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Ion-exchange and permselectivity properties of poly(sodium 4-styrenesulfonate) coatings on glassy carbon: application in the modification of mercury film electrodes for the direct voltammetric analysis of trace metals in estuarine waters

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Abstract

The present work describes the optimisation and characterization of poly(sodium 4-styrenesulfonate)-coated thin mercury film electrodes (PSS-TMFE) for the direct analysis of trace metals in estuarine waters by square-wave anodic stripping voltammetry (SW-ASV). The morphology, thickness and ion exchange ability of the poly(sodium 4-styrenesulfonate) coatings onto glassy carbon were evaluated and these features particularly favoured the incorporation of cationic species, such as dopamine or lead cation. For the case of the heavy metal cations, a simple, sensitive and very reproducible methodology for their SW-ASV analysis could be developed. In fact, with the PSS-TMFE, a significant increase in the sensitivity of the ASV determination of lead was obtained compared both to the uncoated TMFE (ca. 82%) as well as to Nafion-coated electrodes of similar thickness (ca. 43–49%). Furthermore, the permselectivity of the poly(sodium 4-styrenesulfonate) coatings, based both on electrostatic interaction and molecular size, leads to an improved anti-fouling ability against surfactant species. The analytical usefulness of the poly(sodium 4-styrenesulfonate)-coated thin mercury film electrodes is demonstrated by application to the direct ASV determination of trace heavy metals at the low nanomolar level, in estuarine waters with moderate contents of dissolved organic matter, where the uncoated TMFE failed due to fouling.

Keywords: Poly(sodium 4-styrenesulfonate); Ion-exchange; Mercury film electrode; Anodic stripping voltammetry; Lead; Copper; Cadmium

1. Introduction

For over the last three decades, the development of chemically modified electrodes (CMEs) has been a continuously growing scientific area of renewed interest in diverse fields such as analytical chemistry and sensors, electrocatalysis and energy conversion [1–7]. Regarding the applications of CMEs in the voltammetric analysis of trace species, special attention has been paid to the improvement of both sensitivity and selectivity, especially for determinations in complex media, such as natural/industrial waters.

In natural or industrial waters containing significantly high concentrations of natural/anthropogenic organic matter or inorganic colloids, the anodic stripping voltammetric (ASV) analytical signals of trace metals at conventional mercury electrodes are often altered or even suppressed due to the adsorption of those surface active compounds onto the electrode [8,9]. Fouling of the electrode surface can occur also for electrodes other than mercury (i.e., glassy carbon (GC) and graphite) in other complex media such as biological samples where proteins are usually present and thus they become a problem. The most promising procedure to minimize the electrode fouling by surfactants is to prevent the diffusion of the interfering species by coating the electrode surface with a thin layer of a semi-permeable material. The

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purpose is to preclude the income of the interfering species towards the electrode surface, either by size exclusion and/or by electrostatic exclusion. Several different approaches have been studied and applied: covering the electrode with a dialysis membrane [10,11] or cellulosic coatings [12,13] retains colloidal material (usually with molecular weights higher than 1000) but the diffusion of small molecules/ions is frequently hindered, limiting the sensitivity of the voltammetric determinations. On the other hand, coating the electrode surface with ion exchange polymers is widespread: Nafion, the most widely employed cation-exchange polymer [9,14–21], poly(ester sulfonic acid) [22–24], poly(ethyl 3-thiopheneacetate) [16,21], poly(4-vinylpyridine) [25,26] or overoxidised poly(pirrole) [27] are examples of such modifiers. In these cases, the target analyte diffuses selectively throughout the electrode surface by an ionic exchange mechanism. However, the anti-fouling properties of these systems are not completely satisfactory and the preparation procedures often show lack of reproducibility [11,21]. Recently, poly(sodium 4-styrenesulfonate), PSS, was used for coating a thin mercury film electrode, TMFE, and applied to the ASV determination of lead and copper in estuarine water with very low organic matter content [28]. Stable PSS-coated electrodes could be prepared by a very reproducible and easy procedure and presented increased sensitivity to lead and copper cations. Besides, the mechanical stability of the mercury film was improved. The PSS coating prevented to some degree electrode fouling by non-ionic surfactants, e.g., Triton X-100 and agar, and also partially excluded the relatively small surface-active species sodium dodecyl sulfate. Apart from that study, only a brief mention to the use of the acidic form of PSS, poly(styrene sulfonic acid), mixed with Nafion for coating mercury film electrodes has been reported but the coating stability was very low due to the dissolution of poly(styrene sulfonic acid) in water-based electrolytes [20]. No further applications or characterization studies of PSS-coated mercury film electrodes have ever been presented.

On the other hand, PSS coatings on glassy carbon have been prepared by spin-coating of polystyrene and subsequent chemical sulfonation [29]. Also, cross-linked PSS-modified platinum and graphite electrodes were prepared by electropolymerization followed by chemical sulfonation [30]. For both procedures, the resulting electrodes were stable in water but the preparation procedures were intrinsically sluggish and no reproducibility data or permselectivity studies were presented. Modification of platinum electrodes with PSS [31], chlorosulfonated PSS [32] and organosilane–PSS copolymer [33] was applied in experiments in acetonitrile media.

Further, water-insoluble PSS-containing membranes have been applied in electrode modification for the production of amperometric biosensors for glucose, glutamate, H_2O_2 and L-lactic acid [34–38], and for the production of *layer-by-layer* assemblies [39–43]. However, no full characterization of PSS-modified glassy carbon electrodes (GCEs) has yet been reported, namely regarding its permselectivity, ion-exchange and morphological properties.

In the present work, a comprehensive characterization of the PSS coatings on glassy carbon and a detailed analysis of the performance of PSS-coated thin mercury film electrodes, PSS-TMFEs, are performed. Hence, the effects of some experimental parameters, namely the mercury concentration and the PSS loading, are evaluated. The morphology, the cation exchange ability and the permselectivity properties of the PSS coating are also assessed. The PSS-coated mercury film electrodes were successfully applied to the direct determination of dissolved heavy metals in estuarine water samples contaminated with moderate levels of dissolved organic matter. Filtration of the water samples was the only pre-treatment required in accordance to usual procedures for the determination of dissolved metal ions. Furthermore, the present methodology was checked using a certified seawater sample (NASS-5).

2. Experimental

2.1. Instrumentation

All voltammetric measurements were performed with a BAS 100B/W electrochemical analyser (Bioanalytical Systems, West Lafayette, IN, USA) connected to a Cell Stand BAS-C2. The working electrode was a TMFE plated onto a glassy carbon disc, GCE_1 (BAS, MF-2012); the auxiliary electrode was a Pt wire and the reference electrode was Ag/AgCl (saturated KCl). In some studies, three different glassy carbon electrodes were used: GCE_1 and GCE_2 from BAS and GCE_3 from Metrohm. A combined glass electrode (Orion 9104SC) connected to a pH meter (Cole Parmer, Model 05669-20) was used for pH measurements. The microscopic examinations were carried out with an optical microscope (Jenaphot 2000, Zeiss Germany) connected to a video camera (JVC, FK-1085E). Scanning electronic microscopy (SEM) was conducted at a S-4100 HITACHI system.

2.2. Reagents and solutions

Poly(sodium 4-styrenesulfonate), PSS (molecular weight, 70,000, and degree of sulfonation 1.0) and Nafion perfluorinated ion-exchange resin, NA (NA 115, 5 wt.% solution in a mixture of lower aliphatic alcohols and water) were purchased from Sigma–Aldrich and used without further purification. All chemicals were of analytical reagent grade and all solutions were prepared with ultra-pure water (18.2 MΩ cm, Milli-Q systems, Millipore-waters). Sodium chloride (Merck, suprapur), hydrochloric acid, 37% (Fluka, trace select) and 1000 ppm AA-Spectrosol metal ion standards (BDH) were also used. Stock solutions of PSS (25, 50, 75 and 100 mM in monomeric units) prepared in phosphate buffer (0.04 mol dm^{-3} Na_2HPO_4/0.026 mol dm^{-3} KH_2PO_4; pH 7.0, ionic strength 0.15 M) and of Nafion (25 and 11.3 mM

Table 1
Chemical structures of the polyelectrolytes used for coating

Polystyrene sulfonate (PSS)	Nafion (NA)
Monomer mass[a]: 206.196	Monomer mass[b]: 1100

[a] Equivalent weight (g), calculated for the PSS–Na^+ form.
[b] Equivalent weight (g) for the acidic form of NA 115, based on [50] and on the Handbook of fine chemicals and laboratory equipment, Sigma–Aldrich, 2003–2004.

in monomeric units prepared in methanol) were stored at 4 °C. Potassium ferrocyanide, dopamine and L(+)-ascorbic acid solutions (1 mM) were prepared in phosphate buffer. Aqueous stock surfactant solutions, all 0.1% (v/v) (hyamine, HYA, poly(allylaminehydrochloride), PAAHC, and bovine serum albumin, BSA), were also stored at 4 °C.

Schematic representations of the two polymers used for electrode modification are displayed in Table 1. PSS ($pK_a = 1$) [44] is the sulfonate salt of the well-known polystryrene [45]. It is a water soluble, thermally stable polyelectrolyte (decomposition temperature 460 °C [46]), having both hydrophilic parts (sulfonate groups and their counterions) and hydrophobic parts (hydrocarbon backbone and phenyl groups). In aqueous solution, PSS is a linear polyanion [47,48], but in solutions where a simple electrolyte is added (e.g., NaCl), a coiled conformation is observed due to shielding of the polyelectrolyte charges [47]. The same effect has been noticed for electrostatically adsorbed PSS, where highly coiled and thick PSS layers were obtained whenever the deposition proceeds from solutions of high ionic strength, e.g., 0.1–2 M [42,43]. Nafion is a high molecular weight perfluorinated sulfonic acid containing also negatively charged sulfonate groups but these are assembled in hydrophilic clusters surrounded by regions of hydrophobic nature, i.e., the fluorocarbon backbone [18,21,49,50]. This structural conformation contributes to the rigidity and insolubility of Nafion [45]. The ion-exchange capacity of Nafion is about four times smaller than that for other typical sulfonate resins [18].

Polyelectrolyte coatings for modification of glassy carbon electrodes are usually recast from solution by using the drop evaporation method [15,17,28,51,52] or spin coating procedures [53]. The most frequently used value for the recast density of Nafion is 1.98 g cm^{-3} [15,17,21] whilst for PSS, no reference value was found in the literature. Therefore, the value of 0.801 g cm^{-3} available from specifications for the commercial PSS product [46] has been used in the present work. Nevertheless, the actual density of the recast polymers may be lower than the above-mentioned values because their swollen state shall contain more water/electrolyte than the original products [21,52]. This limits the accuracy of the calculation of the thickness of the recast polymer layers.

2.3. Electrode preparation

Prior to coating, the glassy carbon electrode was conditioned following a reported polishing/cleaning procedure in order to obtain a smooth mirror finished, and activated GC surface [28]. The coatings were obtained by the droplet evaporation method [28] placing 3–9 μL of PSS or 6 μL of Nafion solutions on the electrode surface. Otherwise stated, thin mercury films were ex situ plated from a 0.12 mM Hg(II)/0.01 M nitric acid solution by electrodeposition through the polymer coating at −1.3 V for 20 s whilst rotating the solution with a magnetic stirrer (BAS-C2 stand, position 3). The conventional mercury film electrode was obtained in a similar fashion except for the polymer-coating step. The PSS-coated electrodes were ready to use—no pre-conditioning in any electrolyte was necessary. When required, the utilized polymer layer was wiped off with a wet tissue and the GC surface was re-conditioned as mentioned above.

The surface area of the glassy carbon electrodes was measured by chronoamperometry (in 1.02×10^{-3} M ferricyanide/0.5 M KCl solution; diffusion coefficient of ferricyanide 0.763×10^{-5} cm^2 s^{-1} [54]). Four polishing experiments, each one with four replicate determinations, were done. The electrochemically active area was (mm^2): 6.42 ± 0.05 for GCE_1, 7.33 ± 0.04 for GCE_2 and 3.06 ± 0.09 for GCE_3.

2.4. Voltammetric procedures

The ASV experiments for the examination of the analytical performance of the PSS-TMFE were carried out in 10 mL NaCl 0.5 M solutions spiked with lead(II) as a reference metal ion (6.00×10^{-8} M). The deposition step lasted 20 s at −0.8 V, whilst the solution was rotated with a magnetic stirrer (BAS-C2, position 3). After a 5 s quiescent time, the stripping step was initiated at −0.8 V and ended at −0.15 V to prevent the stripping of the mercury film. The instrumental parameters used in the ASV-SW experiments were: frequency 50 Hz, amplitude 25 mV and step potential 5 mV.

For the measurement of the charge under the voltammetric stripping peak of Hg, a linear scan of 0.25 V s^{-1} was applied. That charge is an estimate of the amount of deposited mercury on the GC electrode and is calculated by electronic integration of the linear scan mercury peak [55].

For the ASV determination of heavy metals in natural waters, 10 mL of a filtered sample (0.45 μm membrane filter, Millipore) of estuarine waters (samples A and B) or 10 mL of the unfiltered certified sea water, NASS-5 (National Research Council, Canada), was pipetted into the voltammetric cell. The ASV-SW measurements were carried out promptly with an accumulation step of 3 min at −0.8 V, with a rotation rate corresponding to BAS-C2 position 3. The SW pa-

rameters were the same as described above. Both the TMFE and the PSS-coated TMFE (loading 4.8 μg mm^{-2}) were used as working electrodes. The quantification of trace metals was done by the standard addition method. All peak currents quoted are mean values of five replicate measurements. The estuarine waters had salinities (‰) of 17.3 and 7.3, respectively, for samples A and B, and moderate dissolved organic matter contents (corresponding DOC values of 4 and 10 ppm).

All peak currents and charges quoted are mean values of six replicate measurements. Solutions were purged with pure nitrogen for 5 min prior to analysis. Measurements were carried out at room temperature (18–20 °C).

3. Results and discussion

A previous work [28] has shown that a thin mercury film could be plated on a GC electrode coated with a layer of the cation-exchange polymer PSS. Fig. 1 presents an optical micrograph of a PSS-coated TMFE produced under the proposed conditions (PSS loading 4.8 μg mm^{-2} and q_{Hg} 7.36 μC mm^{-2} [28]). Small mercury droplets were formed onto the GC surface, beneath the PSS film, which looks as a rather open and transparent structure. In order to obtain further information on the characteristics of the mercury film produced at PSS-coated glassy carbon electrodes, the effects of both the mercury concentration in the plating solution and of the PSS loading were evaluated. Besides, electronic microscopy was also used to gain a better insight on the morphological characteristics of the PSS polymer layers.

3.1. Effect of the mercury concentration on the mercury film characteristics at the PSS-coated GCE

The effect of the mercury concentration in the plating solution on the mercury film characteristics was assessed by using both the voltammetric charge corresponding to the amount of plated mercury, Q_{Hg}, and the ASV peak current for lead, $I_{p(Pb)}$. For both the uncoated TMFE and the PSS-TMFE (PSS loading 4.8 μg mm^{-2}), Q_{Hg} increased linearly with the mercury concentration (within 0.05–0.15 mM) with a slope 0.26 C mol^{-1} dm^3 (r = 0.9962, P < 0.05, N = 5) and 0.35 C mol^{-1} dm^3 (r = 0.9988, P < 0.05, N = 5) for the TMFE and the PSS-TMFE, respectively. These results indicate that the mercury deposition through the PSS polymer layer proceeds by a mechanism similar to the one observed for the common deposition process on a bare glassy carbon surface [55,56]. However, the mercury deposition on the PSS-coated electrode is enhanced: in fact, the slope of the plot Q_{Hg} versus [Hg] increased by 35% compared with that for the bare glassy carbon. Also, more reproducible mercury deposits are produced on the PSS-coated electrode: the R.S.D. values decreased from 5.2–6.7% for the uncoated TMFE to 2.4–3.2% for the PSS-TMFE. These results validate the observations previously reported for identical electrodes where the ASV signals of lead were used as the test parameter for reproducibility and sensitivity [28].

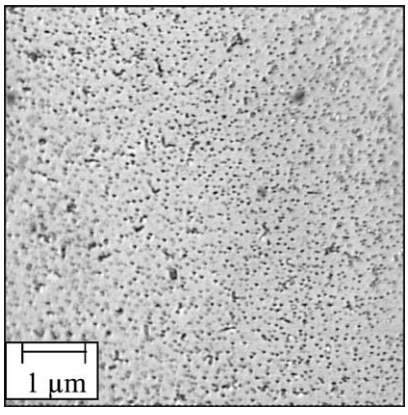

Fig. 1. Optical micrograph (×500) of a thin mercury film (q_{Hg} 7.36 μC mm^{-2}) plated on a GC electrode coated with PSS (loading 4.8 μg mm^{-2}).

Regarding the ASV signals of lead, the $I_{p(Pb)}$ values increased with the mercury concentration, but for [Hg(II)] higher than 0.12 mM, there was no further improvement. Therefore, in terms of the ASV response, there is no advantage in using plating solutions with mercury concentrations higher than 0.12 mM.

Considering the present results, the optimal value for the mercury concentration was set at 0.12 mM. The plating potential was kept at −1.3 V based on a previous study [55]. Under these conditions, the mercury charge density was ca. 7 μC mm^{-2}.

3.2. Effect of the PSS loading

The actual polymer loading used is an important experimental parameter because it affects both the morphology and the compactness of the coating, which, in turn, influence its permselectivity and mass transportation properties. The PSS loading was changed in three different ways, by varying the droplet volume, the number of consecutive drop evaporation steps or the concentration of the PSS polymer solution.

Fig. 2(A and B) shows the charge density, q_{Hg}, and peak current density, $i_{p(Pb)}$, for three different PSS-coated mercury film electrodes. The polymer layer was recasted from a 25 mM PSS solution varying the microdroplet volume (3 μL in experiment 1, 6 μL in experiment 2 and 9 μL in experiment 3) or the number of consecutive evaporation steps (2 + 2 + 2 μL in experiment 4 and 3 + 3 μL in experiment 5, corresponding to a total volume of 6 μL). The values for the uncoated TMFE are also presented for comparison (experiment 6). Three different electrodes (GCE_1, GCE_2 and GCE_3) were used in order to evaluate also the effects of different GC surfaces and different electrode areas. The PSS loadings corresponding to the deposition of 3 μL are 2.4, 2.1 and 4.9 μg mm^{-2}, respectively, for GCE_1, GCE_2 and GCE_3. The corresponding polymer thicknesses are estimated as 3.0,

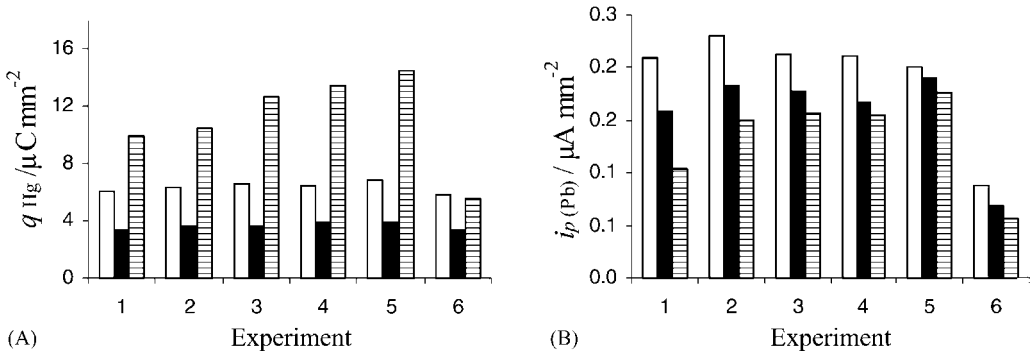

Fig. 2. Mercury voltammetric charge densities (A) and ASV-SW peak current densities of lead (B) for three different GC electrodes, GCE_1 (white), GCE_2 (black) and GCE_3 (horizontal line pattern), and different coating experiments: deposition of a single microdroplet of 3 μL (1), 6 μL (2) and 9 μL (3) and consecutive depositions of 2 + 2 + 2 μL (4) and 3 + 3 μL (5). Experiment 6 corresponds to the uncoated TMFE. PSS solution: 25 mM, in phosphate buffer. Charge determinations: t_{dep} 20 s at −1.3 V; v 250 mV s^{-1}. ASV-SW determinations: t_{dep} 20 s at −0.8 V; a = 25 mV, f = 50 Hz.

2.6 and 6.3 μm. The calculations for 6 and 9 μL are straightforward. For the two BAS electrodes (GCE_1 and GCE_2), the results show that even for identical electrodes, large variations can occur, especially in the amount of deposited mercury where, in some cases, the charge density increased 90%. Conversely, that effect was less significant for the ASV peak current density where the maximum variation was 30%. It must be noticed that for a single GCE, the reproducibility of the PSS coatings is very high [28], so the observed variations cannot be assigned to lack of reproducibility in the coating process. Moreover, those effects were observed also for the bare GC electrodes (experiment 6) and, therefore, they may be related to the intrinsic microstructure of the actual glassy carbon, determining the characteristics of the produced mercury film. In fact, significant differences in the GC microstructure have been reported [57] even for electrodes from the same manufacturer. Surprisingly, the use of a small area electrode (GCE_3) allowed larger amounts of deposited mercury. However, lower ASV peak current densities were observed. Furthermore, for GCE_3, the repeatability of the ASV determinations was slightly poorer (3.2–4.6%) than that for the larger area electrodes (2.2–3.8%).

For the present set of experiments, the overall results show that the variation of the drop volume or the number of deposition cycles did not have a marked effect on the charge and current densities. For 3 μL (experiment 1), the current and charge densities were the lowest and, for the highest droplet volume, 9 μL, the repeatability was slightly worse (R.S.D. values for q_{Hg} changed between 3.7 and 5.6%). In addition, for this higher drop volume, care must be taken in ensuring that the drop does not stay out the electrode surface area. Further, the procedures using sequential depositions (2 + 2 + 2 μL and 3 + 3 μL) did not improve the results and are time consuming. Therefore, and for further studies, it was decided on using GCE_1 and the procedure with the single deposition of a 6 μL droplet.

Changing the concentration of the PSS solution provides a better way to increase the polymer loading. Hence, the PSS concentration was varied from 25 to 50, 75 and 100 mM, corresponding to a four-fold increase in loadings, from 4.8 to 19.2 μg mm^{-2}. Fig. 3 shows the ASV peak current for lead as a function of the PSS loading. For loadings higher than 4.8 μg mm^{-2}, the peak current decreased, reaching the value for the uncoated TMFE at 9.6 μg mm^{-2}, i.e., for an estimated thickness of 9.2 μm. Hence, PSS films thinner than ca. 10 μm present no diffusion restrictions to lead and, actually, the film improves the accumulation of this metal cation. This is quite remarkable for such thick ionomer layers. Usually, polymer layers of ca. 1 μm or less are prepared in order to limit diffusion restrictions [15,17,20,21]; exceptions are reported for polyestersulfonated Eastman AQ 55 [22] and Nafion films prepared without any casting solvent [9] where ca. 5 μm layers were successfully used.

In order to evaluate the cation exchange properties of the PSS coatings, additional experiments were performed without the application of potential during the accumulation period. Hence, the PSS-modified TMFE was equilibrated at open circuit, in a stirred solution of Pb^{2+} (6.0×10^{-8} M) for 20 s. Afterwards, a square wave scan was applied, from −0.8 to −0.1 V, to measure the amount of lead incorporated in the PSS coating (equilibration time of 5 s at −0.8 V). In the absence of any accumulation time, no ASV signal for lead was obtained indicating that the metal ion concentration in solution is too low to contribute to the signal of the incorpo-

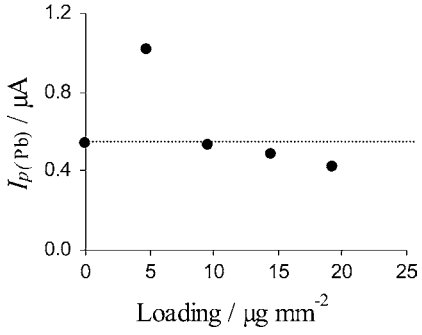

Fig. 3. Effect of the PSS loading on the ASV-SW peak current of lead. t_{dep} 20 s at −0.8 V. SW parameters: a = 25 mV, f = 50 Hz. Concentration of lead, 6.00×10^{-8} M. PSS coatings on GCE_1. Thin mercury films plated ex situ with q = 7.0 μC mm^{-2}.

Table 2
ASV-SW signals of lead (±standard deviations, $N = 6$) accumulated at PSS-coated TMFEs (GCE_1) by application of potential and at open circuit, for different PSS loadings

PSS loading ($\mu g\,mm^{-2}$)	$I_{p(Pb)}$ (μA); t_{dep} = 20 s at −0.8 V	$I_{p(Pb)}$ (μA); t_{dep} = 20 s at open circuit
0	0.55 ± 0.03	0
4.8	1.02 ± 0.03	0.332 ± 0.008
9.6	0.53 ± 0.02	0.203 ± 0.005
14.4	0.48 ± 0.02	0.194 ± 0.005
19.2	0.42 ± 0.01	0.173 ± 0.004

SW parameters: $a = 25$ mV, $f = 50$ Hz.

rated ions. Table 2 presents the $I_{p(Pb)}$ values for PSS-coated mercury film electrodes with different polymer loadings, obtained with and without the application of potential during the accumulation period. These data show that PSS is able to preconcentrate cations due to electrostatic interactions, namely by an ionic exchange mechanism. Even for thicker coatings (>9.6 $\mu g\,mm^{-2}$, i.e., >9.2 μm), that mechanism was responsible for a large fraction of the analytical signal, although there were some restrictions to mass transportation through the polymer layer (the signal at open circuit for the coating with 19.2 $\mu g\,mm^{-2}$ decreased to half the value observed for 4.8 $\mu g\,mm^{-2}$).

SEM images (Fig. 4A and B) highlight the morphological differences for polymer coatings with different loadings. For the PSS coating with 4.8 $\mu g\,mm^{-2}$, the polymer layer looks less compact, presenting wider channels and higher roughness. Nevertheless, all PSS coatings present a rather loose and spongy structure that will certainly facilitate the cation transportation towards the electrode surface and, on the other hand, will allow a more efficient interaction of the target cations with the anionic sulfonate groups of the immobilized polymer. The building of this type of structure may be a consequence of the recasting method via the solvent evaporation of a PSS solution in sodium/potassium phosphate buffer (ionic strength 0.15 M) which may contribute to the coiling of the polyion chain and to the stabilisation of the adsorbed layer, as observed by others [42,43,47]. Therefore, the recasting of sodium–PSS from an ionic solution leads to stable tri-dimensional coatings on glassy carbon and this explains the very low solubility of these PSS-modified electrodes in the electrolyte media used for the voltammetric experiments. Another consequence of the coiling of the PSS polyion chain is the increase of the number of exposed sulfonate groups per unit area, thus intensifying the electrostatic interactions. These considerations associated to the SEM examinations support the observed voltammetric data described above.

3.3. Comparison of the PSS-TMFE with the Nafion-coated TMFE

The characteristics of the PSS-TMFE were compared with those of a Nafion-coated TMFE (NA-TMFE). Both electrodes were prepared by deposition of 6 μL of a 25 mM polymer solution giving loadings of 23 nmol mm^{-2} in monomeric units (i.e., in sulfonate groups). The corresponding mass loadings were 4.8 and 25.7 $\mu g\,mm^{-2}$, respectively, for PSS and NA. The estimated thicknesses of the PSS and Nafion films were 6 and 13 μm, respectively. For the PSS-coated electrode, the mercury charge density was ca. 7 $\mu C\,mm^{-2}$ (corresponding Hg electrolysis time of 20 s, cf. Section 2.3), whereas for the NA-modified electrode, the use of a higher electrodeposition time (40 s) was necessary to achieve a similar charge density. This is indicative of diffusion restrictions to mercury cations through the NA layer and/or a weaker cation exchange

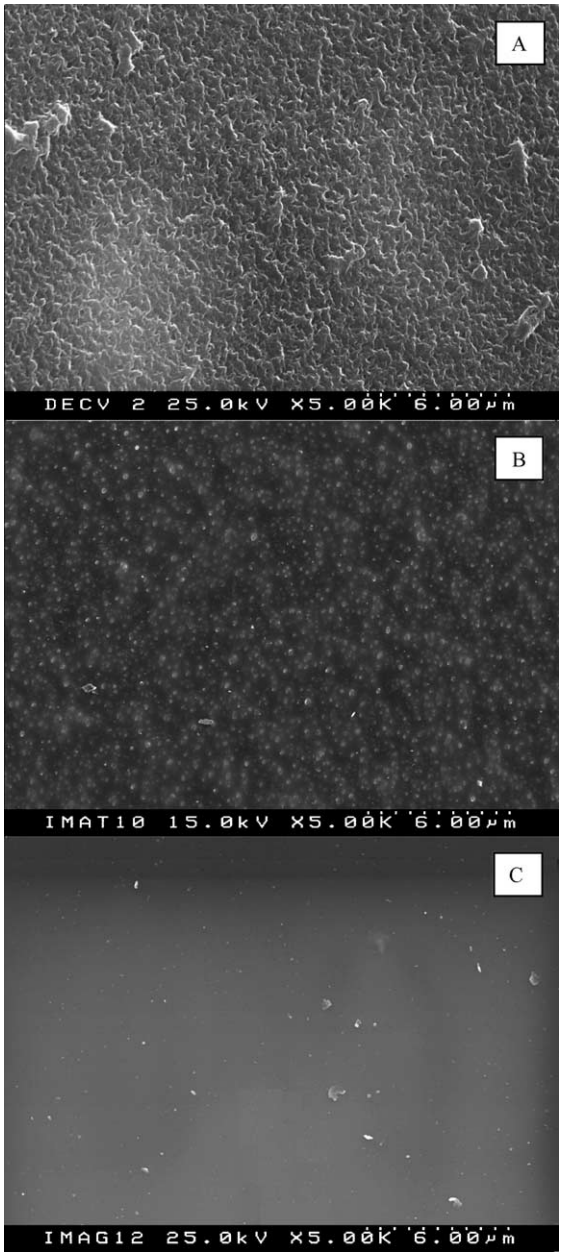

Fig. 4. Scanning electronic micrographs (×5000) of different coatings on GC: (A) PSS, loading 4.8 $\mu g\,mm^{-2}$; (B) PSS, loading 14.4 $\mu g\,mm^{-2}$; and (C) Nafion, loading 11.6 $\mu g\,mm^{-2}$.

ability, comparatively to what occurs for PSS. This fact can be explained by the higher thickness of the NA-coated electrode in spite of both layers having the same concentration of sulfonate groups. A second NA-coated electrode with the same thickness as the PSS electrode (5.9 μm, corresponding to 11 nmol mm^{-2} in monomeric units, deposited from a 11.3 mM solution) was also prepared, and in this case, the mercury electrodeposition time was 20 s (charge density of ca. 5 μC mm^{-2}).

Firstly, the analytical performance was compared. Table 3 presents the calibration data for lead, also compared to that of a bare TMFE. Good calibration curves were obtained for all electrodes. However, a substantial increase in sensitivity (∼45%) for the PSS-coated electrode was observed comparing with the two NA-coated electrodes. Also, all modified electrodes showed improved sensibility to lead compared to the uncoated TMFE. It should be noted that for the present NA coatings, with relatively high thickness, prepared simply by recasting from the commercial NA115 solution, the ASV determination of lead was enhanced, in accordance to the results of Buckova et al. [9]. Nevertheless, doubling the number of sulfonate exchange sites (i.e., the loading) did not bring about a significant improvement of sensitivity, due probably to the increase in thickness. The R.S.D. values of six replicated measurements of I_p for the overall set of standard solutions changed between 0.6 and 2.6% for the NA-TMF electrodes and 0.5 and 1.5% for the PSS-TMFE. The limits of detection were similar for all electrodes, ca. 0.3–0.5 nM (3 s). Nevertheless, the lowest value was observed for the PSS-coated TMFE. All these results demonstrate the enhanced performance of the PSS-coated mercury film electrode for ASV determinations.

Optical micrographs reported for Nafion coatings indicated the formation of compact, transparent layers [15,28]. SEM images for the present Nafion coatings corroborate those observations (cf. Fig. 4C): a rather compact structure was produced with very low roughness. The morphological differences between PSS and Nafion coatings explain, at least partially, the observed variations in the current responses to lead; the denser the polymer coating, the more restricted will be the cation diffusion. Hoyer et al. [17] estimated that ca. 5% of the total peak current of lead, cadmium and copper could be assigned to incorporation by cation exchange within the Nafion polymer (films of 2 μm thickness). That was a rather low value compared with the 30–40% obtained for PSS in the present work (cf. Table 2). Due to the different mass of the monomeric units of the two polymers, the PSS-coated electrode has 4.8 mmol of sulfonate groups per gram of polymer, whereas for the Nafion coating, that value is ca. five times lower. Hence, PSS presents a less compact structure with more sulfonate groups (per gram) available for interaction with cations. All these considerations support the experimental data providing an explanation for the high cation exchange ability and the overall higher sensitivity of the PSS-coated TMFEs for the ASV methodology.

3.4. Ion exchange and permselectivity properties of the PSS coatings

Additional cyclic voltammetric experiments at PSS-coated electrodes with different loadings (4.8, 9.6, 14.4 and 19.2 μg mm^{-2}) were carried out in order to obtain more information on the ion exchange and permselectivity properties of the PSS coating. In this set of experiments, no mercury film was plated. The selected electroactive species were two anions of different molecular weight and charge, $[Fe(CN)_6]^{3-}$ (MW 212) and L(+)-ascorbic acid (MW 176), and dopamine (MW 192). At the working pH 7.0, L(+)-ascorbic acid (pK_a = 4.10) and dopamine (pK_b = 8.87) are anionic and cationic, respectively. Voltammetry at the uncoated GC electrode was also performed for comparison. For all PSS coatings, no voltammetric peaks were detected for $[Fe(CN)_6]^{3-/4-}$ (see Figs. 5A and 6), indicating that the negatively charged film totally excludes ferricyanide ion. This exclusion certainly has an electrostatic nature due to the high charge of that anion but may include also the effect of the semi-permeability of the PSS membranes to molecular size. On the other hand, for the ascorbate anion, decreasing peak currents were observed indicating a progressive exclusion, more pronounced for higher thickness coatings. However, the ascorbate anion was not totally rejected by the PSS films (cf. Figs. 5B and 6), which may be related to the lower molecular weight of this species (lower than that of the ferricyanide anion) and lower anion charge. In contrast, increasing peak currents were observed for dopamine (Figs. 5C and 6), indicating the incorporation of this cationic species into the PSS film. But, for the thicker

Table 3
Calibration data for the SW-ASV determination of lead (2.00–10.0 × 10^{-8} mol dm^{-3}) at PSS- and NA-coated TMF electrodes and at the bare TMFE (using GCE_1)

Electrode	Loading (nmol mm^{-2})	Thickness (μm)	Slope (A M^{-1})[a]	r (N = 5)[b]	L.O.D. (nA)[c]
PSS-TMFE	23	6.0	16.20 ± 0.03	0.9998	0.26
NA-TMFE	23	13	10.92 ± 0.04	0.9998	0.52
	11	5.9	11.30 ± 0.03	0.9997	0.44
TMFE	–	–	8.9 ± 0.6	0.9998	0.41

Deposition time 20 s. SW parameters: a = 25 mV, f = 50 Hz. Mercury charge densities between 5 and 7 μC mm^{-2} (see text for details).
[a] Standard deviations included.
[b] $P < 0.05$ for all calibrations.
[c] Calculated for 3 s.

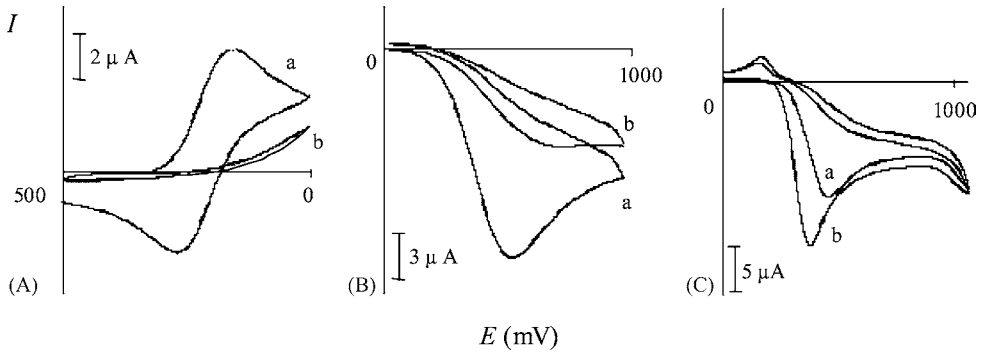

Fig. 5. Cyclic voltammograms of $[Fe(CN)_6]^{3-}$ (A), L(+)-ascorbic acid (B) and dopamine (C) (1 mM solutions in pH 7 phosphate buffer) at the GCE_1 (a) and at the PSS-coated GCE_1 (b). PSS loading: 4.8 μg mm^{-2} (A), 14.4 μg mm^{-2} (B and C). Scan rate, 20 mV s^{-1}.

PSS film, dopamine is being partially excluded, certainly due to diffusion restrictions. Based on these results, the cut-off molecular weight, M_{cut}, of the PSS film with 14.4 μg mm^{-2} (thickness 18 μm) may be estimated as ca. 190, the molecular mass of dopamine. This value is approximately twice the one presented for mixed membranes of PSS and poly-L-lysine [36], which were certainly denser than the present PSS coatings. Nevertheless, a selective determination of dopamine in the presence of equal amounts of ascorbate could not be achieved at any PSS-coated electrode: even for a PSS loading of 14.4 μg mm^{-2}, ascorbate anion contributed to ca. 12% of the oxidation signal. By comparison with published data for NA-coated electrodes, the ascorbate anion is excluded to a lower extent at the PSS layers, which is certainly related to the higher density of the recast nafion coatings [58].

In a previous study, the anti-fouling characteristics of the PSS coatings on glassy carbon were tested using Triton X-100, sodium dodecyl sulfate and agar, by determining the ASV signal of lead at a PSS-coated TMFE (PSS loading 4.8 μg mm^{-2}) [28]. Of those surfactant species, SDS was not completely excluded in spite of being anionic (SDS solutions from 5 to 25 ppm). That observation can now be explained due to the fact that SDS is a mono-negatively charged species with a molecular weight close to the expected M_{cut} value, behaving similarly to the ascorbate anion described above. Conversely, performing the same experiment with an anionic surfactant with a very high molecular weight, e.g., bovine serum albumin (a globular protein with MW 68,000), complete exclusion was observed: only for a 25 ppm BSA solution, the ASV signal of lead (lead concentration 6.00 × 10^{-8} M) decreased slightly, ca. 7%. On the other hand, working in the presence of cationic surfactants may have important effects: for instance, hyamine (HYA, MW 448), in concentrations higher than 3 ppm, unexpectedly produced the total fouling of the PSS-coated electrode in spite of having a molecular weight higher than M_{cut}. The linear conformation of HYA and the presence of the cationic group near the end of the molecule chain may facilitate its transportation throughout the PSS coating. For the uncoated TMFE, HYA also fouled the electrode surface. However, for a 25 ppm solution of poly(allylaminehydrochloride) (MW 15,000), a large molecular weight cationic polymer, no fouling effects were observed, i.e., the ASV peak current of lead remained unchanged compared to that obtained in the absence of any surfactant.

It may be concluded that the PSS coatings are charge selective, as expected for a cation exchange polyelectrolyte, and are also permselective to molecular size. Also, the PSS coatings present anti-fouling properties especially for higher MW tensioactives at moderate concentrations (lower than 25 ppm).

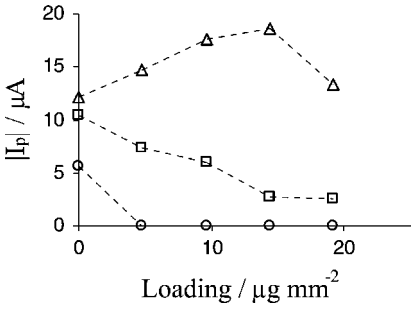

Fig. 6. Effect of the PSS loading on the CV cathodic peak current of $[Fe(CN)_6]^{3-}$ (circles), L(+)-ascorbic acid (squares) and dopamine (triangles). Experimental conditions as in Fig. 5.

3.5. Analysis of real samples using the PSS-coated TMFE

The applicability of the PSS-coated TMFE in the ASV determination of trace heavy metals was checked in contaminated estuarine water containing moderate levels of dissolved organic matter (Fig. 7A and B; Table 4). The results show that the PSS-coated TMFE can be successfully used to quantify trace metals in samples with relatively high DOC, where the bare mercury film electrode fails. This was especially true for sample B (DOC 10 ppm) for which the TMFE was completely fouled. These results highlight the potentialities of the ex situ PSS-TMFE for the direct and sensitive determination of trace levels of dissolved heavy metal ions in samples containing surface-active compounds.

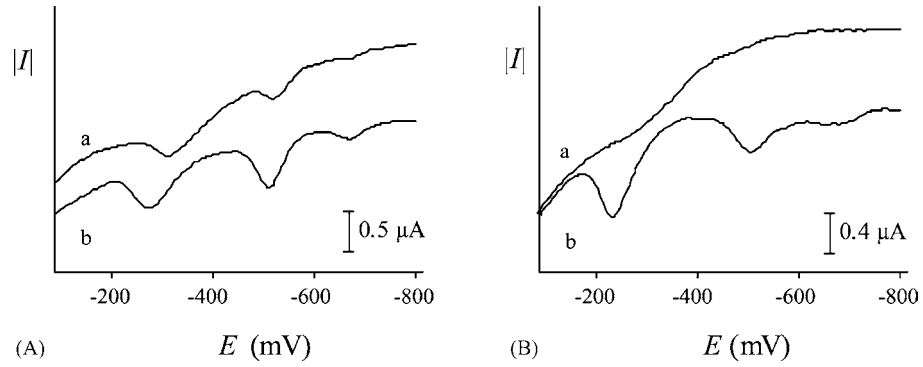

Fig. 7. SW stripping voltammograms of two estuarine waters (samples A and B) at the TMFE (a) and at the PSS-TMFE (GCE_1) (b). PSS loading: 4.8 μg mm^{-2}; SW parameters: a = 25 mV, f = 50 Hz and t_{dep} 180 s at −0.8 V.

Table 4
ASV-SW determinations in contaminated estuarine water samples at the uncoated TMFE and at the PSS-coated TMFE

	Sample A (nM)			Sample B (nM)		
	Cu	Pb[a]	Cd	Cu	Pb[a]	Cd
TMFE	2.69 ± 0.09	3.75 ± 0.08	nd	nd	nd	nd
PSS-TMFE	2.77 ± 0.05	3.83 ± 0.05	1.74 ± 0.06	2.59 ± 0.06	1.31 ± 0.03	0.65 ± 0.02

See Fig. 7 for experimental conditions. nd: not detected.
[a] Values corrected for the blank value (0.12 nM).

The accuracy of the ASV determinations at the PSS-coated TMFE was tested by analysing copper in certified seawater NASS-5. This water sample was used without any pre-treatment. The obtained concentration of copper was 4.64 ± 0.28 nM (N = 3), which compares very well with the certified value of 4.67 ± 0.72 nM. The amount of lead was quantified as (12.0 ± 0.8) × 10^{-11} M (N = 3), which is three times the certified value (40 pM). In spite of our best efforts, the blank level of lead in our laboratory environment could not be lowered further to allow analysis at the pM level. A clean room facility would certainly be necessary to allow such very low level determinations.

4. Conclusion

The use of a PSS coating onto glassy carbon improved not only the formation of the mercury film leading to high amounts of deposited mercury, but also the sensitivity and the reproducibility of the ASV determinations. PSS films thinner than ca. 10 μm presented no diffusion restrictions to lead and were able to pre-concentrate cations due to electrostatic interactions, namely by an ionic exchange mechanism. PSS coatings presented a rather loose and spongy structure, and are mechanically stable and insoluble in aqueous ionic solution. These features are probably a consequence of the coiled conformation of the PSS polyion chains in the evaporation solution, which are maintained through the recasting process. The morphology of the PSS coatings will certainly facilitate the cation transportation towards the electrode surface and improve the cation exchange ability. In fact, there was a substantial increase in the sensitivity of the ASV determinations of lead at the PSS-coated TMFE, compared both with the uncoated TMFE (84%) and with Nafion-coated electrodes (43–49%). Furthermore, PSS coatings were charge selective, as expected for a cation exchange polyelectrolyte, and were also permselective to molecular size. For PSS films of ca. 18 μm thickness (i.e., ca. 14 μg mm^{-2}), the cut-off molecular weight shall be ca. 190. The applicability of the PSS-TMFE in the direct ASV determination of trace heavy metals was demonstrated by analysing lead, copper and cadmium at the low nanomolar level, in estuarine waters containing moderate levels of dissolved organic matter, where the uncoated TMFE failed due to fouling. The accuracy of the ASV determinations with the PSS-coated TMFE was also tested by quantifying copper in certified seawater NASS-5.

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