#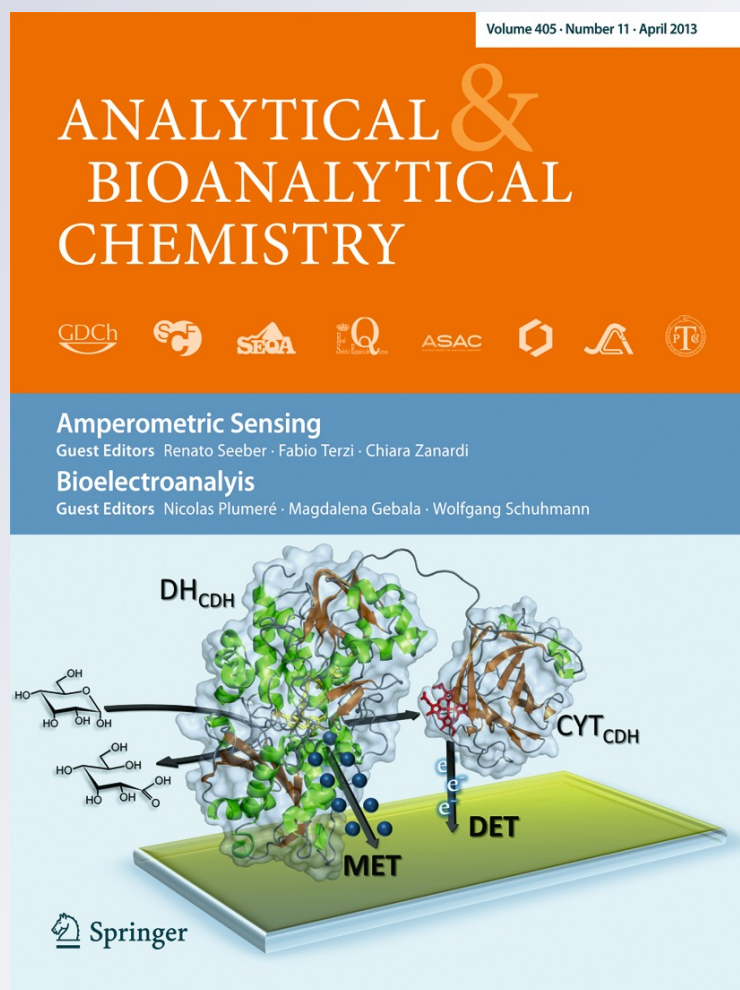 Nafion® as advanced immobilisation substrate for the voltammetric analysis of electroactive microparticles: the case of some artistic colouring agents

## Ligia Maria Moretto, Francesca Montagner, Renzo Ganzerla & Paolo Ugo

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# Nafion® as advanced immobilisation substrate for the voltammetric analysis of electroactive microparticles: the case of some artistic colouring agents

**Ligia Maria Moretto · Francesca Montagner · Renzo Ganzerla · Paolo Ugo**

**Abstract** Voltammetry of microparticles is applied to characterise and to identify solid analytes of interest in the field of cultural heritage. Nafion® is used for the immobilisation of solid microparticles onto the surface of a glassy carbon electrode by exploiting the deposition onto the electrode surface of a micro-volume of a suspension of the micro-sample in polymeric solution. Cyclic voltammetry and square wave voltammetry are applied to characterise and to identify the microparticles immobilised in the Nafion® coating. The analyte studied in this work is Prussian Blue as a typical inorganic pigment, with a relatively simple electrochemical behaviour. The proposed method is applied to a sample of Venetian marmorino plaster. The performance of Nafion® for this analysis is compared with that of the polymer Paraloid B72.

**Keywords** Voltammetry · Microparticles · Nafion® · Cultural heritage · Prussian Blue

## Introduction

The identification of the pigments used in works of art plays a fundamental role in their conservation and restoration. Nowadays, the application of chemical and physical methods of analysis is of increasing interest in the field of cultural heritage and can give the restorers information suitable to

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support scientifically the procedure used in their work. Several instrumental techniques have been used to this aim, and taking into account the uniqueness of each work of art, the techniques of choice are those that are not invasive or micro-invasive. Photographic examinations, including the use of infrared, infrared false colours and ultraviolet, are carried out routinely [1]. For museum collections and other great masterpieces, more precise analyses are often performed. X-ray transmission images provide useful information on the metals used in an artwork, such as the nails connecting the wood panels of tempera paintings. Advanced spectroscopic techniques, such as X-ray fluorescence [2–5], proton-induced X-ray emission (PIXE) [6, 7] and fibre optics reflectance spectroscopy, are used for the non-destructive identification of pigments [8]. In this field, a wide variety of analytical techniques should be used, since each one of them gives partial information to answer questions that are normally very complex.

Considering the uniqueness of a work of art and of archaeological artefacts, it is not possible to apply electrochemical techniques for analysis in solution phase, since this would require relatively high amount of the samples, as well as a treatment for the solubilisation. This drawback can be overcome by the use of voltammetry of microparticles (VMP), a methodology introduced by Scholz et al. in the late 1980s [9]. This technique is based on the principle that the electrochemistry of microparticles of electroactive solid material can be studied through their immobilisation on the electrode surface, recording the electrochemical response of the system electrode/particle/electrolyte [10]. The contact analyte/electrode can also be achieved by mixing small amounts of the solid material with graphite powder and a binder (either electrolytic or not) in the typical carbon paste electrodes [11–13] or by transferring the solid sample by abrasion to the surface of paraffin-impregnated graphite electrodes [14]; this technique is also called "abrasive stripping voltammetry". The voltammetry of

microparticles has been introduced as analytical technique for works of art during the last decade, and a comprehensive view as well as a recent review is available in the literature [15, 16].

Another alternative is based on the incorporation of the microparticles inside Paraloid B72, a co-polymer of ethyl methacrylate (70 %) and ethyl acrylate (30 %), widely applied in the restoration field, thanks to many interesting properties, such as the absence of interaction with pigments, insolubility in water and ability to form thin uniform films with a good adhesion on all kinds of substrates [17]. Domenech-Carbò and co-workers reported on the use of Paraloid B72 to immobilise electroactive analytes on solid electrodes [17, 18]. A drawback in the application of this polymer to electroanalytical methods lies in its insulating properties, as well as in the highly porous structure of the film that can lead to the release of part of the particles of the analyte.

A novel approach which, in principle, is expected to overcome the above limits, constitutes the subject of the present paper, in which an ion conductive ionomer, namely Nafion®, is used instead of an insulating polymer such as Paraloid. In this procedure, the analyte microparticles are pre-mixed with Nafion® hydro-alcoholic dispersion, and a microvolume of the mixture is applied on the electrode surface. After solvent evaporation at room temperature, the modified electrode is dipped in an electrochemical cell containing an inert supporting electrolyte solution, to record finally the voltammogram relevant to the incorporated electroactive species [19]. Nafion® is a perfluorinated ionomer that has been widely used for modifying electrodes, exploiting its ion-exchanger characteristics to preconcentrate cations, as well as to immobilise different analytes such as enzymes, electrocatalysts, electroactive pollutants, etc. [20–28].

Prussian Blue (PB) has a long story [29], and since its production by Diesbach in 1704 [30], it has been widely used as a pigment in the formulation of paints, lacquers and printing inks, due to the interesting characteristics offered by its mixed-valence (iron (III) hexacyanoferrate (II)). PB can be reduced chemically or electrochemically [31], giving a colourless compound containing only iron(II), i.e. $Fe^{II}[Fe^{II}(CN)_6]^{2-}$, that has been differently named: Berlin White (PW), Everitt's salt or Williamson's salt. On the other hand, PB can be oxidised to Prussian Yellow (PY), also named Prussian Brown, which contains only iron(III), i.e. $Fe^{III}[Fe^{III}(CN)_6]$. This redox chemistry was studied on PB films grown on the electrode surface [32–38]. It was shown that voltammetric cycling of PB in $K^+$ containing electrolyte caused the formation of the so-called soluble PB in which the oxidised and reduced forms have the following stoichiometries: $KFe^{III}[Fe^{II}(CN)_6]$ for PB and $K_2Fe^{II}[Fe^{II}(CN)_6]$ for the reduced form PW. The same electrochemical behaviour was observed using the VMP methodology [39–41].

The aim of the present research is to study the voltammetric behaviour of pigments immobilised on the electrode surface by a Nafion® film, in order to develop a simple analytical method for their identification. In particular, we have studied the voltammetric behaviour of Prussian Blue entrapped in a Nafion® film deposited onto a glassy carbon electrode in comparison with PB englobed in Paraloid B72. The application of this method for the identification of a pigment in ancient wall painting is presented.

## Experimental

### Materials and instruments

All chemicals used are of analytical grade quality. The 0.5 % w/v Nafion® solutions are prepared by 1:10 dilution with methanol of 5 % w/v Nafion® solution (Aldrich). Commercially available Paraloid B72 was used to prepare 0.5 % w/v solutions in acetone. Commercially available Prussian Blue (from Kremer Pigmente GmbH & Co. KG) was finely ground in an agate mortar.

All voltammetric measurements, by cyclic voltammetry (CV) and square wave voltammetry (SWV), carried out at room temperature (22±1 °C) under nitrogen atmosphere, were performed with a CH 1200 instrument controlled by its own software. A three-electrode cell was employed: the working electrode was a glassy carbon electrode (GCE) modified with Nafion® or Paraloid; a platinum coil was the counter electrode, and a KCl-saturated Ag/AgCl was the reference electrode.

Absorption spectra in the infrared (IR) region were collected with a Perkin Elmer Spectrum One spectrophotometer. Thirty-two signal averaged scans were acquired on the samples. Few milligrams of each sample were diluted in KBr (IR-grade, Merck) pellet of a diameter of about 13 mm.

Energy-dispersive X-ray spectroscopy (EDS) analyses were carried out using a Jeol (Tokyo, Japan) JMS 5600 LV scanning electron microscope (SEM) equipped with an Oxford Instruments 6587 EDS microanalysis detector. The analyses were performed in low vacuum conditions where samples did not show charging effects. EDS microanalysis was made to obtain information on the elemental composition of the sample.

### Electrodes preparation

Suspensions of the pigments in Nafion® or Paraloid were prepared by mixing few milligrams of pigment in 1 mL of polymer solution. Before use, the suspensions pigment/polymer were treated for 5 min in ultrasound bath. The particles of PB are non-ionic, so in both cases, Nafion® or Paraloid, the particles are just simply entrapped in the film. A homemade polytetrafluoroethylene-shrouded glassy carbon, from Tokai Carbon Japan, grade GC-20S, disk (diameter 5 mm), was initially polished to a mirror finish with graded alumina powder

(0.3 and 0.05 μm). The electrode was modified by casting a microvolume (2 μL, unless otherwise stated) of polymer/pigment suspension on its surface, allowing the solvent to evaporate slowly at room conditions, which takes around 5 min. The Nafion®-coated GCE incorporating the PB particles will be named PB-NCE from hereafter. Before the record of the voltammograms, the PB-NCE was equilibrated for 5 min in the supporting electrolyte.

PB film was prepared in fresh $K_3[Fe(CN)_6]$, $FeCl_3$ solution at pH 2 with HCl by cycling the potential between 1.2 and −0.2 V, scan rate 100 mV/s.

SEM images of the samples indicated that the size of the PB particles is <100 nm; when these particles were immobilised on the electrode surface inside the Nafion® film, agglomerates of particles of the order of 300–500 nm were formed.

### Plaster marmorino sample

Marmorino is a well-known classic Venetian plaster. The sample here analysed was gained in the painted decoration of the Palace Michiel Delle Colonne, Venice (Italy), built in the fifteenth century. Before the analysis, 3 mg of the sample were treated with HCl in order to eliminate carbonate. Afterwards, a suspension of 2 mg of the sample in 1 mL of Nafion® 0.05 % was prepared, and an aliquot of 3 μL was deposited onto the GCE surface.

### Results and discussion

#### Electrochemistry of Prussian Blue at Nafion®-modified electrodes

Figure 1a presents the cyclic voltammogram recorded at a PB-NCE in 0.1 M $KNO_3$ electrolyte solution. Two couples of voltammetric peaks, AA' and CC' in Fig. 1, with $E_{1/2}$ values of 0.200 and 0.860 V, respectively, are detected. The shape of this CV shows features which compare with those observed at GCE modified by direct deposition of a PB film (see Fig. 1b) as described in the "Experimental" section. The CV characteristics of PB film have been already studied [31–34]. By this comparison, the peak systems can be ascribed to the reversible redox reactions 1 (AA' system) and 2 (CC' system) [42, 43].
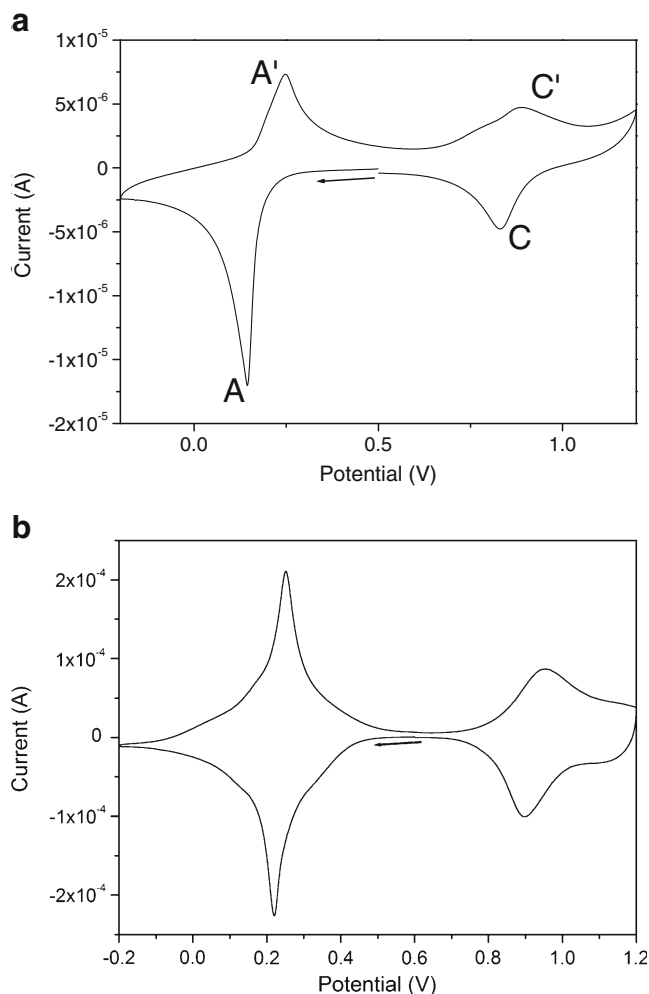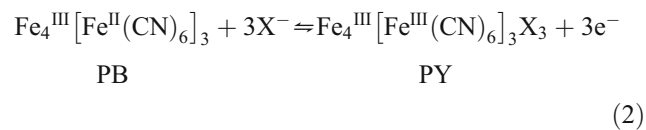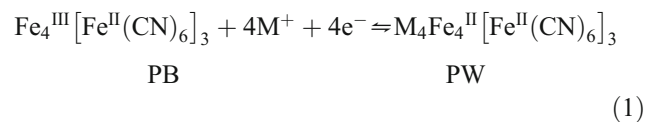
$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4M^+ + 4e^- \rightleftharpoons M_4Fe_4^{II}[Fe^{II}(CN)_6]_3$$

$$\quad PB \qquad\qquad\qquad\qquad PW$$

$$(1)$$

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 3X^- \rightleftharpoons Fe_4^{III}[Fe^{III}(CN)_6]_3X_3 + 3e^-$$

$$\quad PB \qquad\qquad\qquad\qquad PY$$

$$(2)$$



**Fig. 1** **a** CV recorded at a GCE modified with 2 μL of 1.6 mg/mL PB in Nafion® 0.5 %. Supporting electrolyte 0.1 M $KNO_3$, scan rate 50 mV/s. The scan started from 0.5 V in cathodic direction; **b** CV recorded at a GCE modified with PB film. Supporting electrolyte 0.1 M $KNO_3$, scan rate 20 mV/s. Other conditions as above

where $M^+$ and $X^-$ are the supporting electrolyte cation and anion, respectively.

The evidence that at PB-film the peak systems AA' and CC' are shifted at slightly more positive values (0.230 and 0.930 V, respectively) seems to be related to the presence of the Nafion® coating for the PB-NCE. It was indeed demonstrated that [44–47], for redox processes taking place within permselective coatings such as Nafion®, the requirement of uptake of, e.g. cations as a consequence of the redox process (see, for instance, reaction 1) reflects in a shift in the apparent $E_{1/2}$ values, in agreement with what was observed experimentally here.

The voltammetric pattern recorded with the PB-NCE equilibrated in $NaNO_3$ electrolyte is quite different. The CV in Fig. 2 shows that, in the presence of sodium ions, peak A is broader and the relevant peak currents are lower
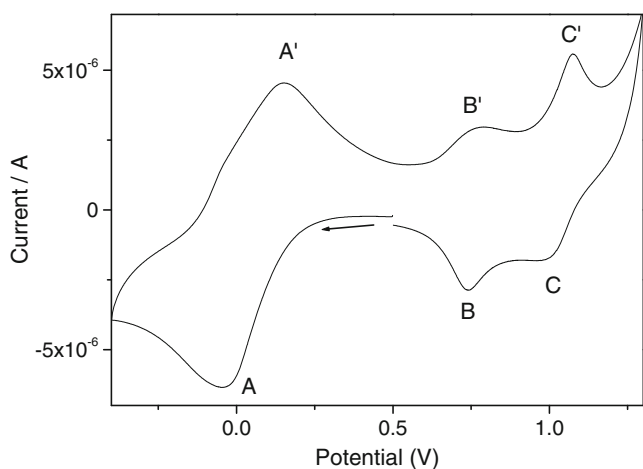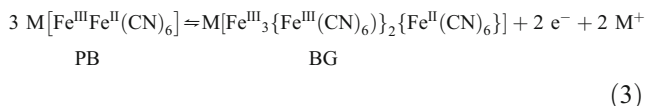
**Fig. 2** CV recorded at a GCE modified with 2 μL of 1.6 mg/mL PB in Nafion® 0.5 %. Supporting electrolyte 0.1 M NaNO$_3$, scan rate 20 mV/s

with respect to the ones recorded in potassium ion solution. Note that the same amount of PB was loaded in the PB-NCE in both cases. Moreover, a new peak system, BB' ($E_{1/2}$ 0.780 V), is now observed. On the basis of previous literature reports [33], this redox system can be correlated to reaction 3.

$$3\,M[Fe^{III}Fe^{II}(CN)_6] \rightleftharpoons M[Fe^{III}_3\{Fe^{III}(CN)_6\}_2\{Fe^{II}(CN)_6\}] + 2\,e^- + 2\,M^+$$

    PB                                    BG

$$\tag{3}$$

The mixed-valence form, named Berlin Green (BG), is an intermediate of the oxidation of PB to PY [42, 48]. In the bulk form, BG is believed to possess the fixed composition presented above; for thin films, there is a continuous composition range between PB and PY, shifting progressively to golden yellow colour in the fully oxidised form [49]. In a recent study, Pajerowski et al. [36] proposed a chemical formula such as $Fe^{III}_4[Fe^{III}(CN)_6]_{1.9}[Fe^{II}(CN)_6]_{1.5}3.6H_2O$ for BG. Our results indicate that BG is stabilised by Na$^+$ cation with respect to K$^+$ and that Na$^+$ is probably the counter-ion M$^+$ neutralising the negative charge of the anion generated by reaction 3.

As shown by reaction 1, the PB reduction process requires a concomitant cation ingress/egress, in order to achieve electroneutrality [37]. The evidence that the current of peak A in the presence of Na$^+$ (Fig. 2) is smaller than in the presence of K$^+$ (Fig. 1a) suggests that diffusion of Na$^+$ in Nafion® can be slower than diffusion of K$^+$. Moreover, to explain the difference in the features of the two voltammograms, one must take into account the fact that, upon reduction, the counter ion must enter also within the PB crystal

structure. In comparison to potassium, the penetration of the larger hydrated sodium cation into the PB lattice is expected to be more difficult [37, 38]. Feldman et al. [43] studied the electron diffusion coefficient ($D_e$) in mixed-valence PB films in various electrolytes and observed a noticeable difference in dependence of the presence of Na$^+$ or of K$^+$ in the supporting electrolyte. Indeed, $D_e$ for Na$^+$ and K$^+$ are equal to $0.80 \times 10^{-9}$ and $3.9 \times 10^{-9}$ cm$^2$/s, respectively [43].

The anion of the supporting electrolyte also plays a role in defining the oxidation of PB (see Eq. 2). As an example, comparing the voltammograms in the presence of chloride and nitrate as anions of the supporting electrolyte, we observed that, in the presence of sodium or potassium, the chloride leads to higher anodic currents. However, in NaCl solution, the oxidation peaks are very broad (CV curves not shown). These behaviours suggest that, in the presence of potassium, BG does not form, since the oxidation of PB gives directly the completely oxidised form of PY. The peak currents are higher in potassium chloride than in potassium nitrate solution while, in the presence of sodium only with nitrate as the electrolyte anion, it is possible to observe better resolved peaks.

The effect of the potential scan rate ($v$) on the cyclic voltammogram patterns was investigated. Figure 3 shows cyclic voltammograms recorded in the same experimental conditions as those in Fig. 2a but at scan rates varying from 5 to 500 mV/s. The plots of the peak current of the peaks A and A' as a function of $v$ are linear at low scan rate (up to 50 mV/s) and become linear with the square root of the scan rate for higher $v$ values. Such a behaviour indicates that, at low scan rates, thin layer like conditions hold, while, for
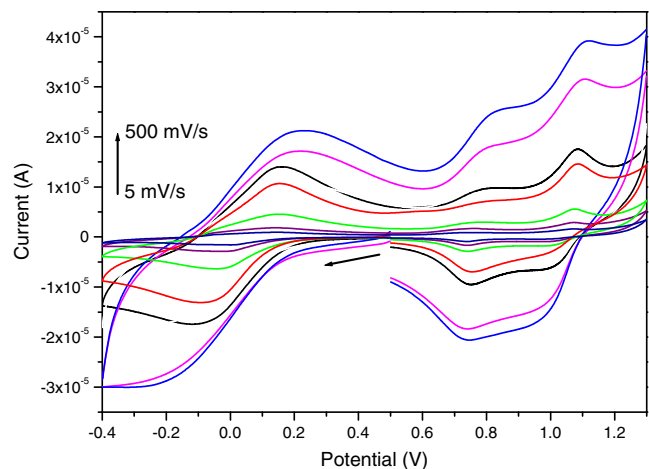


**Fig. 3** CVs recorded at a GCE modified with 2 μL of 1.6 mg/mL PB in Nafion® 0.5 %. Supporting electrolyte 0.1 M NaNO$_3$ at scan rates from 5 to 500 mV/s. Other experimental conditions as in Fig. 2

higher scan rates, a diffusion-controlled voltammograms are recorded [20].

In order to define the best amount of PB microparticles to deposit onto the electrode, suspensions of PB in Nafion® with 1.6, 3.6 and 12.8 mg/mL were prepared. Afterwards, 3 µL of each suspension were deposited on the electrode, and the relative CVs were recorded; such voltammograms (not shown) indicate that the increase of the suspension concentration leads to less defined and broader peaks. Therefore, the study was carried out with PB/Nafion® suspensions of 1.6 mg/mL.

The volume of PB/Nafion® dispersion deposited on the electrode surface was optimised recording cyclic voltammograms at GCEs with different volumes of the suspension deposited by drop casting. Figure 4 shows the CVs recorded at electrodes modified with 2, 3, 8 and 12 µL of 1.6 mg/mL PB in Nafion® 0.5 %. The application of 2 or 3 µL of the suspension corresponds to the best compromise to obtain a cyclic voltammogram with all the peaks well separated and characterised by high enough currents. In these conditions, the amount of sample deposited on the electrode surface is in the order of 1.2–1.6 µg.

In order to improve the signal/noise ratio and to obtain better resolved peaks, the use of pulsed techniques was studied. Figure 5 presents the SWV curves recorded at a PB/NCE in (a) $KNO_3$ and (b) $NaNO_3$ solution. In $NaNO_3$ solution, the voltammogram is characterised by a peak at around 0.05 V and a peak at around 1.04 V, with a shoulder around 0.8 V; when potassium is used as the counter ion (Fig. 5a), only two peaks are present, in agreement with the
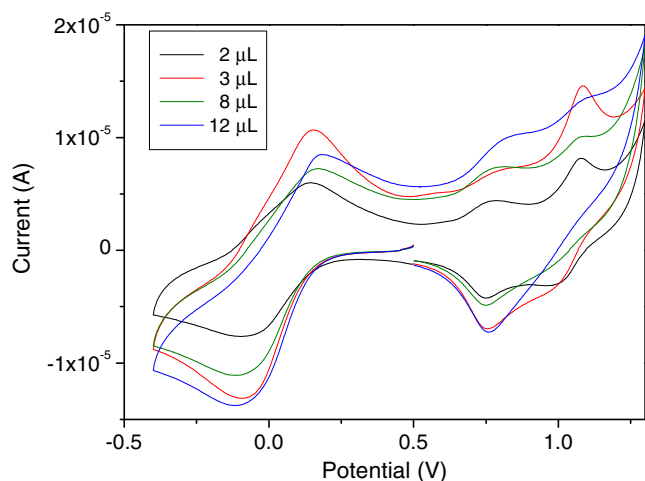


**Fig. 5** SWVs recorded at a GCE modified with 3 µL of 1.6 mg/mL PB in Nafion® 0.5 %. Supporting electrolyte: **a** 0.1 M $KNO_3$, and **b** 0.1 M $NaNO_3$. Instrumental parameters: frequency 15 Hz and pulse height 25 mV

cyclic voltammetric results. As expected, SWV peaks are better resolved with respect to the background current.

Comparison with Paraloid modified electrodes

The cyclic voltammogram of PB immobilised at GCE with a film of Paraloid, in $NaNO_3$ solution, is shown in Fig. 6a. The pattern of the cyclic voltammogram is similar to that observed at Nafion®-modified electrode; however, the peaks are less resolved and the peak current intensities are lower. The comparison of the curves of PB immobilised at Nafion® (Fig. 6b, full line) and Paraloid (Fig. 6b, dashed line) on GCEs indicates that the peak current observed at Nafion® electrode is almost one order of magnitude higher. Also applying pulsed techniques, the immobilisation of PB with Nafion® leads to voltammograms with higher currents



**Fig. 4** CVs recorded at a GCE modified with different volumes of 1.6 mg/mL PB in Nafion® 0.5 %. Supporting electrolyte 0.1 M $NaNO_3$, scan rate 50 mV/s
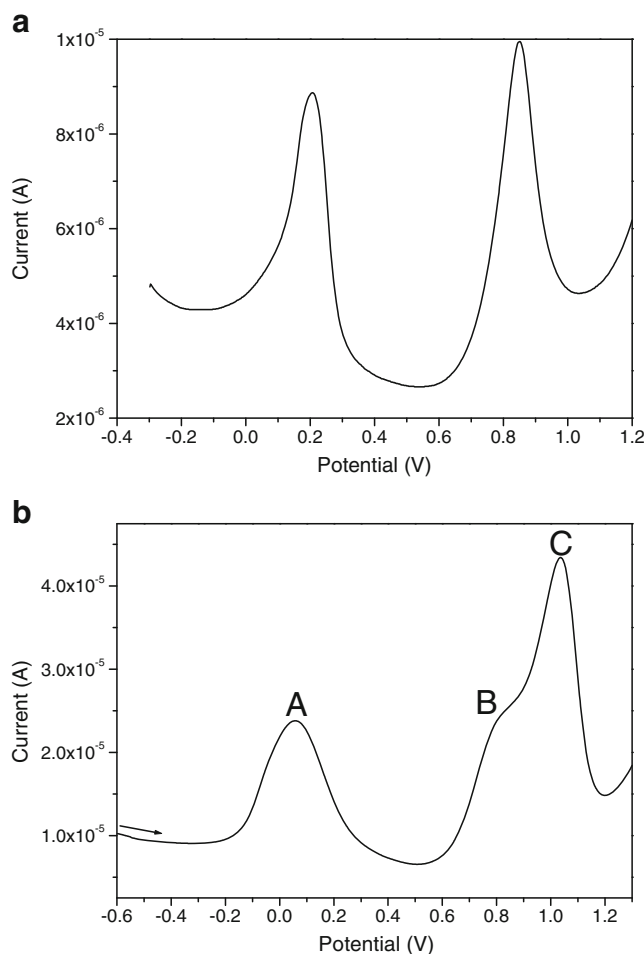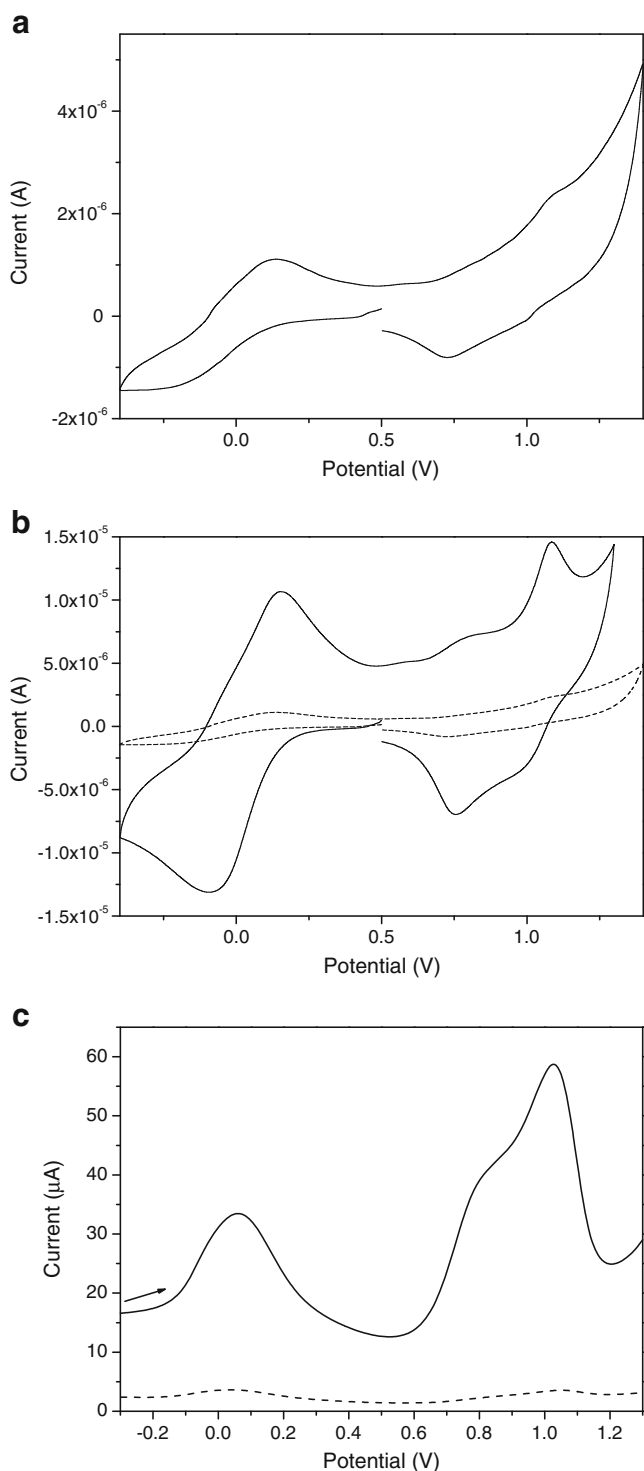
**a**



**b**



**c**



Fig. 6 **a** Cyclic voltammogram recorded at GCE modified with 3 μL of 1.6 mg/mL PB in Paraloid B72; **b** same voltammogram of (**a**) (*dotted line*) and GCE modified with 3 μL of 1.6 mg/mL PB in Nafion® (*full line*), supporting electrolyte 0.1 M NaNO$_3$, scan rate 50 mV/s; **c** SWV recorded at a GCE with PB immobilised with Paraloid and Nafion® films as in (**b**); supporting electrolyte 0.1 M NaNO$_3$, frequency 50 Hz, pulse height 50 mV

and better resolved peaks than with Paraloid, as shown in Fig. 6c. This behaviour could be ascribed to some of the characteristics of Polaroid and Nafion®. Paraloid presents low electrical conductivity and a very porous structure of the film [17], while Nafion® solutions deposited on the electrode surface form very thin and homogeneous films covering all the electrode surface, and due to its ionic character, Nafion® presents good electrical, namely ionic, conductivity [50]. The ionic conductivity of the film, in particular of cations, since Nafion® is a cation exchanger, is responsible for the easy flow of ions inside the film. As shown in Eqs. 1–3, the flow of ions plays an important role in the oxidation and reduction processes of PB because they are necessary to maintain electroneutrality.

Application to real samples: PB in Venetian marmorino plaster

During the work of restoration of the Palace Michiel Delle Colonne, from the fifteenth century, in the Canal Grande of Venice (Italy), some blue wall paintings were found. These samples were analysed in order to identify the nature of the pigments used. The Fourier-transform infrared (FTIR) spectrum (see Fig. 7a) of the blue samples of this plaster suggested the presence of two blue pigments: ultramarine blue (peaks at 669 and 1,014 cm$^{-1}$, ascribable to Si-O stretching) and Prussian Blue, with a characteristic peak at 2,093 cm$^{-1}$, due to C≡N stretching. This result was unexpected, since no record is found about repairs in this wall painting after the eighteenth century, when Prussian Blue was first synthesised. EDS analysis of the sample before the acid treatment (Fig. 7b, dotted line) indicates the presence of Fe ascribed to PB, as well as of residues of C and Ca from the carbonate; after HCl treatment, practically all the carbonate residue was eliminated (Fig. 7b, full line), while Fe was still detected.

These samples were analysed to verify the applicability of the proposed electroanalytical approach. Considering the possible presence of two blue pigments, PB and ultramarine blue, it is worthy to note that, among these two pigments, only PB is electroactive. Figure 8 shows the cyclic (a) and the SW (b) voltammograms recorded in 0.1 M KCl solution at a GCE modified with a suspension in Nafion® of the sample treated as described in the "Experimental" section. These voltammograms are characterised by two redox systems with $E_{1/2}$ values around 0.15 and 0.75 V, respectively, in agreement with those recorded with pure Prussian Blue in the same experimental conditions (see Fig. 1). Other cations
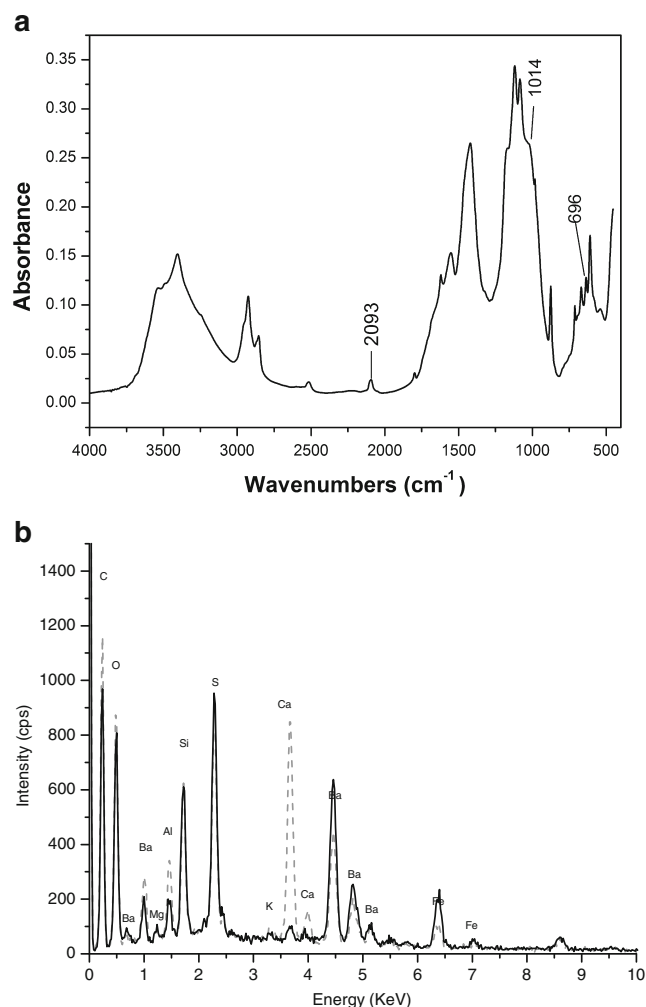
Fig. 7 **a** FTIR spectrum of the marmorino sample; **b** EDS analysis of the marmorino sample before (*dotted line*) and after (*full line*) HCl treatment



Fig. 8 **a** CV recorded at a GCE modified with 3 μL of a 3 mg/mL of marmorino in Nafion® 0.5 %, in 0.1 M KCl, scan rate 50 mV/s; **b** SWV at the same electrode as (**a**), frequency 25 Hz, pulse height 50 mV

besides potassium from the supporting electrolyte, in particular, sodium from the original sample, can be present, introducing some modification of the oxidation peaks of PB. Differences are observed in the shape of the peaks and their potentials. According to Garcia et al. [50], it was observed that the degree of hydration as well as of crystallisation can be responsible for this behaviour. Old samples, such as those here analysed, can present modification in the crystalline structure that are responsible for the shift in potential. This behaviour could be a negative point with respect to the electroanalytical approach to the analysis of archaeological samples. However, it is known that archaeometric studies normally require the combination of different analytical techniques, each one useful to answer some questions and/or confirm different hypotheses [16].
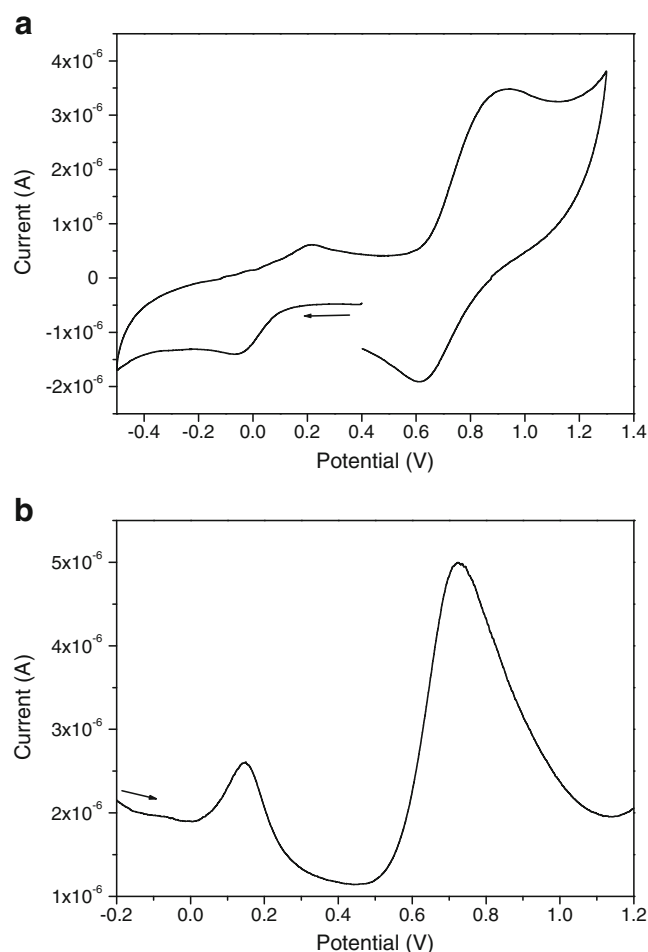
## Conclusions

This study points out the good performances of Nafion® film to immobilise electroactive microparticles on electrode surfaces. Studying the case of PB as the analyte of interest, the possibility to follow its reduction to PW and oxidation to PY, through an intermediate species BG in the presence of sodium as the cation of the supporting electrolyte, was evidenced.

The proposed procedure requires a very small amount of the sample (in the order of few micrograms), resulting to great interest in the field of cultural heritage. In view of applications in the field, the methods have been tested on real samples, namely, a marmorino plaster.

The electroanalytical method developed can compete with procedures that require longer execution times, larger samples

and much more expensive instrumentation. Indeed, it is known that the use of portable electrochemical instrumentation commercially available can constitute a remarkable added value to this kind of analytical technique. Preliminary experiments performed on other artistic materials such as malachite and grisailles gave very promising results. Further studies are in progress in our laboratory, and finding a suitable quantification procedure will constitute the next step along this line of research.

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