SIMULTANEOUS IDENTIFICATION OF LEAD PIGMENTS AND BINDING MEDIA IN PAINT SAMPLES USING VOLTAMMETRY OF MICROPARTICLES

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ABSTRACT: *Voltammetry of microparticles is applied to the simultaneous determination of lead pigments and binding media in paint samples. The mechanical attachment of a few nanograms of sample to a paraffin-impregnated graphite electrode produced well-defined square wave voltammetric responses for model paint specimens containing lead white, minium and Naples yellow associated with linseed, sunflower and poppy oils and casein, egg, and bovine gelatin. The use of a multiparametric fitting of the electrochemical data allows for the simultaneous identification of the lead pigment and binder in synthetic paint specimens.*

KEYWORDS: lead pigments, binding media, voltammetry of microparticles, conservation, paintings

INTRODUCTION

The identification of the components of paint samples is an obvious analytical objective which is carried out during the scientific examination of works of art. In recent years, a novel methodology, the voltammetry of microparticles (VMP) has been added to the existing techniques for pigment identification. This methodology developed by Scholz et al. (Scholz and Meyer, 1998) is based on the attachment of a few micrograms of solid sample to the surface of an inert electrode and the recording of its voltammetric response in contact with a suitable electrolyte. In prior works, this methodology has been applied to the identification of inorganic pigments in pictorial samples (Doménech et al., 2000, 2001, 2002, 2007).

Interestingly, voltammetric profiles are sensitive to the presence of other materials in the sample, in particular, binding media. As it is well known, the pigments in such samples are accompanied by bindings and other materials, namely proteinaceous materials and drying oils, either alone or mixed together. Proteinaceous tempera (milk or casein, egg and animal glue) have been used since ancient times, while drying oils were first used in Europe some time before 13th century[Mills and White, 1994; Matteini and Moles, 1989]. In addition, *tempera grassa*, which consists of an emulsion of oil and egg or, less frequently, oil and casein or gelatin, was often used to obtain particular chromatic effects (Matteini and Moles, 1989; Mills and White, 1994). Proteinaceous materials undergo hydrolysis reactions followed by oxidation, crosslinking, condensation and dehydration of amino acids (Genestar and Pons, 1995) while oil paint films undergo crosslinking reactions, the oxidation of unsaturated acids and the hydrolysis of glyceride bonds (Erhardt et al., 2005).

The proteins are rather stable and undergo little chemical change under normal conditions of temperature and humidity [Mills and White, 1994]. Moisture, however, produces the slow hydrolysis of the peptide linkages and eventually permits the action of fungi and bacteria. Ageing possibly yields some changes in the protein structure (van der Weerd et al., 2005), while exposure to light, particularly ultraviolet, can produce the breaking of crystalline and peptide linkages. Protein and amino acids can form complex species with metal cations. In fact, complexation seriously interferes with the chromatographic determination of binders in pictorial samples (Colombini et al., 1999; Scott et al., 2004; Kuckova et al., 2005).

Following Erhardt et al. (2005), 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 crosslinking process), unsaturated fatty acids and short-chain fatty or diacids formed by the scission reactions of unsaturated fatty acids. The acids 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 (Meilunas et al., 1990; Boon et al., 1996). Boon et al. (1996) proposed that pigment alteration results in the physical change of the paint layer to a hardened, brittle system. These authors describe this hardened system as a polyanionic network in which the carboxylic acid groups are stabilized by the metal ions, the pigments being the most probable source. Accordingly, the pigment particles can be surrounded by an ionomeric layer resulting from the reaction of the pigments and the products of oil hydrolysis, carboxylate salts (referred to as soaps in the case of fatty acids) (Boon et al., 1996) or free carboxylic acids (Erdhardt et al., 2005), considered the main components of the paint layer.

In this report, VMP has been applied to simultaneously identify lead pigments and binding media using a series of synthetic specimens prepared by combining different lead pigments (lead white, Naples yellow, minium) with oils (linseed, sunflower and poppy oils) and proteinaceous binders (bovine gelatin, egg, casein).
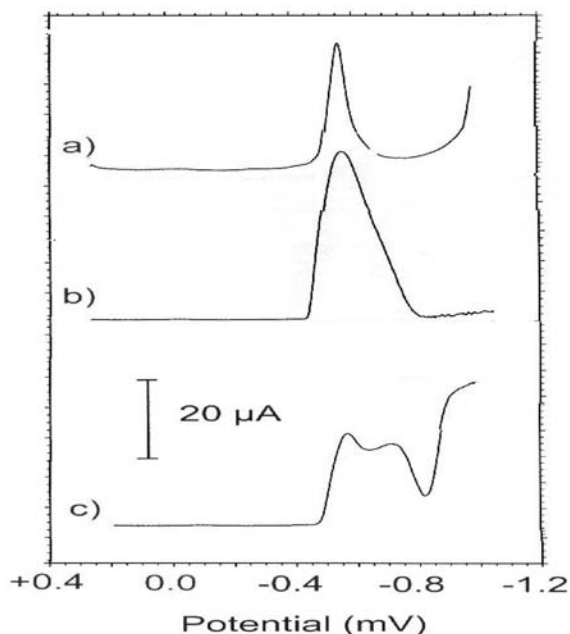
Figure 1. SQWVs of microsamples of: a) Naples yellow, b) lead white, and c) minium attached to paraffin-impregnated graphite electrodes. Electrolyte: 0.50 M acetic/acetate buffer, pH 4.85. Potential step increment of 4 mV; square wave amplitude of 25 mV; frequency of 15 Hz Figure 1. SQWVs of microsamples of: a) Naples yellow, b) lead white, and c) minium attached to paraffin-impregnated graphite electrodes. Electrolyte: 0.50 M acetic/acetate buffer, pH 4.85. Potential step increment of 4 mV; square wave amplitude of 25 mV; frequency of 15 Hz

EXPERIMENTAL

Commercially available pigments were used: minium (Pb_3O_4, Probus), lead white ($2PbCO_3.Pb(OH)_2$, Sigma-Aldrich, Steinheim, Germany), and Naples yellow ($Pb_3[SbO_4]_2$, Kremer). Natural, cold pressed linseed oil (Kremer) supplied by AP Fitzpatrick, London, England, bovine gelatin supplied by Sigma-Aldrich (Steinheim, Germany) and ox-gall used in Fine Art works supplied by Dr. Luis Angel de La Fuente (Bilbao, Spain) were used to prepare the model paint specimens.

Acetic acid (Panreac) and sodium acetate (Merck) in a total concentration of 0.50 M were used in nanopure water for the electrolyte preparation.

Electrochemical experiments were performed using paraffin-impregnated graphite electrodes modified with the samples. Measurements were performed at 298 K in a three-electrode cell under an argon atmosphere using a AgCl (3M NaCl)/Ag reference electrode and a platinum-wire auxiliary electrode. Cyclic and square wave voltammograms (CVs and SQWVs, respectively) were obtained with CH I420 equipment.

A first series of model paint specimens was prepared by mixing the pigments with the appropriate amount of oil (Meyer, 1993). As a result, pictorial dispersions at 14% (w/w) were obtained and then spread as a thin layer (average thickness, 50-80 um) on glass slides. The model paint specimens were stored at room temperature (24±2 ºC) during 4 weeks and subsequently analyzed.

Similar to the above model oil paint specimens, a second series of model paint specimens was prepared by mixing the pigments with the appropriate amount of a previously prepared aqueous solution (70 g/L) of proteinaceous binder (Meyer, 1993). The resulting pictorial dispersions at 14% (w/w) were obtained and processed as above.

RESULTS AND DISCUSSION

Figure 1 compares the square wave voltammograms for: a) Naples yellow, b) lead white and c) minium attached to paraffin-impregnated graphite electrodes immersed in acetate buffer. The lead pigments exhibited a prominent reduction peak ca. -550 mV corresponding to the reduction of the corresponding lead compound to lead metal as previously described (Doménech et al., 2007).

Different electrochemical parameters were used for pigment characterization, based on criteria used by Sybrandt and Perone (1972) for pattern recognition in cyclic voltammetric curves: i) peak potential, E_p, ii) half-peak width, $W_{1/2}$, iii) semi-half-peak widths, defined as the differences between the peak potential and the potentials of the above points in the increasing and decreasing portions of the voltammetric peak, and, iv) the quotient r between the above two parameters, representative of the symmetry of the voltammetric peak. Values of the parameters for the lead pigments studied are summarized in Table 1.

SQWVs of lead white plus: a) casein, b) egg, c) bovine gelatin, d) sunflower oil and e) poppy oil are shown in Fig. 2. While the response of the pristine pigment consisted of a unique peak at -555 mV (Fig. 2b), the model specimens provided significantly-binder-dependent profiles. Thus, for casein, peaks appeared at -430, -535 and -615 mV, while for egg a unique peak appeared at -590 mV preceded by a weak shoulder at ca. -450 mV. For bovine gelatin, overlapping peaks appeared at -480, -550, and -620 (shoulder) mV. For oil-containing specimens, the SQWVs provided a sharp peak at -475 mV followed by a shoulder at -555 mV (poppy oil) or -665 mV (sunflower).

This voltammetry is sensitive to changes in the electrochemical parameters, in particular, to variations in the frequency, f. This can be seen in Fig. 3, where the SQWVs of lead white plus casein at are shown: a) 5, b) 20 and c) 50 Hz. On increasing frequency, the voltammetric profile tends to that displayed by the pristine pigment; consisting of a main peak at -550 mV. This is in agreement with prior cyclic voltammetric results in the AFM cell (Doménech et al., 2007), the effect of the binder is more intense at short-time experiments; i.e., at low potential scan rate CVs or low frequency SQWVs.
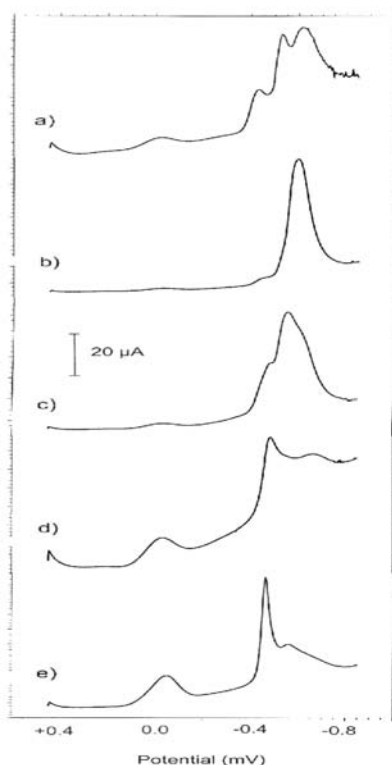

Figure 2. SQWVs for model specimens containing lead white plus: a) casein, b) egg, c) bovine gelatin, d) sunflower and e) poppy immersed in 0.50 M acetic/acetate buffer, pH 4.85. Potential step increment of 4 mV; square wave amplitude of 25 mV; frequency of 15 Hz
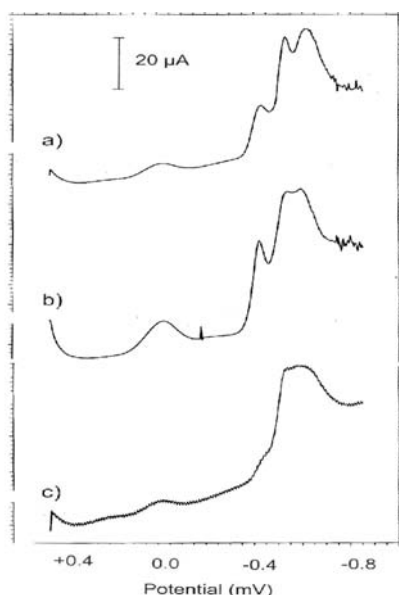
Figure 3. SQWVs of lead white plus casein specimens immersed in 0.50 M acetic/acetate buffer, pH 4.85. Frequency: a) 5, b) 20, c) 50 Hz. Potential step increment of 4 mV; square wave amplitude of 25 mV

Pigment	E_p (mV)	$W_{1/2}$ (mV)	$(\Delta E_{p/2})_1$ (mV)	$(\Delta E_{p/2})_2$ (mV)	r
Lead white	-555	180	65	115	0.56
Minium	-545	155	50	105	0.48
Naples yellow	-540	65	30	35	0.86

Table 1. Diagnostic criteria for characterizing lead pigments via voltammetry of microparticles using pristine pigment deposits on paraffin-impregnated graphite electrodes. Data from SQWVs at potential step increment of 4 mV, square wave amplitude of 25 mV, and frequency of 15 Hz. All potentials referred to a AgCl (3M NaCl)/Ag electrolyte, 0.50 M acetate buffer, pH 4.85.

System	E_p (mV)	E_p (mV)	E_p (mV)	E_p (mV)	E_p (mV)
Lead white +bovine gelatin		-35sh	-480	-520	620sh
Lead white + casein		-15sh	-430	-535	-615
Lead white + poppy oil		-45	-465	-555	
Lead white + egg		-40sh	-450sh	-590	
Lead white + sunflower		-30	-485		-665sh
Naples yellow + poppy oil	+200	-35	-465	-505	-630
Naples yellow + linseed oil			-495		
Naples yellow + sunflower		-30	-475sh	-550	-620sh
Minium + casein				-520	-695
Minium + egg				-505sh	-615
Minium + bovine gelatin				-565	-635

Table 2. Peak potential data for lead pigment plus binder specimens attached to paraffin-impregnated graphite electrodes. Data from SQWVs at a potential step increment of 4 mV, square wave amplitude of 25 mV, and frequency of 15 Hz. All potentials referred to AgCl (3M NaCl)/Ag electrolyte, 0.50 M acetate buffer, pH 4.85. sh: shoulder.

The data for the different pigments plus binding specimens are summarized in Table 2. In general, three peaks (I-III) can be discerned. Peak I appears at potentials between -400 and -500 mV, while the second peak (II) appears between -475 and -550 mV, retaining the electrochemical parameters obtained for the pristine pigments. Finally, the broad peak (III) appears at potentials between -550 and -650 mV, and frequently appears as a broad wave. Examination of these data indicates that proteinic binders produce such additional peaks while the main reduction peak becomes lightly shifted (either cathodically or anodically) along the potential axis. The effect of oil binders was more drastic: here the main peak was displaced 100-150 mV in the positive direction while a cathodic shoulder appeared at more negative potentials.

The above voltammetric responses can be rationalized by assuming that the response of the grains of the pristine pigments is superimposed to that of the ionomeric layer containing lead-binder compounds. For $PbCO_3$ this can be represented as:
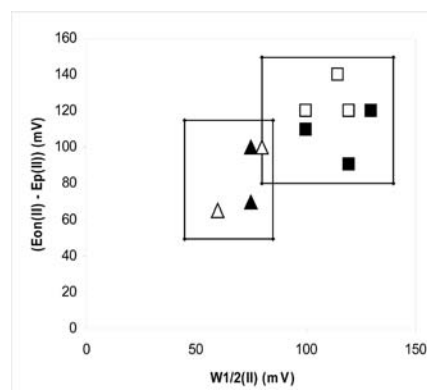

Figure 4. Plot of Eon(II) – Ep(II) vs. W1/2(II) for the different pigments plus binder samples: lead white plus proteinaceous binders (squares), minium plus proteinaceous binders (solid squares), lead white plus oils (triangles), and Naples yellow plus oils (solid triangles), from SQWV data using the same conditions as in preceding figures
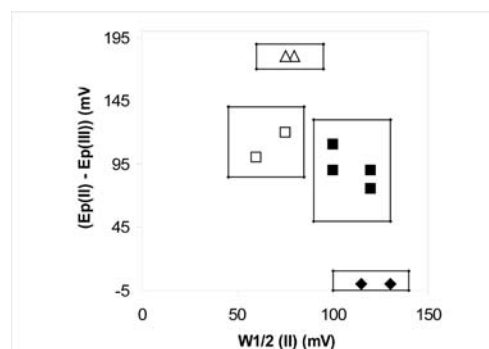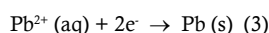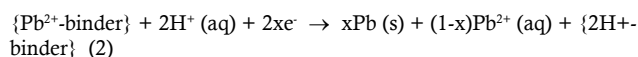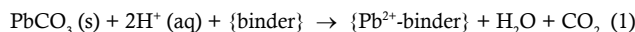

Figure 5. Plot of Ep(II) – Ep(III) vs. W1/2(II) for the different pigments plus binder samples: solid squares: casein or bovine gelatin plus lead white or minium; squares: lead white and Naples yellow plus poppy oil; triangles: sunflower plus lead white and Naples yellow; solid rhombs: egg plus lead white and minium, from SQWV data using the same conditions as in precedent figures

$$PbCO_3\ (s) + 2H^+\ (aq) + \{binder\} \rightarrow \{Pb^{2+}\text{-binder}\} + H_2O + CO_2 \quad (1)$$

$$\{Pb^{2+}\text{-binder}\} + 2H^+\ (aq) + 2xe^- \rightarrow xPb\ (s) + (1\text{-}x)Pb^{2+}\ (aq) + \{2H+\text{-binder}\} \quad (2)$$

$$Pb^{2+}\ (aq) + 2e^- \rightarrow Pb\ (s) \quad (3)$$

In these equations, {} represents species confined in the ionomeric layer surrounding the grains of pigment. In the case of proteinaceous binders, Pb^{2+} ions are probably coordinated to any extent to the donor sites of the binder, so that Eq. (3) should be replaced by:

$$Pb^{2+}\text{-}\{binder\} + 2e- \rightarrow Pb\ (s) + \{binder\} \quad (4)$$
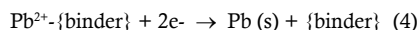
Additionally, the ionomeric layer can form a barrier for charge diffusion surrounding the particles of pigment. As a result, the rate of the overall electrochemical process described by Eqs. (1)-(3) is modified. Our data suggest that the peak at ca. -450 mV is attributable to the reduction of free (Eq. (3)) or binder-coordinated (Eq. (4)) Pb^{2+} ions, while peaks at ca. -650 mV must correspond to the reduction scheme described by Eqs. (1) and (2).

The examination of the electrochemical parameters suggests that the first peak (I) can be attributed to the reduction of free or binder-coordinated Pb^{2+} ions (Eq. (4). The second peak (II), appearing between -475 and -550 mV, can be assigned to the reduction of pristine pigment particles in direct contact with the basal electrode. Finally, the broad peak (III) appears at potentials between -550 and -650 mV, and can be assigned to the reduction of species in the ionomeric layer surrounding the pigment particles (Eqs. (1)-(3)).

Figure 4 shows a two-dimensional diagram corresponding to the plot of $E_{on}(II) – E_p(II)$ vs. $W_{1/2}(II)$ for lead white plus proteinaceous binders (squares), lead white plus oils (triangles), minium plus proteinaceous binders (solid squares) and Naples yellow plus oils (solid triangles).

In this diagram, one can see that the data points for pigment plus proteinaceous binder samples fall into a region separate from that where the data points for pigment plus oil binders are grouped.

The characterization of the binding media can be improved using plots of the potential separation between peaks II and III, $E_p(II) - E_p(III)$, vs. $W_{1/2}(II)$. As shown in Fig. 5, the data points for the two proteinaceous binders, casein and bovine gelatin, and for the different pigments (lead white, minium, Naples yellow) fall into a narrow central region of the diagram. The data points for sunflower oil, poppy oil, and egg are, in turn, grouped in other, well-separated regions of the diagram.

In these cases, the pigment identification can be obtained, as previously described (Doménech et al., 2007), by modifying the electrochemical conditions so that the signals for the pristine pigment largely prevail or by submitting the sample to mechanical abrasion to facilitate the exposure of the pigment grains to the electrolyte/electrode interphase.

In summary, the use of voltammetry of microparticles provides direct information on the pigment and binder composition of paint layers, based on the detailed examination of electrochemical parameters.

ACKNOWLEDGEMENTS

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Versión española

TITULO: *Identificación simultanea de pigmentos de plomo y aglutinantes en muestras de pintura usando la voltametría de micro-partículas*

RESUMEN: *La voltametría de micropartículas se aplica para la determinación simultánea de los pigmentos de plomo y aglutinantes en muestras de pintura. Tras la adhesión mecánica de unos microgramos de la muestra a unos electrodos de grafito impregnados de parafina, se obtuvieron respuestas voltamétricas de onda cuadrada bien definidas para muestras de modelos de pintura que contenían naranja de plomo, amarillo de plomo, blanco de plomo, litargirio, minio, amarillo de Nápoles, y el estaño-plomo Amarillo, asociados al aceite de linaza y gelatina de bovino. El uso de ajustes multiparamétricos en los datos electroquímicos permite identificar simultáneamente pigmentos de plomo y aglutinante en las muestras de pintura sintética.*

PALABRAS CLAVES: .*pigmentos de plomo, medio aglutinante, voltametría de micropartículas, conservación, pinturas*..