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Electrochemical Determination of Bisphenol A with Pencil Graphite Electrodes Modified with Co(II), Ni(II), Cu(II) and Fe(II) Phthalocyaninetetrasulfonates

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Pencil graphite electrodes modified with Co(II), Ni(II), Cu(II) and Fe(II) metallophthalocyaninetetrasulfonates (MePcTSs) were investigated for an electrochemical determination of bisphenol A (BPA). The electrochemical performances of the modified electrodes for different pH values in phosphate and the Britton–Robinson buffers were determined by cyclic voltammetry; the electrode performances were better in the Britton–Robinson buffer. NiPcTS and CoPcTS modifications of the electrodes had remarkable enhancements on their performances. The differential pulse voltammetry parameters for the electrodes were optimized, and we found that the electrochemical response *versus* the concentration of BPA is linear from 5.0×10^{-7} to 1.0×10^{-5} M for the NiPcTS and CoPcTS modified electrodes. The detection limits of these modified electrodes are 2.9×10^{-7} and 4.3×10^{-7} M, respectively, and the effects of interfering species are less than 5%. The results show that NiPcTS and CoPcTS modified pencil graphite electrodes could be used for electrochemical determinations of BPA for analytical purposes.

Keywords Bisphenol A, electroanalysis, sensor, metallophthalocyaninetetrasulfonate, modified electrode, pencil graphite electrode

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Introduction

Bisphenol A (BPA) is an industrial monomer, which is especially used for the production of polycarbonate plastics and epoxy resins.[1,2] The annual production of BPA is more than 3 million tons.[3] Due to its common usage, it is generally detected in waste and drinking water and food packages.[4,5] In addition, many things commonly used in daily life include BPA: baby bottles, toys, eye glasses, lenses, some water bottles, CDs and DVDs, auto parts, car lights, medical equipment and food and beverage containers.[6] BPA included waste materials are the reason why BPA is present in nature, especially in water,[7] and its uptake by dermal and respiratory pathways, even in low amounts, could cause health problems.[8-12]

BPA analysis is very important considering its presence in daily life and adverse effects to nature and human health.[13,14] In the literature, BPA analyses have been generally carried out with liquid chromatography equipped with a mass-spectroscopy detector[15-18] or an electrochemical detector[15-19] and gas chromatography equipped with a mass spectroscopy detector.[18-20] In addition, sensors and biosensors have also been investigated for BPA analysis.[21] It appears that the development of simpler, faster and more economical methods for BPA analysis in samples is needed. Therefore, electrochemical methods could be a good alternative to these complex and expensive methods.

In the literature, a few investigations in which metallophthalocyanines were used to modify some electrodes for BPA analysis were published. Metallophthalocyanines have a good electrocatalytic activity and can adsorb very effectively on carbon based electrodes.[22,23] Moreover, metallophthalocyanine-based electrodes are chemically and electrochemically stable.[23,24] A Co(II) phthalocyanine modified carbon paste electrode,[14] a Ni(II) tetraaminophthalocyanine modified gold electrode,[25] Ta(IV) phthalocyanine, conjugated with gold nanoparticles and carbon nanotubes, modified gold electrodes[26] and Zn(II) phthalocyaninetetrasulfonic acid-functionalized graphene nanocomposite modified glassy carbon electrode[27] were prepared and used for BPA analysis. Nearly in all cases these studies the modified electrodes for BPA analysis was investigated in basic or neutral media. Of the metallophthalocyanine modified electrodes, various modified electrodes were also prepared and used for BPA analysis.[28-32]

Pencil graphite electrodes (PGE) are very preferable for many analytic applications owing to their high electrochemical activity, mechanic stability, low cost, small dimension, and facility of modification and application.[33-35] They could be used

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for the determination of very low concentrations of contaminates in low volume because of their high surface areas.[36] Moreover, the analysis time could be very short by using disposable PGE.[37]

To the best of our knowledge, electrochemical determinations of BPA using PGE modified with water-soluble metallophthalocyaninetetrasulfonates (CoPcTS, NiPcTS, CuPcTS and FePcTS) were not investigated before. The effects of the pH and type of buffer, the linear concentration range, the detection limits and the effect of interfering species on PGE modified with these metallophthalocyaninetetrasulfonates were determined, and the results were discussed.

Experimental

Electrodes and metallophthalocyaninetetrasulfonates

The electrochemical experiments were performed using a three-electrode system in a 5-port electrochemical cell. A Pt plate ($10 \times 10 \times 0.25$ mm, Aldrich 99.9%) was used as the counter electrode, a PG (diameter: 0.70 mm, Faber Castell (2B), Germany) as the working electrode (1.0 cm long part was dipped in the solution) and Ag/AgCl electrode (in 3.0 M KCl) as the reference electrode. A pencil (Noki model, Japan) was used as a PGE holder. Electrical contact with the PGE was obtained by soldering a metallic wire to the metallic part of the pencil. Tetra sodium salts of NiPcTS and CuPcTS were bought from Aldrich (99+%). Tetrasodium salts of cobalt(II) and iron(II) phthalocyaninetetrasulfonates were synthesized by the Weber and Busch method.[38]

Equipment

A potentiostat-galvanostat instrument (Reference 600 ZRA model, Gamry, USA) was used for all cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements. Data analyses were evaluated by using the Echem Analyst software of the instrument. Deionized water was used for all experiments. Before the measurements, electrolytic solutions were purged with nitrogen gas for 10 min. All electrochemical measurements were performed at room temperature. A pH meter (Orion 3 Star model, Thermo Scientific) was used for hydronium-ion activity measurements. Phosphate and Britton-Robinson (BR) buffers were used as electrolyte solutions. BR buffer consists of a mixture of 0.04 M H_3BO_3, 0.04 M H_3PO_4 and 0.04 M CH_3COOH, and has been titrated to the desired pH with 0.20 M NaOH.

Preparation of the modified PGEs

PGEs were ultrasonicated in water and acetonitrile for 5 min, sequentially, and dried in an oven at 50°C for 90 min. Cu(II), Co(II), Ni(II) and Fe(II) metallophthalocyaninetetrasulfonates (1.0 mM) were adsorbed on the surfaces of the PGE by dipping the electrodes into their solutions for various periods of time (1 – 90 min). After that, the modified electrodes were left in air for 15 min at room temperature to stabilize them. The structure of metallophthalocyaninetetrasulfonates and the modification procedure of the PGEs with MePcTS are shown in Fig. S1 in Supporting Information. The modified electrodes were coded as PGE/MePcTS(Xmin) where Me is Co, Ni, Cu or Fe and X is the time used for adsorption of MePcTS on the PGE.

Results and Discussion

The effect of pH

Initially, the anodic peak current behavior of BPA by varying the pH in the phosphate and BR buffers for all electrodes was investigated by CV measurements. A plot of the obtained results at different pH values in phosphate buffer (0.10 M) and in the presence of 0.25 mM BPA is given in Fig. S2a. It was found that the anodic peak currents of the modified electrodes were higher than that of the PGE. The performances of the modified electrodes were very high, especially at low pH values. For instance, PGE/CoPcTS(30min) showed a current 2.2-times higher than that of the PGE at pH 3. Figure S2b shows cyclic voltammograms of BPA by using the PGE and modified PGE in the phosphate buffer at pH 3.

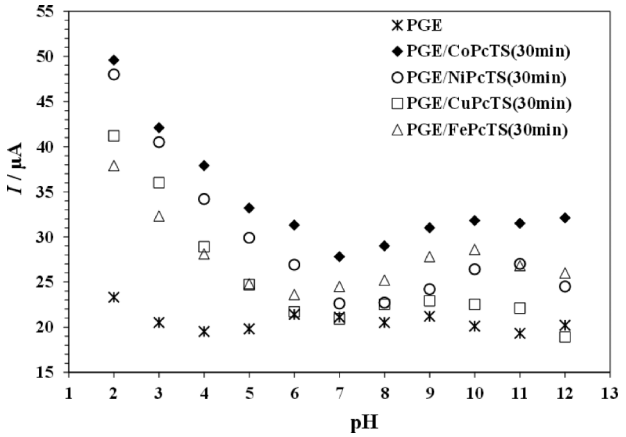


Fig. 1 Anodic peak current values of BPA (0.25 mM) for different pH values in the BR buffer (0.10 M) for the electrodes.

The high current values were also obtained at low pH values in the BR buffer (Fig. 1). The highest current value (*ca.* 49 µA) was obtained by using a PGE/CoPcTS(30min) electrode at pH 2. This current value is 2.1-times higher than that of the unmodified electrode. Moreover, the current values were higher in the BR buffer with respect to those in the phosphate buffer. Figure S3 shows cyclic voltammograms of BPA by the PGE and modified PGE in the BR buffer at pH 2 in the presence of 0.25 mM BPA.

It is known that the supporting electrolytes could enhance the electrocatalytic response by increasing the redox activity on the modify electrode surface.[14,39] Yin *et al.* showed that the anodic peak current of a Co-phthalocyanine modified carbon-paste electrode for BPA analysis increased after the addition various salts to the phosphate buffer.[14]

Because the CoPcTS and NiPcTS modified electrodes showed better performances than the FePcTS and CuPcTS modified ones, these modified electrodes were used in further investigations for BPA analysis in the BR buffer.

Adsorption time optimization

It is well known that metallophthalocyanines adsorb very efficiently on carbon-based electrodes.[22,23] Furthermore, metallophthalocyanine modified electrodes are efficient catalysts for redox reactions because they have a planar π-conjugated skeleton structure similar to biological molecules, such as chlorophyll and hemoglobin.[27] Hydrophobic metallophthalocyanines could aggregate in aqueous solutions owing to their π-conjugations with each other, whereas water-soluble metallophthalocyanines could be ordered on the electrode surface without aggregation.

In order to determine the optimal times of the adsorptions of CoPcTS and NiPcTS on the surface of the PGE, a series of

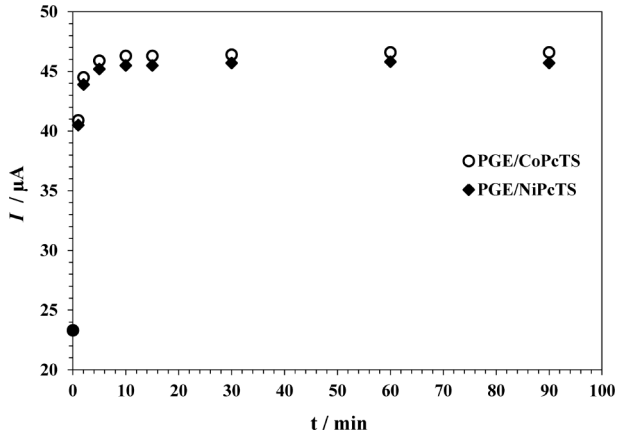


Fig. 2 Peak-current values of BPA (0.25 mM) in BR buffer (pH 2) by using modified electrodes that were prepared by the adsorption of CoPcTS and NiPcTS on PGE for different times.

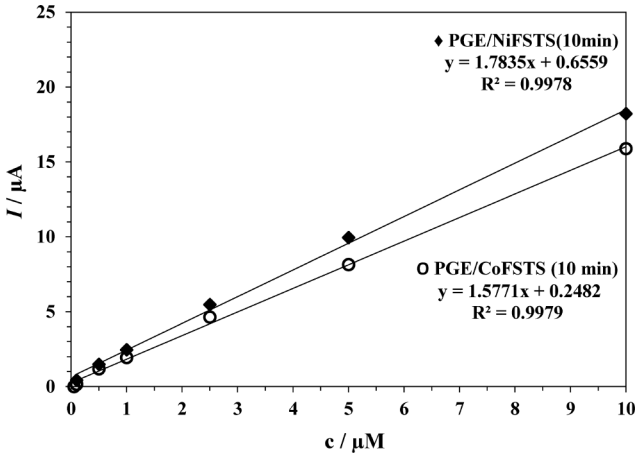


Fig. 3 Current values *versus* the BPA concentration using PGE/CoPcTS(10min) and PGE/NiPcTS(10min) electrodes at pH 2 in the BR buffer for low concentrations.

experiments were performed. In these experiments, the PGEs were dipped in 1.0 mM CoPcTS and 1.0 mM NiPcTS solutions for different adsorption times (1 – 90 min). After the period of adsorption, the electrodes were allowed to dry for 15 min at room temperature before measurements. The plot of the peak current values by CV in the BR buffer at pH 2 *versus* time is given in Fig. 2. The zero time in the figure corresponds to the current value of the PGE. The curves are Langmuir type until 10 min of adsorption time, at which the current values reached a maximum, and then remained nearly constant for both CoPcTS and NiPcTS adsorptions. Therefore, it was concluded that the optimum adsorption times of CoPcTS and NiPcTS on the PGE are about 10 min, and thereafter a 10-min adsorption time was used to prepare the modified electrodes for following experiments. Based on our findings, it appears that a 10-min adsorption time is sufficient to cover most, maybe all, of the PGE surface.

The optimization of DPV parameters

The pulse size (amplitude, A), step size (pulse increment, E_s), pulse time (width, W) and sample period (pulse period, T) parameters of DPV were optimized for PGE/CoPcTS(10min) and PGE/NiPcTS(10min) electrodes in a 0.10 mM BPA solution at pH 2 (Fig. S4). These optimized parameters for both electrodes were 60 mV, 10 mV, 0.02 s and 0.2 s, respectively. Thereafter these DPV values were used for following experiments.

The effect of the BPA concentration on the electrochemical response

The effect of the BPA concentration on the electrochemical response was investigated by DPV using PGE/CoPcTS(10min) and PGE/NiPcTS(10min) electrodes at pH 2 in the BR buffer for the concentration range from 0.10 to 500 µM. A plot of the currents as a function of the BPA concentrations is given in Fig. S5. The anodic peak current values changed linearly with respect to the BPA concentration just for its low concentrations (5.0×10^{-7} to 1.0×10^{-5} M) for both modified electrodes (Fig. 3). These results show that the modified electrodes could be used for BPA analysis at micromolar concentrations. Moreover, the detection limits of BPA, obtained from the data of electrochemical analysis, are 4.3×10^{-7} and 2.9×10^{-7} M at 3σ for PGE/CoPcTS(10min) and PGE/NiPcTS(10min), respectively. Figures 4 and S6 shows differential pulse voltammograms

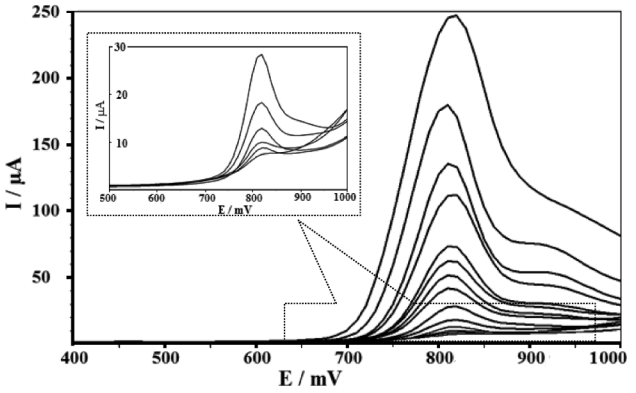
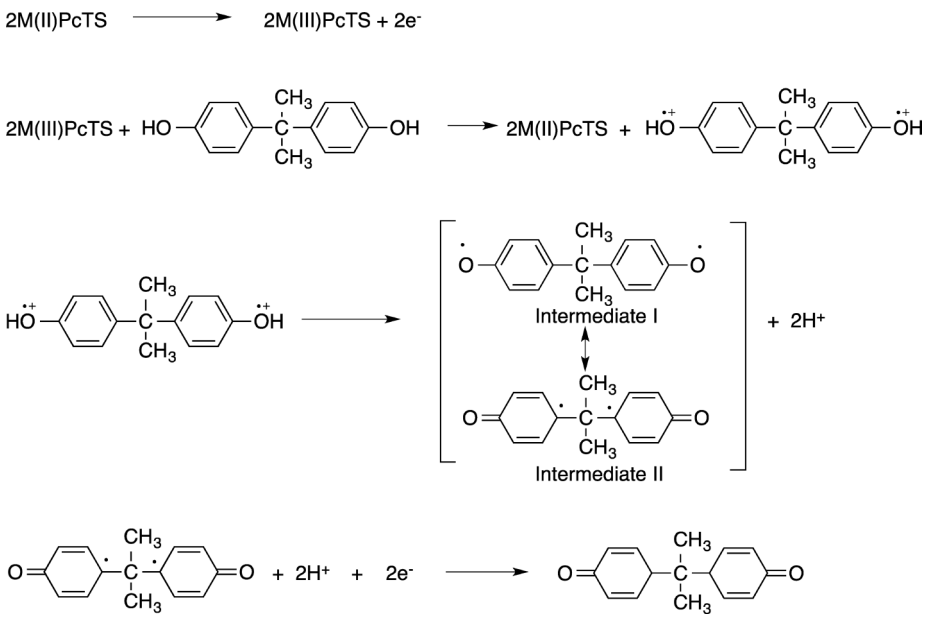


Fig. 4 Differential pulse voltammograms obtained by varying the BPA concentrations by using a PGE/NiPcTS(10min) electrode. Insets show the linear relation part of *I vs. C* (until 10 µM). The peaks (from top to down) correspond to 500, 250, 150, 100, 50, 40, 30, 20, 10, 5, 2.5, 1, 0.5 µM concentrations of BPA.

obtained by varying the BPA concentrations for PGE/NiPcTS(10min) and PGE/CoPcTS(10min), respectively.

In the literature, a few investigations in which metallophthalocyanines were used to modify the electrodes for BPA analysis were published. The linear ranges reported for BPA analysis were 8.75×10^{-8} – 1.25×10^{-5} M,[14] 7×10^{-4} – 3×10^{-2} M,[25] 1×10^{-6} – 8×10^{-6} M,[26] and 5×10^{-8} – 4×10^{-6} M.[27] All in these works the modified electrodes for BPA analysis have been investigated in basic or neutral media. In most of these studies, nanomaterials were also utilized for modification. This is the reason why some the results in the literature are better than ours. However we modified the PGE by four different metallophthalocyaninetetrasulfonates without the use of any nanomaterials. Therefore, our modified electrodes are simple and cheap based on considering their preparations; the cost of BPA analysis with them is low and the analysis time is short. Moreover, different from the results of the literature works, our electrodes showed better performances in an acidic medium compared to those of neutral or basic media.

It is well known that oxidations involving Co(II) or Ni(II) phthalocyanine complexes proceed *via* the central metal, and that the electrochemical activity of metallophthalocyanine



Scheme 1 Proposed mechanism for the electrocatalytic oxidation of BPA by the metallophthalocyanines in acidic media.

Table 1 Anodic peak, cathodic peak and peak-to-peak separation values of the electrodes

Electrode	Anodic peak (E_{pa})/mV	Cathodic peak (E_{pc})/mV	$\Delta E_p(E_{pa} - E_{pc})$/ mV
PGE	315	175	140
PGE/CoPcTS(10min)	540	–140	680
PGE/NiPcTS(10min)	545	–140	685
PGE/CuPcTS(10min)	495	–110	605
PGE/FePcTS(10min)	460	5	455

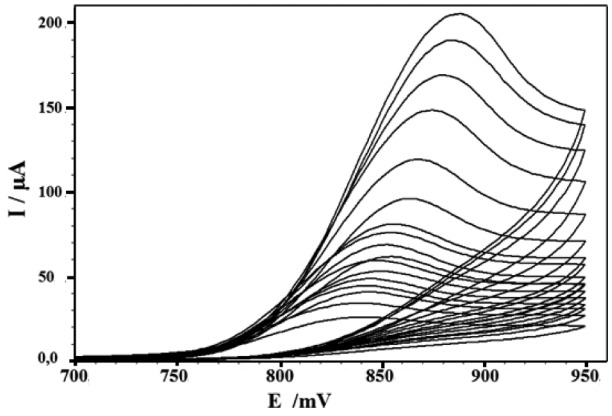


Fig. 5 Cyclic voltammograms of BPA by PGE/NiPcTS(10min) electrode for different scan rates ([BPA] = 0.25 mM in BR buffer).

complexes for many reactions is reported to depend on the M(III)/M(II) redox couple.[40-42] The pH of the medium could have an effect on the efficiency of the M(III)/M(II) redox couple and the strength of the π-π interaction between Pc and BPA. According to Maree and Nyokong, the potential for the electrocatalytic oxidation of cysteine is related to the Co(III)/Co(II) couple in acidic media, whereas to the Co(II)/Co(I) couple in basic media.[43] Chen *et al.* reported higher reaction rates for the oxidation of organic dyes by a supported $CoPc/H_2O_2$ catalytic system in acidic solutions.[44] Yin *et al.* argued that the Co(II)Pc/Co(III)Pc step occurs first, and that then Co(III) in Co(III)Pc coordinates axially to the oxygen atom of the phenolic OH in BPA before its oxidation.[14] Based on these reports, we propose the mechanism on the electrocatalytic oxidation of BPA catalyzed by our metallophthalocyanines in acidic media given in Scheme 1. In the first state, M(II)PcTS oxidises to M(III)PcTS. Then, BPA donates two electrons ($1e^-$ from the oxygen atom of each OH group) to two M(III)PcTS complexes, which is followed by $2H^+$ losses to give Intermediate I. The resonance structure of the Intermediate I (Intermediate II) converts the quinoid product of BPA.

The electrochemical characteristics of the modified electrodes

The electrochemical behavior of the PG and modified PGE was investigated by using CV in 5.0 mM $K_3(Fe(CN)_6)$ and 0.10 M KCl solutions. Table 1 reports ΔE_p values of the electrodes. The peak-to-peak separation (ΔE_p) value of the redox couple for the PGE is 140 mV, while this value for the modified ones is higher, *ca.* 680 mV. This result is attributed to interactions between the metallophtalocyanines and PGE, which indicate that modification occurred.[27]

In order to determine whether the current is diffusion or adsorption controlled, the cyclic voltammograms of PGE/CoPcTS(10min) (Fig. S7) and PGE/NiPcTS(10min) (Fig. 5) electrodes were studied in 0.25 mM BPA solutions at pH 2 for different scan rates (20 – 700 mV/s).

Figure 6 gives plots of the anodic peak current values *versus* the square root of the scan rate of PGE/NiPcTS(10min) and PGE/CoPcTS(10min).[45] It is evident that the current is diffusion controlled, since the correlation coefficient of the graphics are close to 1 (0.9976 and 0.9981 for PGE/NiPcTS(10min) and PGECoPcTS(10min), respectively).[46]

A plot of the logarithm of the current *versus* the logarithm of the scan rate of PGE/NiPcTS(10min) and PGE/CoPcTS(10min)

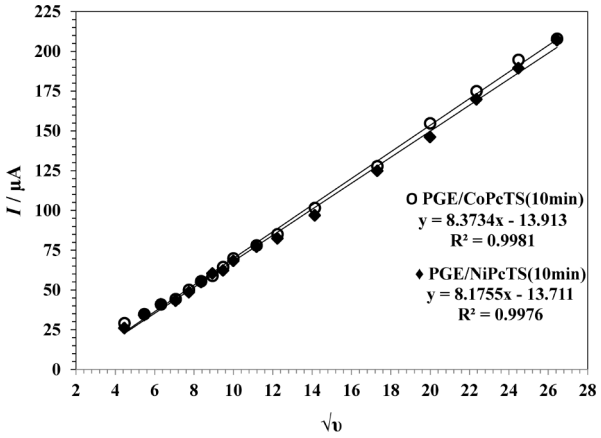


Fig. 6 Anodic peak current values *versus* the square root of the scan rate of PGE/NiPcTS(10min) and PGE/CoPcTS(10min) electrodes.

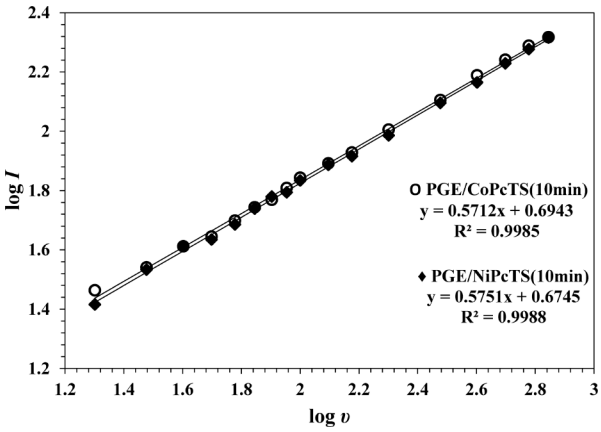


Fig. 7 Logarithm of current *versus* the logarithm of the scan rate of PGE/NiPcTS(10min) and PGE/CoPcTS(10min).

is shown in Fig. 7. The values of the slopes are 0.575 and 0.571, respectively. This is another evidence that the current is diffusion-controlled, because the slopes are close to 0.5.[46] Because the current is not adsorption controlled, using stripping methods could not provide extra improvements in the performances of the electrodes. Therefore, it is sufficient to use differencial pulse voltammetry for BPA analysis.

The effect of interference species

The concentration of BPA was kept constant at 10 µM, while the concentrations of various metals, which are possible interference species, were chosen to be 100 fold higher: 1.0 mM. The peak current values, obtained by DPV in the presence of these interference species, were compared with that in their absence. The results by using PGE/NiPcTS(10min) and PGE/CoPcTS(10min) are reported in Table 2. Because the effects of the interference species are lower than 5%, the modified electrodes could be used selectively for BPA analysis in water sources or waste waters.

Reproducibility of PGE/NiPcTS(10min) and PGE/CoPcTS(10min) electrodes

The reproducibility of the PGE/NiPcTS(10min) and PGE/CoPcTS(10min) electrodes were tested in 20 µM BPA solution at pH 2 using different modified electrodes. The relative standard deviation of the peak-current values of DPV are 2.30 and 2.85% for PGE/NiPcTS(10min) and PGE/CoPcTS(10min), respectively by using 7 measurements of each new electrode.

Table 2 Effect of interference species in the presence of modified electrodes in [BPA] = 10 µM

Modified electrode	Interference species (1.0 mM)	Current/ µA	Current difference/ µA	RSD, %
PGE/NiPcTS(10min)	—	18.22	—	—
PGE/NiPcTS(10min)	Pb^{2+}, ($Pb(NO_3)_2$)	17.90	–0.32	2.88
PGE/NiPcTS(10min)	Al^{3+}, ($Al_2(SO_4)_3$)	19.43	1.21	2.14
PGE/NiPcTS(10min)	Cu^{2+}, ($CuSO_4$)	17.65	–0.57	2.63
PGE/NiPcTS(10min)	Ni^{2+}, ($NiSO_4$)	18.44	0.22	1.29
PGE/NiPcTS(10min)	Zn^{2+}, ($Zn(Ac)_2$)	18.46	0.24	1.39
PGE/NiPcTS(10min)	Fe^{3+}, ($Fe(NO_3)_3$)	19.39	1.17	4.33
PGE/NiPcTS(10min)	K^+, (KCl)	19.44	1.22	3.19
PGE/CoPcTS(10min)	—	15.89	—	—
PGE/CoPcTS(10min)	Pb^{2+}, ($Pb(NO_3)_2$)	15.94	0.05	2.56
PGE/CoPcTS(10min)	Al^{3+}, ($Al_2(SO_4)_3$)	16.02	0.13	3.95
PGE/CoPcTS(10min)	Cu^{2+}, ($CuSO_4$)	16.02	0.13	1.40
PGE/CoPcTS(10min)	Ni^{2+}, ($NiSO_4$)	16.20	0.31	3.79
PGE/CoPcTS(10min)	Zn^{2+}, ($Zn(Ac)_2$)	15.90	0.01	1.98
PGE/CoPcTS(10min)	Fe^{3+}, ($Fe(NO_3)_3$)	16.69	0.80	4.80
PGE/CoPcTS(10min)	K^+, (KCl)	16.71	0.77	2.80

Conclusions

PGE modified with Ni(II), Co(II), Cu(II) and Fe(II) metallophthalocyaninetetrasulfonates was investigated for electrochemical BPA analysis by CV. The kind of metal in the phthalocyanine, the pH, the type of buffer, the adsorption time of metallophthalocyanines on PGE, the DPV parameters and the linear concentration ranges were optimized for the electrochemical analysis of BPA. The electrochemical characteristics of the modified electrodes were determined. Moreover, the effect of the interference species and the reproducibility of modified electrodes were analyzed. The results show that NiPcTS and CoPcTS modified electrodes showed better performances than CuPcTS and FePcTS modified ones. NiPcTS and CoPcTS modified electrodes could be used for the electrochemical determination of BPA concerning analytical purposes, especially in an acidic medium. By considering simplicity, low cost and a quick response of these disposable electrodes, they could find applications concerning electrochemical BPA analysis. We think that the performances of NiPcTS and CoPcTS modified electrodes could be improved by using nanomaterials in their modifications. Our work is in progress concerning this perspective.

Acknowledgements

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Supporting Information

SI includes figures concerning the structure of metallophthalo-

cyaninetetrasulfonates and the modification procedure of the PGE, electrochemical performances of the modified electrodes for different pH values in phosphate and BR buffers, the optimization of DPV parameters, the current values *versus* BPA concentrations for large range, differential pulse voltammograms obtained by varying BPA concentrations by using PGE/CoPcTS(10min) electrode and the cyclic voltammograms of BPA by PGE/CoPcTS(10min) for different scan rates. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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