty or diacids formed by scission reactions of unsaturated fatty acids. The acid groups formed by hydrolysis may react with metal ions from pigments to produce carboxylate salts, whose presence has been reported in pigmented linseed oil paints [82, 83]. Boon et al. [83] proposed that a change in the physical constitution of the paint layer results from pigment to a hardened, brittle system. These authors describe this hardened system as a polyanionic network in which several carboxylic acid groups are stabilized by metal ions provided presumably from the pigment particles. Accordingly, pigment particles can be surrounded by an ionic layer resulting from the reaction of pigments and the products of oil hydrolysis, carboxylate salts (referred to as soaps in the case of fatty acids) [83], or free carboxylic

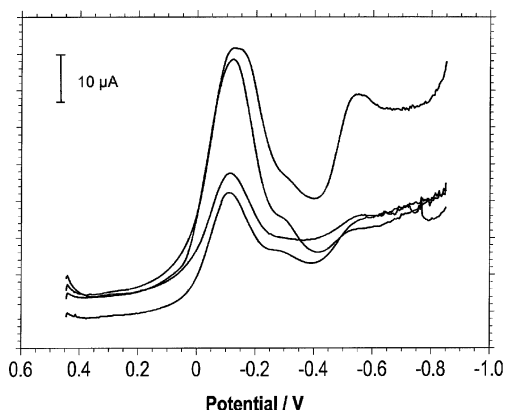
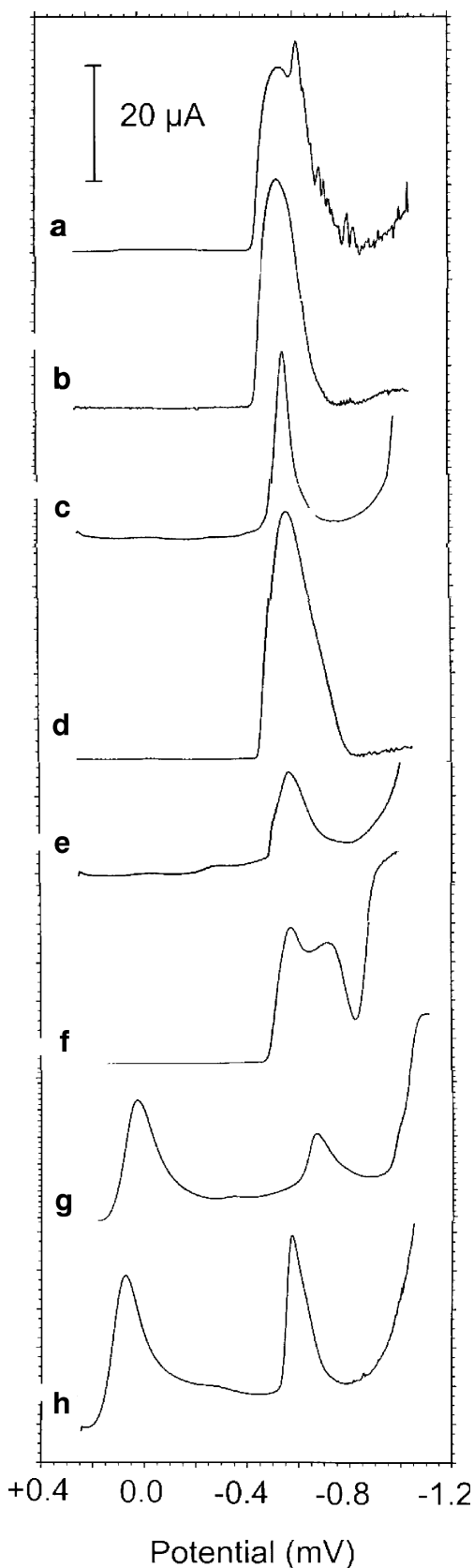


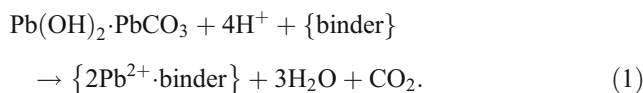
Fig. 4 Square wave voltammograms for azurite pigments (from top to bottom): Kremer10260, Kremer10280, Kremer10201, and Kremer10203, attached to PIGEs in contact with 0.50 M aqueous potassium phosphate buffer, pH 7.0. Potential scan initiated at +0.45 V in the negative direction. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 5 Hz

Fig. 5 Square wave voltammograms for: a lead white, b minium, c litharge, d massicot, e Naples yellow, f tin-lead yellow, g chrome yellow, h chrome orange attached to PIGEs in contact with 0.50 M aqueous sodium acetate buffer, pH 4.75. Potential scan initiated at +0.45 V in the negative direction. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 5 Hz

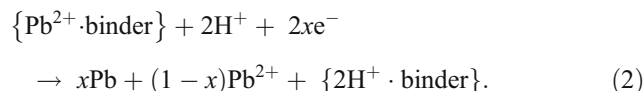


acids [77], being considered the main components of the paint layer.

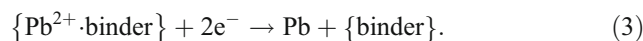
The presence of organic binders forming an ionomeric layer surrounding the grains of pigment can distort the response of the pigment, as schematically depicted in Fig. 6. Taking lead white as a typical material, the formation of an ionomeric layer can be represented as [22, 84]:



First of all, it should be noted that the ionomeric layer surrounding the particles of pigment can form a barrier for charge diffusion resulting in the alteration of the kinetics of the electrochemical process. Apart from this, two general mechanisms can be proposed depending on the nature of the binder [22, 84]. For oil-type binders, the ionomeric layer (represented by { }) is electrochemically reduced as:



In this process, the rate of the overall electrochemical process could be probably controlled by the diffusion of protons and/or hydroxide ions and/or water molecules through the ionomeric layer. In the case of proteinaceous binders, there is opportunity for a strong coordination of metal ions to donor sites of the binder. The reduction process can be represented as:



Here, the rate-determining step should be the dissociation of the metal–binder complex.

On considering that the ionomeric layer partly covers the particles of pigment as schematized in Fig. 6, both the responses of the pristine pigment and the ionomeric layer can eventually be superimposed. As far as the kinetics of both processes are different, these responses can be identified by varying electrochemical parameters such as potential scan rate in linear and cyclic voltammetries or frequency in square wave voltammetry. This offers opportunity for discerning not only between pigments, but also between binders [16, 22, 84]. As an example, square wave voltammograms for paint specimens prepared from lead white plus (a) caseine, (b) egg, (c) bovine gelatine, (d) sunflower oil, and (e) poppy oil in contact with aqueous acetate buffer, are shown in Fig. 7. The response of the pristine pigment is significantly modified in paint specimens prepared with the different binders. On first examination, distinction between proteinaceous and oil-type binders can be made [84].

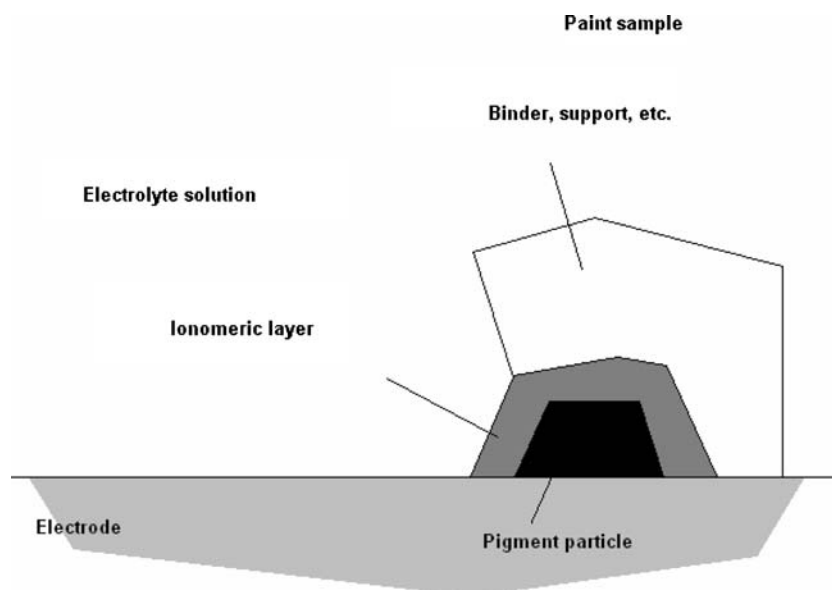


Fig. 6 Schematics for a paint sample consisting of a pigment particle surrounded by ionomeric layers attached to an inert electrode

Analytical strategies

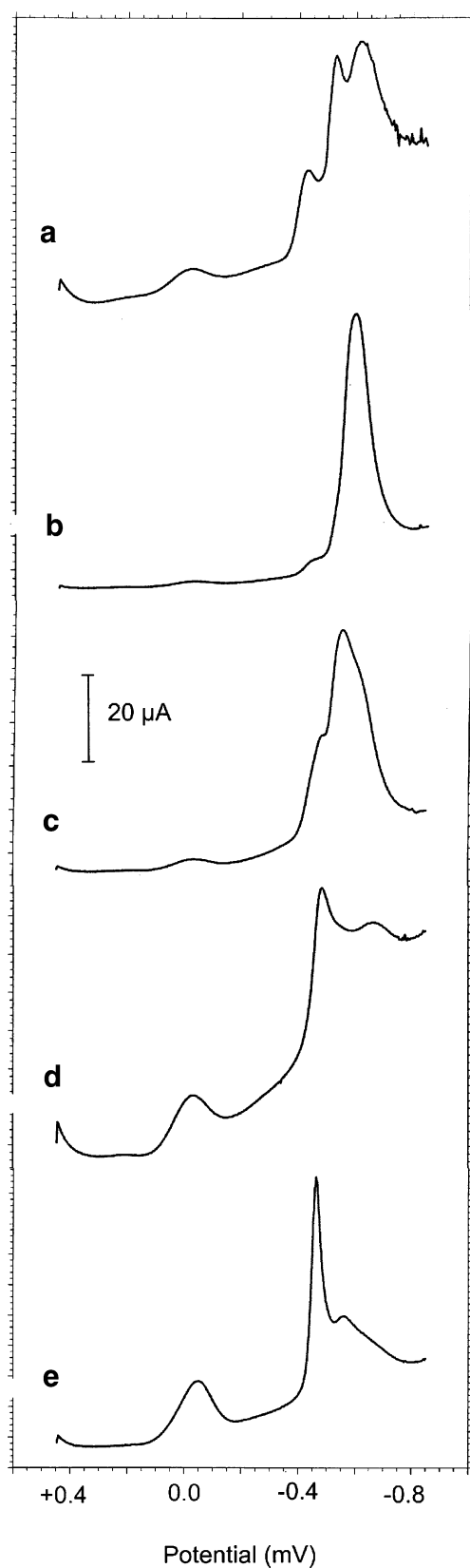
In most cases, identification of species is made difficult by the close similarity between the voltammetric patterns of possible materials in the sample and/or by the same complexity of the voltammetric response of the components. This is the case of, for instance, anthraquinonic dyes, having in common an anthraquinone core with variable substituent groups, preferentially, $-OH$ units. For such compounds, the main electrochemical process occurring in contact with aqueous electrolytes is the proton-assisted reduction of the quinone core to the corresponding diphenol (see Scheme 1). The potential of this process is modulated by the type, number, and position of the substituents, so that peak potential and peak profile slightly vary from one dye to another. Additionally, other substituent-dependent electrochemical processes can be superimposed, typically, the oxidation of *o*-diphenol units to the corresponding quinone (see also Scheme 1), thus facilitating dye characterization.

Further, several available analytical strategies can be used for identification purposes. Roughly, these can be divided into “chemical” or “electrochemical”. The most evident electrochemical strategies can consist of varying the electrochemical parameters, typically potential scan rate in linear and cyclic voltammetries, or frequency in square wave voltammetry. Additionally, one can apply constant potential steps resulting in the formation of new products whose electrochemical response can also be typified. In the case of organic dyes in contact with aqueous electrolytes, coupled proton-transfer, electron-transfer processes occur resulting in the formation of a narrow oxidized or reduced layer in the external regions of the crystals of the pristine

pigment, as indicated by chronoamperometric data [57] and AFM examination of dye deposits during electrochemical turnovers [58]. Then, the response of the electrochemically modified sample exhibits characteristic features which can be applied, for instance, for characterizing flavonoid dyes [29].

Chemical strategies are based on changing the composition of the electrolyte and/or the solvent. For instance, anthraquinonic dyes display recognizable responses in contact with both aqueous and non-aqueous (MeCN, DMF, DMSO) electrolytes [27]. The most typical chemical strategies are the pH change and/or the addition of a complexing agent to the electrolyte. The complexant can modulate the voltammetric response of the analytes, thus increasing the differences between one or another compound and/or, eventually, blocking and/or promoting several voltammetric signals. This is the case of aluminum chloride and boric acid added to aqueous electrolytes with regard to the identification of flavonoid dyes [29]. Borate units form strong complexes with *o*-diphenol groups, while Al^{3+} ions bind to quinone plus alcohol units. As a result, the response of a given dye can significantly vary or not from, for instance, aqueous acetate buffer to boric acid plus acetate buffer. Figure 8 compares the response of purpurin, an anthraquinonic dye, in aqueous potassium phosphate buffer with those recorded upon addition of increasing concentrations of boric acid to the electrolyte. The voltammogram of the pigment exhibits a main oxidation

Fig. 7 Square wave voltammograms for paint specimens prepared from lead white plus: *a* casein, *b* egg, *c* bovine gelatin, *d* sunflower oil, and *e* poppy oil, immersed into 0.50 M aqueous sodium acetate buffer, pH 4.85. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 15 Hz



peak at +0.30 V, attributable to the oxidation of the *o*-diphenol unit and a weak signal at -0.60 V, corresponding to the reduction of the quinone group (notice that in square wave voltammetry, both anodic and cathodic processes are simultaneously recorded). As can be seen in Fig. 8, the voltammetric response of the pigment becomes significantly modified upon increasing the concentration of boric acid, the main oxidation process being apparently blocked as a result of the coordination of *o*-diphenol units by borate. On the contrary, the reduction of the quinone group at -0.60 V is progressively enhanced and accompanied of secondary signals at -0.20 and -0.35 V on increasing the concentration of boric acid in the electrolyte solution. The use of this strategy leads to an increase in the number of electrochemical parameters able to be used for identifying the pigment.

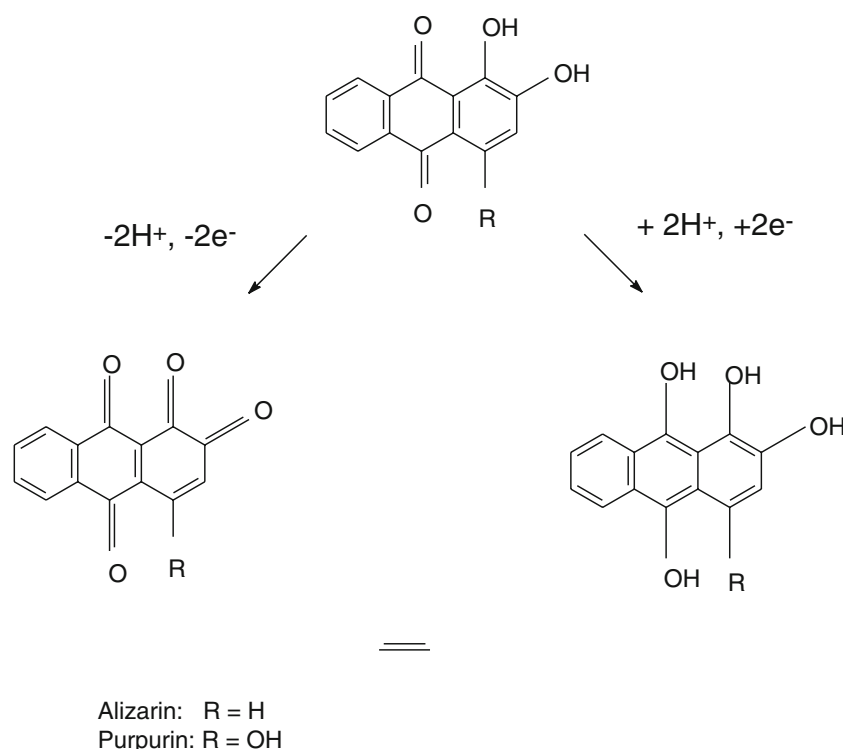
In several instances, the change in the supporting electrolyte can cause differences in the electrochemical response by virtue of the size selectivity imposed by the tested material, as occurring in pigmenting systems formed by dye attachment to certain clays (*vide infra*).

Speciation

The term speciation can be applied to the distinction between different mineral varieties and/or electroactive centers in different oxidation states. Examples of the first type of speciations are the identification of different manganese dioxide and iron oxide forms in weathered layers of archaeological glass and glazed materials [31, 36, 37]. By the second token, identification of Pb(II) and Pb(IV) centers in medieval glazes [38], Sn(II) and Sn(IV) [33] and Fe(III) and Fe(II) in ceramics [39, 40], has been carried out.

In general, that speciation involves not merely the detection of the presence of different species, but also the determination of their relative amount in the sample. In the case of reversible voltammetric signals, this quantification can be derived from the analysis of voltammetric curves following the methods devised by Scholz and Hermes [85] and Doménech et al. [39, 86].

A case of particular interest was that of Maya blue, a pigment widely used by the Mayas and other ancient peoples in Mesoamerica whose peculiar hue, ranging from turquoise blue to green, and brightness, and its enormous stability, has attracted attention during decades [87]. This attention, increased by the fact that there are no sources describing the preparation procedure used by the ancient Mayas [88], has been recently focused on the pigment characteristics as a nanostructured hybrid organic–inorganic material [89]. It is believed that the ancient Mayas could prepare Maya blue either by means of “dry” and “wet” procedures from the leaves of *Indigofera suffruticosa* and



Scheme 1 Molecular diagram for the main electrochemical processes involving anthraquinone-type dyes in contact with aqueous electrolytes

other species and palygorskite (or attapulgite) a local fibrous phyllosilicate [90–94]. More recently, Arnold et al. [95] have proposed that burning incense was one way in which the ancient Mayas made the pigment in the context of ritual ceremonies.

The reasons for the peculiar hue of and durability of Maya blue (resistant to the attack of acids, alkalis, organic solvents, and biodegradation), however, have become controversial [96–104]. Thus, José-Yacamán et al. attributed it to Mie-type light dispersion due to the presence of iron and iron oxide nanoparticles in Maya blue [96]. The most extended view, however, attributed Maya blue color to bathochromic shift of the indigo absorption bands as a result of the association of the dye to the inorganic support [100–104].

In this context, application of VMP methods, reinforced by ^{13}C NMR, visible and infrared spectroscopies, permitted to introduce a new piece into the above scenario [105]: dehydroindigo, the oxidized form of indigo (see Scheme 2). Thermochemical parameters calculated from temperature variation of electrochemical data indicated that dehydroindigo could be formed by aerobic oxidation of palygorskite-associated indigo during the preparation of the pigment by crushing indigo and palygorskite [100–104]. The simultaneous presence of indigo and dehydroindigo anchored to the palygorskite matrix could explain the peculiar hue of the pigment and its relatively high variability, because the amount of dehydroindigo relative to indigo should be

controlled by varying the temperature during the crushing process [105–107]. Using VMP, the presence of Maya blue in wall paintings of the Substructure IIC in the archaeological site of Calakmul, dated in the Late Postclassical period, was detected, thus anticipating significantly the date of use of the pigment with regard to the currently accepted period [105]. Analysis of a set of samples from different archaeological sites in Yucatán and Campeche (Mexico) suggested that the preparation procedure of Maya blue varied with time along the life of the Maya civilization [107–109]. Application of different thermal treatments, eventually including the use of additives such ochres during the preparation of the pigment would be used by the Mayas, thus anticipating several contemporary chemistry techniques such as hybrid inorganic–organic synthesis, thermal control of reactivity, and template synthesis [107]. Further, electrochemical monitoring of indigo preparation following the ancient Maya's recipes provides information on the possible mechanisms of formation of the dye from their precursor compounds in plants [108].

In a wide sense, the term speciation can also be applied for distinguishing between differently coordinated species, an idea that also applies to the Maya blue case. Here, it was proposed that the indigo molecules could anchor into the channels of palygorskite [93], or to be adsorbed onto the external surface of the clay [92]. More recently, it has been proposed that the structure of Maya blue involves the formation of hydrogen bonds between the carbonyl and

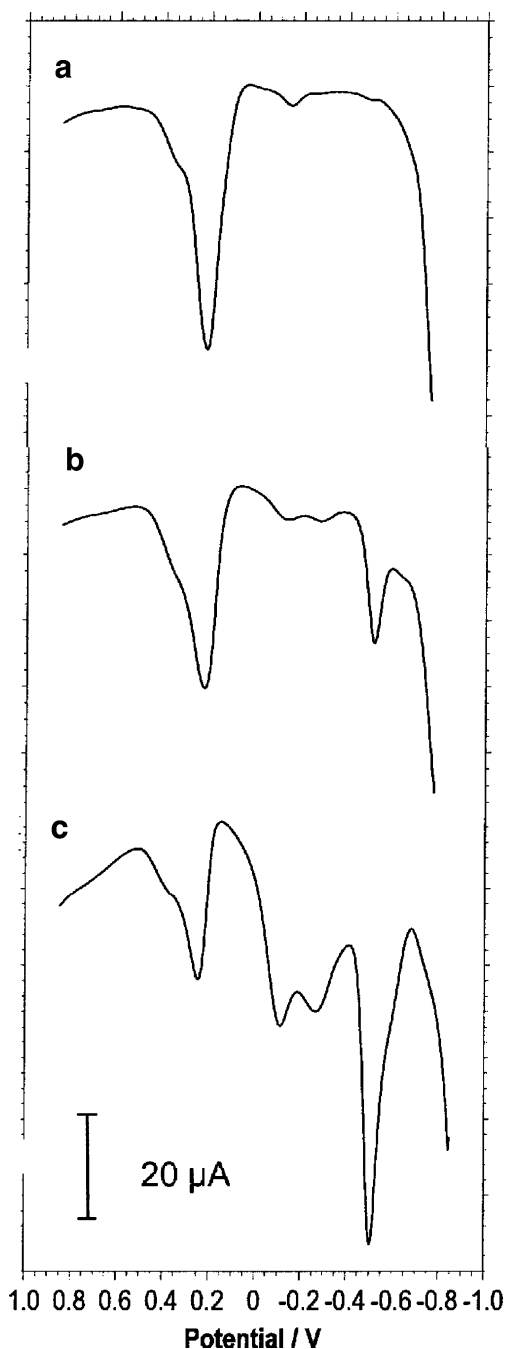


Fig. 8 Square wave voltammograms for purpurin attached to PIGE immersed into: *a* 0.50 M aqueous potassium phosphate buffer (pH 7.0), *b* id. plus 0.01 M boric acid, and *c* id. plus 0.10 M boric acid. Potential scan initiated at -0.85 V in the positive direction. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 5 Hz

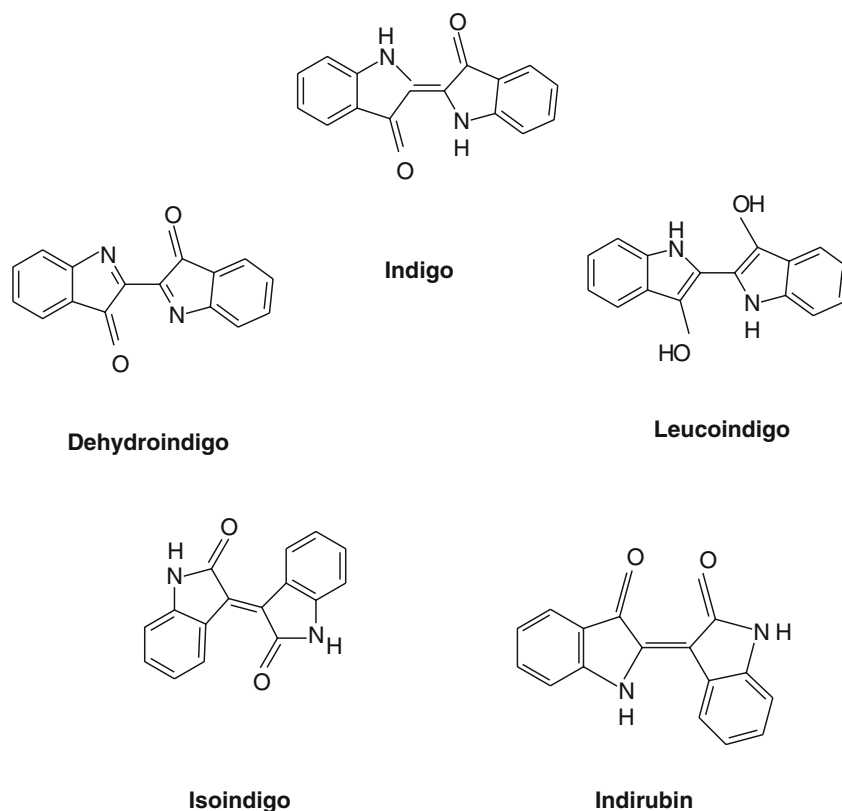
amino groups of indigo with edge silanol units of the clay, thus blocking the entrances of indigo molecules to the palygorskite channels [97]. Studies on molecular modeling, however, suggested a description of the indigo–palygorskite in terms of the formation of hydrogen bonds between C=O of indigo molecules and structural water molecules, but further spectroscopic data, however, suggested that hydro-

gen bonding between structural water molecules and N–H units of indigo occur [102]. Other studies concluded that, in addition to hydrogen bonding, van der Waals interactions and a direct interaction between indigo and clay octahedral cations, not mediated by structural water, could also play an important role in anchoring indigo molecules [98].

More recent data from VMP, combined with polynuclear magnetic resonance and visible and infrared spectroscopies, indicate that different topological redox isomers should occur [109–111]. This concept, which arises in the context of the photochemistry [112] and electrochemistry [113–115] of zeolite-associated species, reflects the presence of guest molecules occupying different positions in the host matrix. VMP data clearly suggest that different topological isomers of indigo and dehydroindigo, each one having a different type of attachment with the palygorskite framework, should exist in Maya blue. This means that the Maya blue pigment should be regarded as a complex system where different dye molecules (indigo, dehydroindigo, and possibly others like indirubin) are placed in different sites in palygorskite crystals so that possibly different coordinative arrangements are involved [111]. Additionally, the variation of the concentration of the different species with the depth in the crystals of palygorskite can be calculated from electrochemical data [109].

Identification and speciation via chemometric methods

As previously noted, in several cases, there is a possibility of obtaining highly characteristic electrochemical responses enabling for the identification of selected materials. This can be illustrated by the case of hematite in contact with HCl media, displaying a cathodic peak at about -0.40 V vs. AgCl/Ag. The appearance of such peak in: (a) a paint sample from the Palomino's frescoes in the *Sant Joan del Mercat* church in Valencia (Spain), (b) the corrosion layer of a steel sculpture in the campus of the Polytechnical University of Valencia, and, (c) a sample of weathered glass from Manises (Valencia, Spain, sixteenth to seventeenth centuries) can be seen in Fig. 9. Characterization of individual components can be of considerable interest for elucidating, for instance, preparation procedures. This is the case of the application of VMP to samples of medieval *socarrats*, ceramic tiles characteristic of the Valencian region whose preparation details remain uncertain, in particular, with regard to the application of a firing process and the nature of pigments. Figure 10 shows the voltammetric responses obtained for three samples each one providing from a different archaeological site in Manises (Valencia, Spain) in contact with HCl. The first sample (a) exhibits a clear signal for hematite while the second and third (b, c) samples present a voltammetric profile characteristic of hematite plus ochre mixtures [73, 74]. These features suggest that sample a was



Scheme 2 Molecular diagrams for indigoid compounds potentially related with Maya blue electrochemistry

submitted to a firing process determining the entire conversion of goethite into hematite, whereas samples b and c do not undergo a comparable process.

In most cases, however, the electrochemical response of the sample is complicated, as shown in Fig. 11 which compares the square wave voltammetric responses for two paint samples from the frescoes in the vault of the *Sant Joan del Mercat* church in Valencia (Spain), attributed to Antonio Acisclo Palomino, and dated ca. 1707. In the first sample (Fig. 11a), a main reduction peak appears at -0.10 V vs. AgCl/Ag, accompanied by weaker signals at -0.28 and -0.46 V. In the second sample (Fig. 11b), peaks at -0.10 and -0.28 V are followed by two intense, highly overlapping signals at -0.46 and -0.56 V. In the first sample, application of oxidative stripping analysis indicated the presence of cobalt and copper pigments, while for the second sample, cobalt, copper, and lead pigments were found to be present.

Comparison with voltammograms for different reference materials allowed to attribute the signals at -0.10 and -0.28 V to the superposition of reduction processes for azurite and cobalt smalt; the cathodic process at -0.45 V was assigned to the reduction of tenorite, CuO, an alteration product of copper pigments, while the signal at -0.56 V was attributed to Naples yellow. The presence of tenorite was derived from the thermal alteration of copper pigments

due to the gunfire experienced by the vault during the Spanish Civil War in 1936 [75].

Application of bivariate and multivariate chemometric techniques can enhance the analytical performance of VMP applied to conservation and restoration. This is of particular interest for identification of purposes in cases where: (a) the voltammetric responses of the different possible analytes are similar, so that single examination of peak potentials and related parameters does not offer an unambiguous characterization of the material, and (b) the voltammetric response of the analyte is intrinsically complicated.

Both situations apply for iron earths, an extensive family of pigments used since pre-historical times. The majority of earths are natural pigments, but several pigments such as Venetian red are manufactured materials. From the mineralogical point of view, earth pigments can be divided into clayey yellow earths, calcium sulfate-based earths, umbers, and iron silicates. Clayey earths are mainly composed by Al-substituted goethite (and/or hematite), kaolinite, and quartz, whereas gesso-type yellow and red earths are composed by goethite and/or hematite accompanied by gypsum, anhydrite, and clay minerals. Umbers or dark earths are goethite-based pigments probably originating from weathering of iron minerals such as iron sulfides, whereas green earths contain iron silicates such as glauconite and celadonite [20, 116].

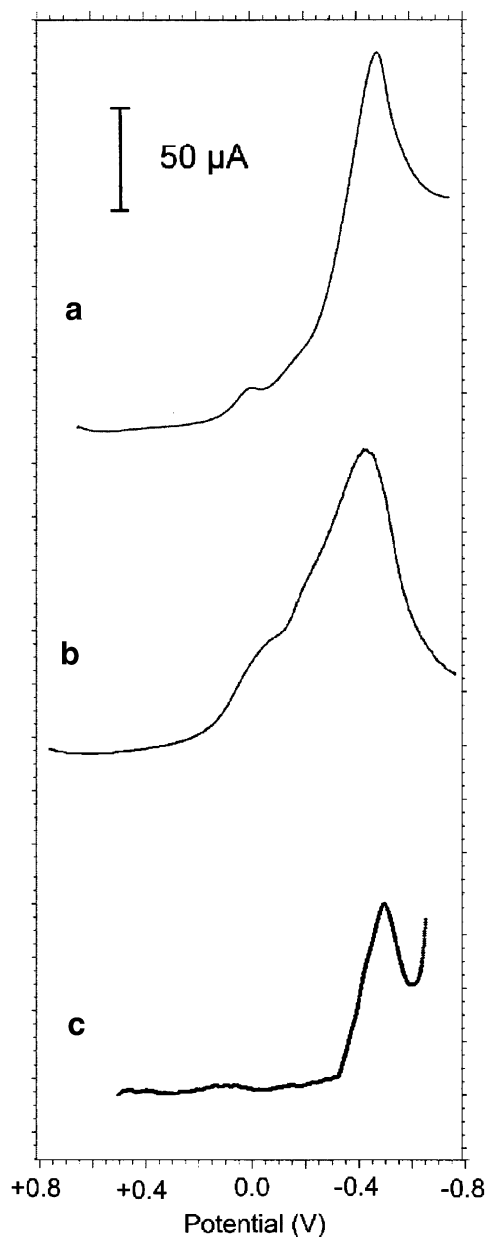


Fig. 9 Square wave voltammograms for PIGEs modified by: *a* a paint sample from the Palomino's frescoes in the *Sant Joan del Mercat* church in Valencia (Spain), *b* the corrosion layer of a steel sculpture in the campus of the Polytechnical University of Valencia, and *c* a sample of weathered glass from Manises (Valencia, Spain, sixteenth to seventeenth centuries) immersed into 0.10 M HCl. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 5 Hz

Iron oxide-based earths are, therefore, multicomponent materials whose hue is due to the absorption associated to the charge transfer between the oxo ligand (OH^- and O^{2-}) and the Fe^{3+} ion contained in goethite and/or hematite, and depends significantly on the shape and size distribution of particles [117]. As a result of this complex composition, pigment characterization by means of XRD and FTIR techniques is made difficult by the coexistence of numerous

and strongly overlapping signals due to the different components in the sample [116]. In contrast with such techniques, only iron-centered signals are obtained in VMP, thus simplifying notably data analysis.

Unfortunately, the voltammetric response of iron oxide materials, based, as previously noted, on reductive dissolution processes [19–22, 64–74], is relatively complicated because voltammetric peaks depend on the composition, degree of hydration, crystallinity, and shape and size distribution of iron oxide grains. Thus, hematite- and goethite-based voltammetric peaks are shifted cathodically by increasing Al-for-Fe substitution, increasing particle size, and anodically with increasing departures of stoichiometry, the wider peaks hence indicated less consolidated, and hence probably more heterogenous iron oxides [20]. As a result, voltammograms of earths in contact with acidic

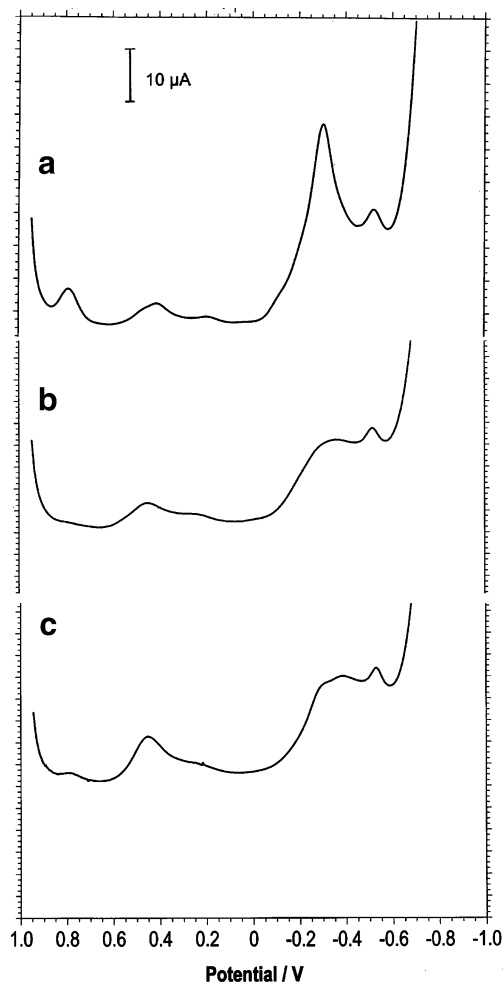


Fig. 10 Square wave voltammograms of PIGEs modified with three different samples of medieval *socarrats* from different archaeological sites in Manises (Valencia, Spain). Voltammograms for samples *a* S-4, *b* S-14, and *c* S-16, immersed into 0.20 M HCl. Potential scan initiated at +0.95 V in the negative direction. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 2 Hz

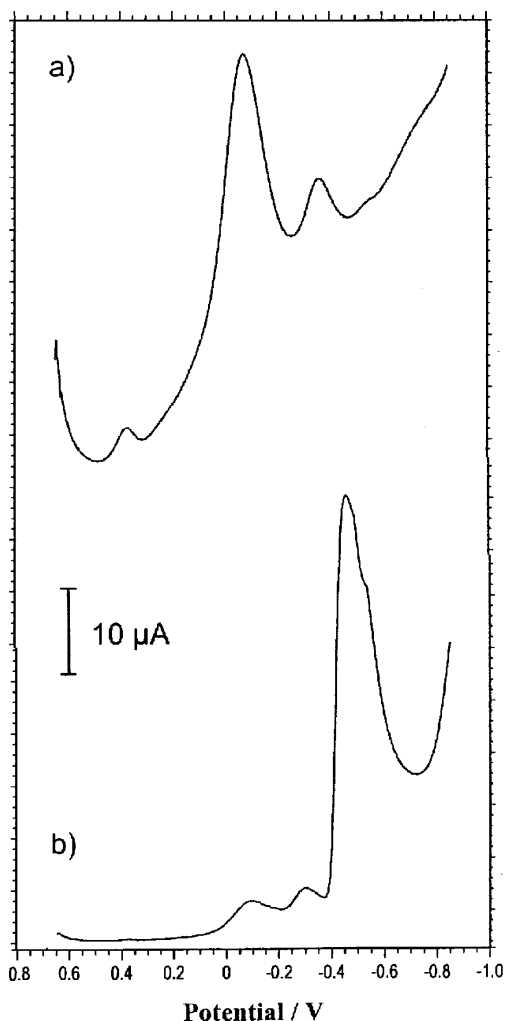


Fig. 11 *a, b* SQWVs for two samples taken from different locations in the vault of the *Sant Joan del Mercat* church in Valencia (Spain) attached to PIGEs in contact with 0.50 M potassium phosphate buffer at pH 7.0. Potential scan initiated at +0.65 V vs. AgCl/Ag in the negative direction. Potential step increment 4 mV, square wave amplitude 25 mV, frequency 5 Hz

aqueous electrolytes (typically HCl) consist of several overlapping peaks in the potential range between +0.50 and -0.80 V vs. AgCl/Ag [19, 20]. Interestingly, manganese oxides, often accompanying iron oxides in earths, display signals at more positive potentials.

In these cases, bivariate characterization of pigments was achieved from two-dimensional diagrams where selected peak current ratios were used [72–74]. The idea is that, although absolute peak currents depend on the amount of electroactive species existing in the electrode, the quotients between the currents for different peaks are representative of the voltammetric profile, thus being usable for characterizing the iron oxide material. Multivariate chemometric methods, cluster analysis in particular, can accordingly be used from a matrix of several peak current ratios in order to identify earth pigments [72, 74] and

products of alteration in steel sculptures [73]. Remarkably, the use of chemometric techniques permitted to explain the general reddening observed in carnations in the aforementioned Palomino's frescoes in the *Sant Joan del Mercat* church as a result of the conversion of goethite into hematite as a result of the firing stress suffered by the paints [74]. Figure 12 shows a two-dimensional diagram where two different peak current ratios in square wave voltammograms in contact with HCl allow for distinguishing between different earth pigments. Solid squares correspond to data points for samples providing from the Palomino's frescoes in the *Sant Joan del Mercat* church. Their position in the diagram can only be understood as the result of goethite into hematite transformations due to thermal stress.

Similarly, bivariate and multivariate analyses can be applied to previously described shape-dependent parameters of voltammetric signals [22] and Tafel parameters which will be reviewed in the next section [75, 76].

Quantification

Relative quantification of components in work of art samples is of obvious interest in archaeometry and conservation science. As described by Scholz et al. [10–15, 118–122], using VMP, relative quantification for two particular electroactive components in solid samples can be obtained from the quotients between the areas and/or peak currents of the respective voltammetric peaks. Additionally, coulometric data can be used for relative quantification purposes [118–122]. As far as coulometric measurements are always more demanding than voltammetric ones, because coulom-

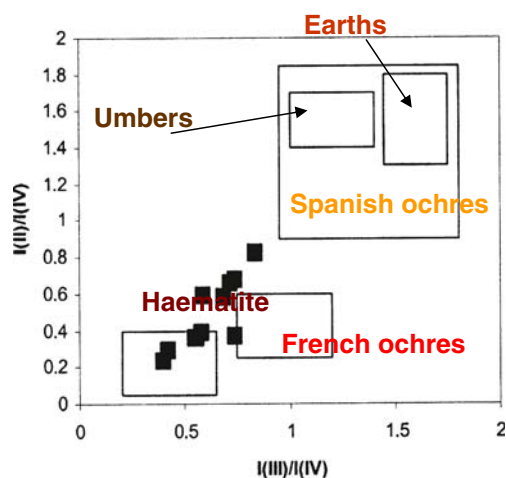


Fig. 12 Two-dimensional diagram using two different peak current ratios determined in square wave voltammograms of samples from the *Sant Joan del Mercat* church in Valencia (solid squares) immersed into 0.10 M HCl. Experimental details in [74??]

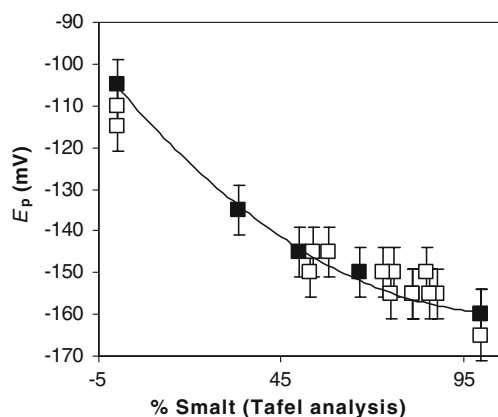


Fig. 13 Shift in the peak potential of the main reduction peak obtained from square wave voltammograms of azurite plus cobalt smalt mixtures (*solid squares*) and samples from the *Sant Joan del Mercat* church in contact with aqueous phosphate buffer (conditions such as in Fig. 11) as a function of the smalt/azurite ratio determined from Tafel analysis. The values of the peak potential vary from -105 mV for azurite to -155 mV for smalt

etry offers opportunity for more pronounced systematic errors, the use of coulometric measurements is recommendable for cases where voltammetry fails [122]. In this context, quantification of CdS in cadmium pigments (cadmium sulfide and cadmium sulfoselenide) relative to added AgCl [48] and quantification of ferric oxides relative to that of an internal manganese oxide standard [46] have been reported. Quantification of pigmenting species in ceramic glazes relative to lead has been described using stripping peaks for oxidative dissolution of metal deposits obtained after a reductive electrodeposition step [47].

Eventually, the variation in other electrochemical parameters can be used, after calibration with adequate standards, for relative quantification. This is the case of peak potentials in the case of mixtures of electroactive species displaying highly overlapping voltammetric peak, illustrated in Fig. 13. Here, the peak potential data is plotted vs. the smalt/azurite molar ratio determined using Tafel analysis of the rising portion of voltammetric curves (*vide infra*) using square wave voltammograms of azurite plus cobalt smalt mixtures in contact with aqueous phosphate buffer.

In most cases, the identification and quantification of the analyte are possible using the analysis of Tafel of the rising portion of voltammetric peaks, characterized by a linear dependence of $\log(\text{current})$ on the applied potential [75, 76, 123]. This relationship is strictly valid for irreversible charge transfer processes involving species in solution phase [124, 125], reductive/oxidative processes for surface-confined species [126]. Using square wave voltammetry, Tafel relationship applies for reversible electron transfer processes involving species in solution phase [127, 128] and can be extended to several cases of electron transfer processes involving species immobilized on the electrode surface

[129–131]. In several cases, one can assume that the rising portion of the voltammetric curve can reasonably be described in terms of an equation of the type [75, 76, 123]:

$$i \approx q_0 k \exp\left(-\frac{\alpha n_a F}{RT} E\right). \quad (4)$$

In this equation q_0 represents the total charge involved in the complete reaction of the electroactive solid, αn_a the product of the coefficient of electron transfer (α) by the number of electrons (n_a) involved in the rate-determining step, n the total number of electrons involved in the electrochemical reaction, and k the heterogeneous electrochemical rate constant at the zero potential. Equation 4 predicts that plots of $\ln i$ vs. E should fit to a straight line whose slope is function of the αn_a factor, and the ordinate at the origin depends on the electrochemical rate constant and the amount of sample transferred to the electrode surface. Accordingly, the slope of the Tafel representation is characteristic of the electroactive compound and, therefore, usable for identification purposes. To avoid the dependence of the ordinate at the origin on the amount of sample deposited onto the electrode surface, currents can be normalized with respect to the peak current of the voltammetric peak. This is based on the assumption that the peak current, i_p , can in general be taken as [19, 75, 76, 123]:

$$i_p = G q_0 \left(\frac{\alpha n_a F}{RT}\right) \quad (5)$$

Where G represents an electrochemical coefficient of response depending on the technique and parameters such as the potential sweep rate. Combining Eqs. 4 and 5, one obtains a normalized Tafel relationship:

$$\ln(i/i_p) = \ln\left(\frac{kRT}{G\alpha n_a F}\right) - \frac{\alpha n_a F}{RT} E. \quad (6)$$

Here, both the slope and the ordinate at the origin of the Tafel representation become independent on the amount of sample deposited on the electrode surface. Accordingly, such parameters can be used for characterizing materials [19, 75, 76, 123].

In the cases where two components exhibit overlapping voltammetric peaks, Tafel plots of the logarithm of the current vs. the applied potentials yield straight lines whose slope and intercept can be taken as representative of the composition of the sample. The relative amount of both components can be determined from the Tafel analysis of voltammetric curves as described by Doménech et al. [75]. This methodology allowed to solve cobalt blue plus azurite mixtures in wall paintings from the *Sant Joan del Mercat* church in Valencia (Spain).

Remarkably, relative quantification of components in samples from works of art can provide useful information for style characterization and authentication. Thus, the smalt/

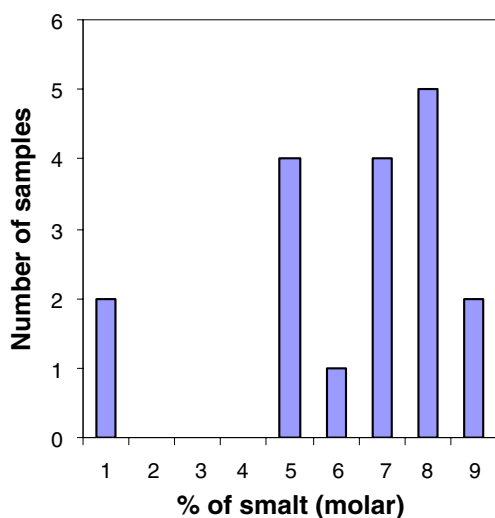


Fig. 14 Smalt/azurite dosages determined in samples for Palomino's frescoes in the vault of Spain) using VMP

azurite ratios determined in samples from Palomino's frescoes in the aforementioned *Sant Joan del Mercat* church in Valencia were grouped in selected dosages, as shown in Fig. 14.

Absolute quantification requires the addition of an electroactive standard so that the relative sample/standard amount was known. This is due to the fact that it is not possible to control the exact amount of materials transferred to the electrode surface in VMP experiments. When a unique analyte or more than one analyte displaying well-separated voltammetric signals are involved, the standard additions method can be used for absolute quantification [49]. The voltammetric signal for the standard has to be separated from those of the analytes and a linear variation of peak current or peak area with the amount of the respective species is desirable. When two analytes displaying strongly overlapped signals are involved, the H-point standard additions method can be used for absolute quantification of both analytes [50, 51].

Future developments

The next future in the application of the VMP methodology to conservation science can be viewed in three complementary fields: analytical, electrochemical, and conservation/restoration. Analytical field is focused on analytical methods for conservation science, whereas the electrochemical field is devoted to the purely electrochemical aspects involved in VMP. The conservation/restoration field comprises the specific demands and applications of VMP in the conservation science frame.

With regard to the analytical field, several aspects can be developed: (a) standardization, with study of reference materials (desirable database creation, for instance, for

pigments and alteration products); (b) development of specific methods of multivariate analysis; (c) application of hyphenated techniques; (d) development of programs of quality assessment such as inter-laboratory trials; and (e) research for developing non-destructive sampling.

Developments in the electrochemical field should include: (a) investigation on specific theoretical models to be applied for describing complex processes occurring in work of art samples, (b) studies on the influence of matrix materials in the electrochemical response (for instance, the modification of the response of pigments by effect of binding media), (c) development of indirect and competitive methods (i.e., recording signals for species different from the desired analyte), and (d) application of other electrochemical techniques to VMP configurations (electrochemical impedance spectrum, electrochemical noise).

Future research in the conservation/restoration field could be focused in aspects such as: (a) extension to new materials (such as marbres [132]), (b) improving procedures for translating electrochemical information to archaeometry/conservation/restoration information, (c) increasing complementarity with non-electrochemical techniques for problem solving, (d) oriented research for preservation/conservation treatments, (e) extension to, for instance, environmental analysis, and (f) generation of new perspectives from the capabilities of VMP for gain information on dosages, speciation, etc.

In this sense it is pertinent to remark that:

- (a) VMP can be considered as a technique complementary—not substitutive—of existing non-electrochemical

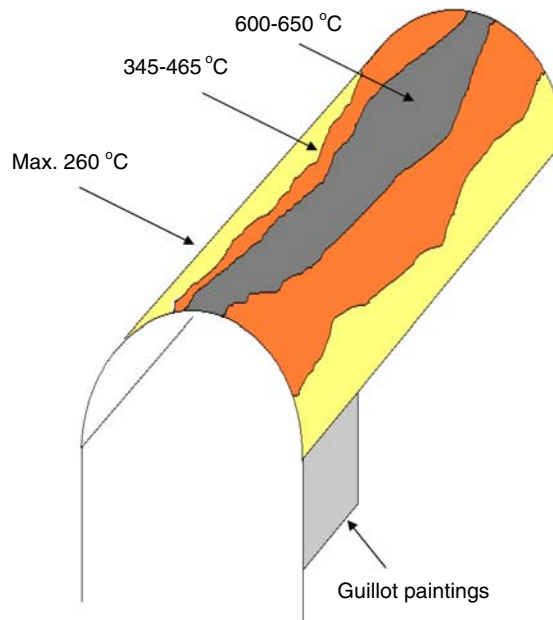


Fig. 15 Temperature profiles during the firing process suffered by the vault of the *Sant Joan del Mercat* church in Valencia (Spain) determined from VMP data

techniques of analysis. The analysis of samples from historical artifacts and works of art should be regarded in terms of a synergistic use of different techniques rather than focused in few “universal” techniques [133].

- (b) VMP can offer interesting information for restoration and conservation that cannot be directly obtained (or is not easily derived) from other techniques. Identification of components, determination of dosages in paint samples [75], and composition changes due to alteration processes [75, 76, 123] become easily accessible to VMP and can be used for obtaining historic and archaeometric information. As a paradigmatic example of the wide possibilities of VMP, temperature profiles were estimated for the firing process suffered by the vault of the *Sant Joan del Mercat* church in Valencia, depicted in Fig. 15. Threshold temperatures were determined from the goethite into hematite thermal transformation and lead carbonate and azurite thermal decomposition processes crossing thermochemical with electrochemical data.

Final considerations

VMP methods can offer analytical information of interest in the fields of archaeometry, conservation, and restoration of works of art. Application to mural and oil paintings, textiles, ceramic materials and glasses, metals and alloys and other materials in historical pieces, archaeological artifacts, and work of art samples is currently possible, involving minimal amounts of sample. Identification of components and alteration products, mineral and chemical speciation, distribution of components, and relative and absolute quantification of components in samples are possible using the VMP methodology.

A judicious combination of VMP with other techniques can lead to complementary information to be achieved. Relevant data for authentication, identification of pristine materials and techniques, schools, alteration products, etc. can be derived from VMP analysis of samples from works of art and archaeological artifacts, in turn providing information of historical, anthropological, and artistic interest.

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