

Solid-Phase Microextraction and Ion Chromatographic Analysis of Anions Based on Polypyrrole Electrode

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ABSTRACT: The polypyrrole (PPy) film was used for the selective extraction of trace levels of chloride, nitrite, and nitrate ions by solid phase micro-extraction (SPME). PPy film was electrochemically prepared from aqueous solutions of pyrrole and LiClO_4 under N_2 atmosphere at constant potential of +0.80 V (versus Ag/AgCl). The anion uptake and release properties of the PPy film electrodes were examined under both open circuit and controlled potential conditions for prospective applications in electrochemically controlled solid-phase microextraction (EC-SPME). Applied positive and negative potentials facilitated

the extraction and desorption of anions, respectively. Ions were desorbed into sample aliquot and were determined by ion chromatography (IC). The effect of uptake/release parameters, potential, time, pH of the uptake solution, on EC-SPME of anions was investigated. The method was validated using a standard reference material and tested for the determination of the ions in water samples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3298–3304, 2008

Key words: electrochemically controlled solid phase microextraction; polypyrrole; anion exchange; ion chromatography

INTRODUCTION

Nowadays, solid-phase extraction (SPE) is a well established technique and, due to its advantages over other sample preparation techniques, it has been used for the preconcentration and clean-up of numerous different classes of compounds in a variety of matrices. SPE is a convenient and solventless sample preparation method that utilizes a thin polymer film coated on a silica fiber as an extraction phase.^{1–5} SPE has advantages of simplicity, low cost, ease of use and rapid preconcentration and extraction of analytes that exist in low concentrations. The method successfully combines sample cleanup and preconcentration into one step. However, the neutral charge of commercially available SPE coatings results in a low coating/sample partition coefficient and poor analyte recoveries, which limited its application. Chemical modification of the sample or fiber's surface by derivatization or by the addition of complexing agents can increase the extraction efficiency. But, these reactions require expensive and toxic reagents and sometimes produce unstable products. The most promising alternative for the extraction of ionic compounds is the use of conduc-

tive polymers as the extraction phase. The electroactivity and reversible redox properties of conductive polymers, especially PPy, have attracted great interest in the development of electrochemically controlled delivery devices and separation systems for charged species.^{6–8} Electrochemical redox of the polymer is accompanied by the movement of dopants in and out of the polymer film for charge balance. The oxidized conducting polymeric macromolecular chain has positive charges, and the charge must be balanced by the dopant (counter ion). When it is reduced, the dopant will be released from the polymer. Under the principle, the PPy has been used to control release a variety of anions. The anions are first electrochemically entrapped into PPy films during oxidation and then released during electroreduction.⁹

The electrochemical doping/undoping features of certain conducting organic polymer electrodes could be advantageous as SPE films for preconcentration and matrix separation of anionic,^{3,6} cationic,^{3,7,10} and neutral analytes.^{11,12} PPy and its derivatives, have attracted great interest in the development of electrochemically controlled solid phase microextraction (EC-SPME) as ion exchange material for charged species.^{3,7,13} The main advantage of using conducting polymers in SPME is that the charge of the coatings can readily be controlled by oxidation and reduction of the polymers. PPy with small counterions, e.g., Cl^- , ClO_4^- , NO_3^- mainly exhibits anion exchanger behavior due to the high mobility of these

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ions in the polymer matrix. Cation exchanger behavior can be achieved by incorporating large polyanionic counter-ions, such as polystyrene sulfonate (PSS), because of their immobility in the polymer matrix.¹⁴

The aim of this work was to study the application of electrochemically controlled solid phase micro extraction based on polypyrrole modified electrodes. This work describes method for the use of polypyrrole film to obtain extraction and selective determination of trace levels of chloride, nitrite, and nitrate ions by ion chromatographic system. The developed method is straightforward and suitable for the extraction and analysis of anionic species in aqueous samples.

EXPERIMENTAL

Chemicals and reagents

Pyrrole (Py) (Aldrich, 99%, Milwaukee, WI, USA) was distilled repeatedly under vacuum until a colorless liquid was obtained, and kept under nitrogen in darkness at 4°C prior to use. HCl, NaOH, LiClO₄, NaNO₃, NaNO₂, and NaCl were obtained from Aldrich. All the chemicals were of analytical reagent grade and used without further purification. All solutions were prepared by appropriate dilution from stock solutions using predistilled 18 MΩ cm⁻¹ deionized water. The solutions were prepared daily and were filtered through a 0.45 μm membrane filter before use.

Preparation of the PPy electrode

Polymer film formation was achieved in a conventional one-compartment three-electrode cell. PPy was electrochemically prepared from aqueous solutions of 0.1M monomer (distilled Py) and 0.2M LiClO₄ as supporting electrolyte under N₂ atmosphere. Electropolymerization was performed on 1.0 × 1.0 cm² Pt foil electrodes at constant potential of +0.80 V (versus Ag/AgCl) during 8 min. Growth of the films was controlled based on the amount of charge passed. After the electropolymerization process, the PPy film electrodes washed with water to remove the excess Py and LiClO₄ and dried at room temperature before the experiments. All experiments were carried out at ambient temperature. When the coated electrodes were not in use, they were stored in 1.0 × 10⁻³M LiClO₄ at room temperature.

Instrumentation and analytical conditions

The electrochemical instrumentation consisted of an Autolab PGSTAT-100 Potentiostat/Galvanostat with GPES software (EcoChemie, The Netherlands). Elec-

trochemical measurements were carried out under N₂ atmosphere in a conventional one-compartment three-electrode cell for the reference electrode (Ag/AgCl) and the counter electrode (Pt spiral). Prior to each electrochemical measurement, the working electrode was polished with an aqueous suspension of 0.05 μm gamma alumina powder (CH Instruments), washed with deionized water and alcohol to eliminate the alumina and cleaned by holding it in a flame for a few minutes after that dried.

Determination of the released anion species were carried out by ion chromatography. Chromatographic measurements were carried out using a Dionex DX100 Model ion chromatography (Dionex, Sunnyvale, CA), with 25 μL sample loop, consisting of an isocratic pump, an anion separator column (Dionex, IonPac AS9-SC) coupled with an anion self-regenerating suppressor (Dionex, ASRS, 4 mm), a conductivity detector, and a computer. The mixture of 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃ buffer solution was used as an eluent at a flow rate of 1.0 mL min⁻¹. Peak area of the anions signal was used for quantitation. The IonPac AS9-SC column (4 × 250 mm²) is an 8.0-μm diameter ethylvinylbenzene crosslinked with 55% divinylbenzene. The substrate bead is coated with a quaternary ammonium-functionalized, as an anion exchanger that permits elution of monovalent and divalent anions with dilute eluents. The response of the detector was measured with a ChromaSimple software program (Dizge Analitik, Turkey) and AC/DC convertor to obtain a full chromatogram.

Scanning electron micrograph (SEM) of the PPy film was performed by using field emission gun scanning electron microscope (FEG-SEM) (Oxford Instruments-7430).

EC-SPME of anions

The PPy film electrodes were washed with water to remove excess electrolyte and pyrrole before the experiments. It was then transferred to 10 mL sample of aqueous target solutions for extraction, by applying a positive potential (3 min for Cl⁻, 2 min for NO₂⁻, and 3 min for NO₃⁻). After extraction, the electrode was washed with water and then transferred to 10 mL cell containing 0.01M LiClO₄ solution where the analyte was released at negative potential (4 min for Cl⁻, 3 min for NO₂⁻, and 4 min for NO₃⁻). The uptake potentials were +1.25 V, +0.20 V, and +0.75 V for Cl⁻, NO₂⁻, and NO₃⁻, respectively. And the released potential was -0.50 V for all anions versus Ag/AgCl reference electrode. All data points reported in this work represent the average of three replicates. The effect of the solution pH the uptake of the anions was investigated by

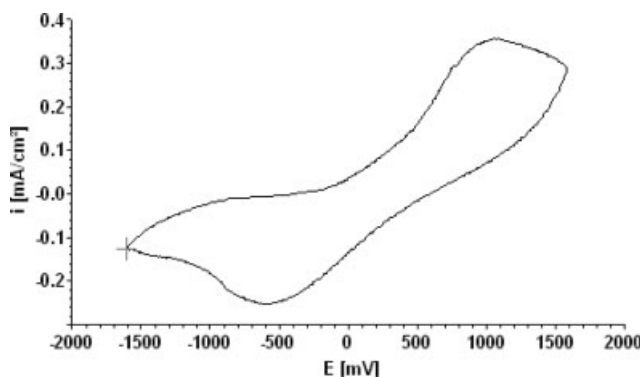


Figure 1 Cyclic voltammetric behavior of PPY film electrode in 0.1M LiClO₄ solution with a scan rate at 100 mV/s.

adjusting the pH with hydrochloric acid and sodium hydroxide solutions.

RESULTS AND DISCUSSION

Electrochemical behavior of PPY film electrode

The electrochemical behavior of the electrodeposited film was studied by potential cycling between -1.60 V and $+1.60$ V (versus Ag/AgCl) in 0.1M aqueous solution of LiClO₄ (blank solution) (Fig. 1). A broad oxidation peak was observed at the peak potential of $+0.90$ V and reverse cathodic peak was seen at a peak potential of -0.60 V (versus Ag/AgCl). This oxidation and reduction process shows that the polypyrrole film has an electroactive characteristic in aqueous solution.

The effect of the polymer thickness on the extracted amounts of ions

The amount of analyte accumulated on the film coating is a function of the distribution coefficient, concentration of analyte in matrix, and volume of polymer film. The amount of analyte extracted onto the polymer coating accessible for analyte extraction should also be crucial. We investigated the effect of the polymer film thickness on the extracted amounts of ions in our previous work.¹⁵ The polymer film thickness influences the extraction efficiency due to the increased surface area. Thickness is highly effective on the surface area up to a certain value due to porous structure of the film. After certain thickness value diffusion limitation starts to limit the extraction amount. It is shown that as the film thickness increases, the sensitivity will also increase. Thicker coatings have therefore higher ion exchange capacity and results in larger dynamic range before the coating becomes saturated.

Surface morphology

The morphologies of the PPY film were investigated by scanning electron microscopy (SEM) (Fig. 2). Figure 2(a) shows the SEM picture of the PPY film which was grown from electrode surface to the solution/film interface (solution side). The porous surface structure and “cauliflower” morphology of PPY film can be seen easily in this figure. The electrode/film interface (electrode side) of the PPY film has a cavity structure [Fig. 2(b)]. The physical adhesion of the film to the bare platinum foil surface was also affected by the electrodeposition process. These two images clearly show that the electrode and solution side greatly influence the surface morphology. The surface morphology affects the anion uptake selectivity.

Calibration method

The calibration curves of Cl⁻, NO₂⁻, and NO₃⁻ were obtained by preparing standards in deionized water.

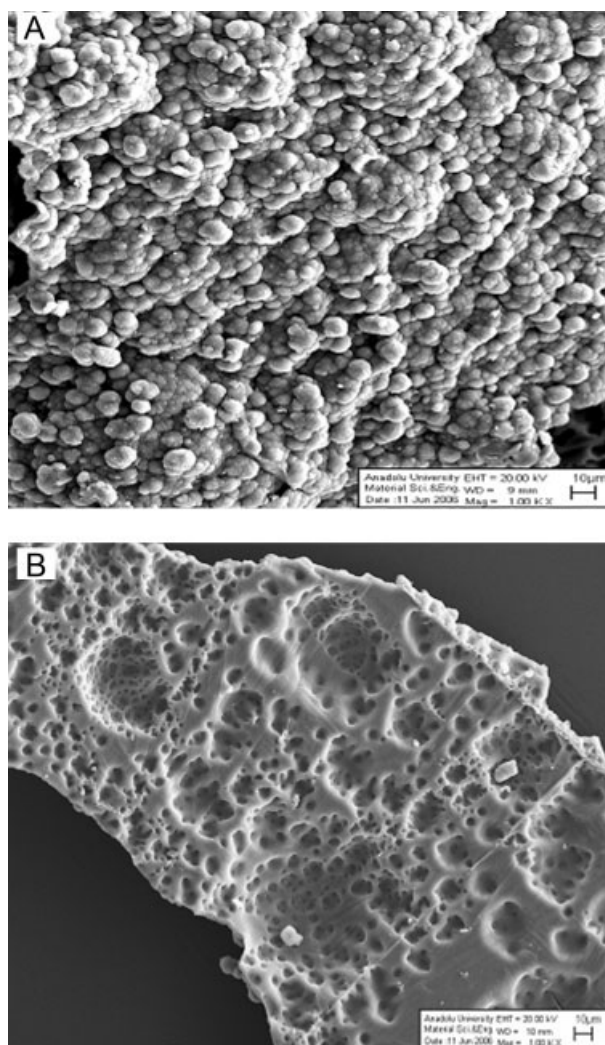


Figure 2 Scanning electron micrographs of the PPY film: (a) solution and (b) electrode side.

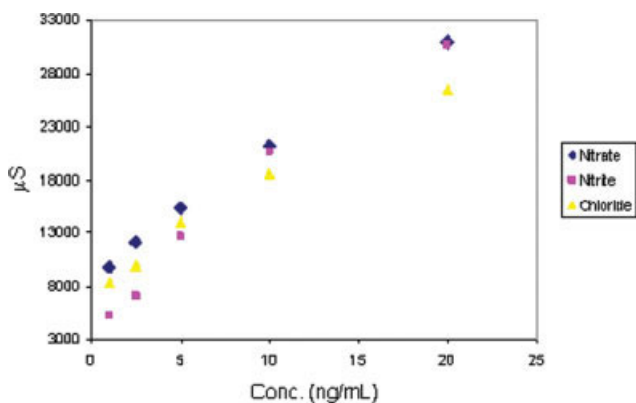


Figure 3 Calibration curves for Ion Chromatographic measurements of (\blacktriangle) Chloride, (\blacksquare) Nitrite and (\blacklozenge) Nitrate ions after EC-SPME process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

To determine the detector linearity for Cl^- , NO_2^- , and NO_3^- ions by using of this method, a series of standard solutions of these ions in the concentration range of 10^{-4} to 10^{-8}M were tested. Calibration curves were observed by measuring the peak height versus the concentration of each ion. Their correlation coefficients were between 0.977 and 0.995. From these results we concluded that PPy could reliably be used as an SPME element for anions such as Cl^- , NO_2^- , and NO_3^- . These values were obtained from IC by using aqueous samples of analytes. The results are summarized in Figure 3.

Effect of uptake and release time

Uptake and release time profiles of a given analyte of the coating element are critical factors that allow the extracting system to be used in ion chromatography. The transition of a specific analyte from the ma-

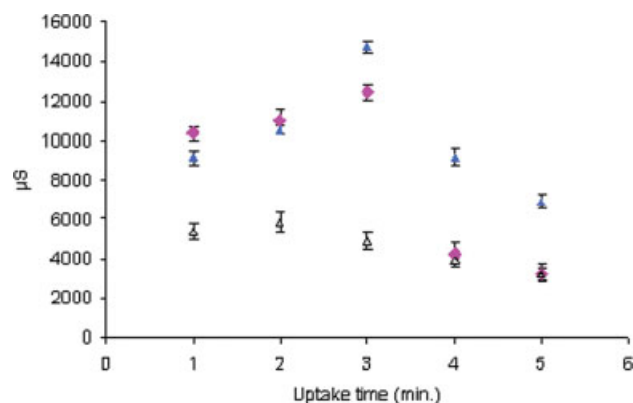


Figure 4 Uptake time profiles of 10 ng mL^{-1} of (\blacklozenge) Cl^- , (\triangle) NO_2^- , and (\blacktriangle) NO_3^- at PPy films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

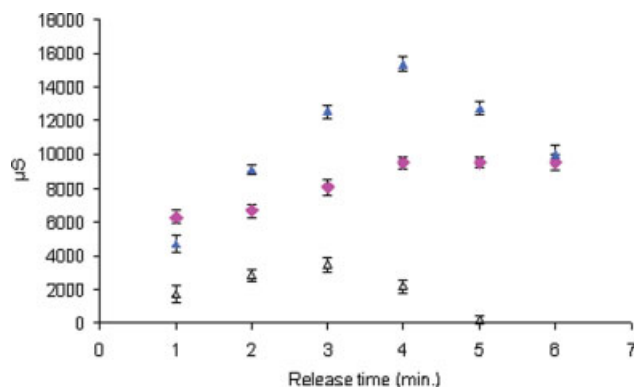


Figure 5 Release time profiles of 10 ng mL^{-1} of (\blacklozenge) Cl^- , (\triangle) NO_2^- , and (\blacktriangle) NO_3^- at PPy films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

trix into the extraction medium (i.e., the polymer film) should start instantaneously and terminate within a reasonable time. This is achieved when a rapid distribution equilibrium is established for the analyte at the solution/film interface. During all experiments, and, for simplicity, we will assume that the extraction time, is equivalent to the time needed to reach equilibrium at the coating/matrix interface for a given polymer film thickness. The uptake and release time profiles of 10 ng mL^{-1} of Cl^- , NO_2^- , and NO_3^- at PPy films are given in Figures 4 and 5, respectively. From the data depicted in Figure 4, an optimum time used for of Cl^- , NO_2^- , and NO_3^- uptake were 3, 2, and 3 min, respectively. The extraction time used in this work was kept 3 min. for Cl^- and NO_3^- ions and 2 min for NO_2^- ion, respectively. Figure 5 shows that the optimum times to be used for release Cl^- , NO_2^- , and NO_3^- were 4, 3, and 4 min, respectively. The film used in this study as SPME coatings, showed remarkable equilibration time (within minutes) for the analyte uptake and release.

Effect of uptake and release potential

Accumulation and release were achieved by the applied positive and negative potentials, respectively. The anion exchanger PPy electrode was oxidized and thus takes up Cl^- , NO_2^- , and NO_3^- ions from the solution. The accumulation and release process is based on the electrochemical oxidation and reduction of the PPy, respectively. In the anode, during the oxidation of polypyrrole, the positive charges were formed on the PPy chain and were used to extract the anions from the solution. In the cathode, the charge of the PPy changed to neutral form and then releases the anions. Anion-exchange ability of this film was found to be influenced by the applied uptake and release potentials. The positive charges

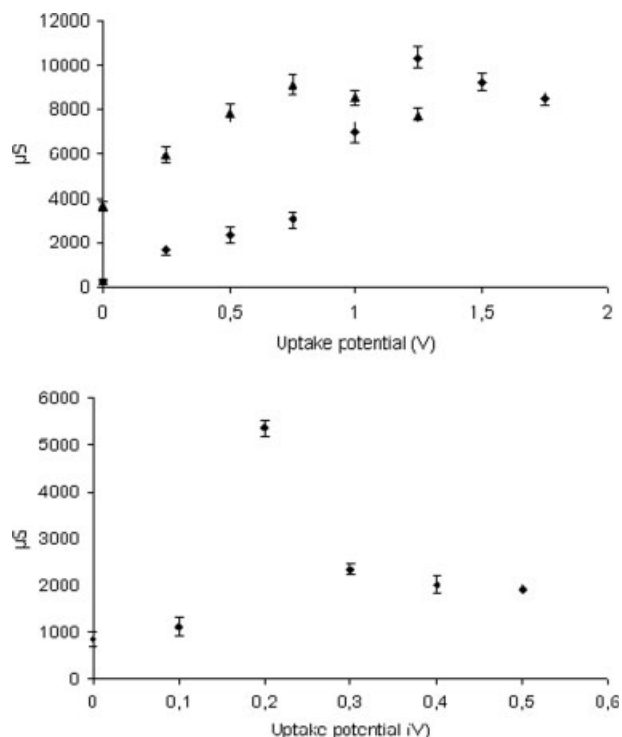


Figure 6 Uptake potential profiles of 10 ng mL^{-1} of (a) (\blacklozenge) Cl^- , (\blacktriangle) NO_3^- and (b) NO_2^- at PPy films.

of the PPy films were responsible for accumulation of anionic species. To determine the effect of uptake and release potential on the anion uptake and release capacity of the polymer film, different positive and negative potentials were applied during the extraction step for uptake and release of the ions, respectively. The uptake of the ions to the film was found to increase with increasing anodic potentials up to $+1.25 \text{ V}$, $+0.20 \text{ V}$, and $+0.75 \text{ V}$ (versus Ag/AgCl) for Cl^- , NO_2^- , and NO_3^- , respectively, [Fig. 6(a,b)]. There was considerable decrease in the yield of extraction below and above these potentials. Accumulation potential of $+1.25 \text{ V}$, $+0.20 \text{ V}$, and $+0.75 \text{ V}$ was found to give the highest responses for Cl^- , NO_2^- , and NO_3^- ions, respectively. The optimum release potential was found -0.50 V for all ions during the extraction step. Figure 7 shows the effect of the applied potential on the release of Cl^- , NO_2^- , and NO_3^- ions monitored by IC.

The pH of the uptake solutions has a significant influence on the extraction yield of the PPy film. Figure 8 illustrates the response of a polypyrrole modified electrode in a aqueous solution with LiClO_4 at different pH values. The signal of the polymer should be maximum to increase the uptake capacity of the film. Accumulation pH of 7 and 6 was found to give the highest responses for NO_2^- , NO_3^- , and Cl^- ions, respectively, while at more acidic and basic pH there was considerable decrease in the uptake capacity of the PPy electrode below and above this

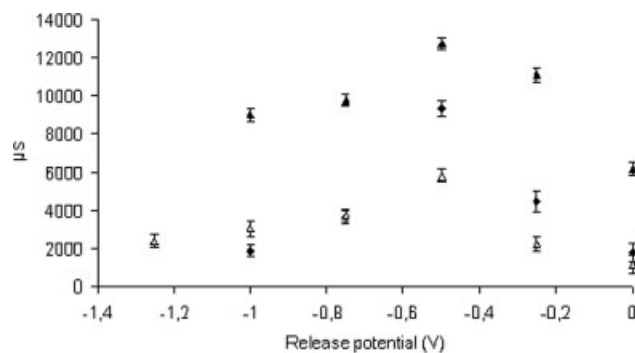


Figure 7 Release potential profiles of 10 ng mL^{-1} of (\blacklozenge) Cl^- , (Δ) NO_2^- , and (\blacktriangle) NO_3^- at PPy films.

pH values. Because of the competition between the acid anion and analyte anion, the extraction yield decreases in acidic medium. This competition increases with increasing of acid concentration (or decreasing pH value) of the uptake solution. Basic solutions are generally used for desorption of anions in an anion exchange process. The accumulated anions to the electrode surface desorbs into the extraction solution in basic medium. Therefore the optimum pH of the uptake solution was found to be 6 which are closed to neutrality. For this reason the pH of the medium in which the measurement with the polypyrrole-modified electrode was adjusted to 7.0.

Interference effects

The performance of the polymer film studied in this work was evaluated in presence of some potential interfering anions. Oxidation of conductive polymers produces positive charge on the polymer chains. The positive charges at polymer chain are balanced by the dopant anions. Accompany with the oxidation/reduction reaction, doping/dedoping process happens. The forces between positive polymer chain and dopant anions are determined by the size and the number of charges of the dopant anions. It can

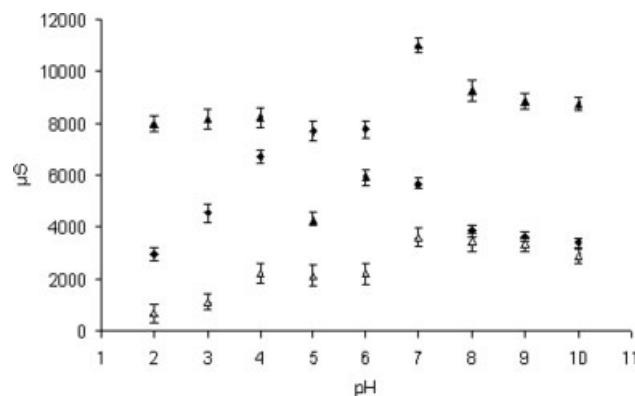


Figure 8 pH effect profiles on uptake solutions of 10 ng mL^{-1} of (\blacklozenge) Cl^- , (Δ) NO_2^- , and (\blacktriangle) NO_3^- at PPy films.

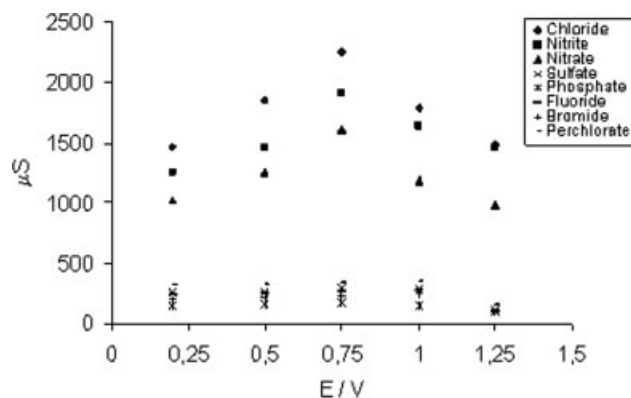


Figure 9 Relationship between the applied potential and extraction efficiency in a solution containing 10 ng mL^{-1} of Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , F^- , Br^- , and ClO_4^- anions at PPy films.

be predicted that the dopant anions that have higher charges will have much larger electrostatic forces than the ions that have lower charges. Thus coexisting anions will compete with the doping site with analyte ions.⁹ The response signal was found to decrease with increasing the high charge and concentration of the coexisting ions. The low doping degree of analyte ions also caused to decrease of the response signal. On the other hand, coexisting ions can increase the viscosity of the test solution, and thus decrease the amount of analyte ion comes to the electrode surface.⁹ Figure 9 shows the relationship between the applied potential and extraction efficiency in a solution containing 10 ng mL^{-1} of Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , F^- , Br^- , and ClO_4^- anions at PPy films. This figure indicates that the corresponding signal of analytes (Cl^- , NO_2^- , NO_3^-) is getting less with the presence of SO_4^{2-} , PO_4^{3-} , F^- , Br^- , and ClO_4^- . This can be explained by the decrease doping degree of Cl^- , NO_2^- , NO_3^- anions with the increase of the SO_4^{2-} , PO_4^{3-} , F^- , Br^- , and ClO_4^- . The decrease doping degree of Cl^- , NO_2^- , NO_3^- will result in the reduction of extraction yield.

The extracted amounts of anions are given in Table I. About 3.2 ng mL^{-1} of chloride, 6.8 ng mL^{-1} of nitrite, and 8.8 ng mL^{-1} of nitrate were extracted

TABLE I
Amount of Anions Extracted and Recovery Studies of Analytes using the PPy Film

Anion ^a	Amount of anion extracted (ng mL^{-1}) ^b	Recovery (%)
Chloride	3.2	32
Nitrite	6.8	68
Nitrate	8.8	88

^a Anion concentrations in the sample are 10 ng mL^{-1} .

^b The relative standard deviations (R.S.D.) are between 2 and 4% ($n = 3$).

from 10.0 ng mL^{-1} solution using polypyrrole doped LiClO_4 . As the concentration in the polymer should be proportional to the concentration in the sample solution, a larger extracted amount should be expected for a higher sample concentration. The extraction recoveries on the proposed method for the studied anions were found between 32 and 88% using the PPy film as shown in Table I. The extraction efficiency could be increased by using larger polymer electrode or different properties of the electropolymerized polypyrrole film. The obtained values showed good agreement with the certified values with good precision.

Real water samples

EC-SPME method was applied to the determination of Cl^- , NO_2^- , and NO_3^- anions in two different real water samples, Porsuk River (Eskisehir, Turkey) and tap water of Eskisehir, using IC method according to the procedure given in experimental section. To determine the extraction yield, first real water samples were analyzed by IC without any process (extraction, preconcentration, etc.). The water samples were only filtered before analysis. Second, after the EC-SPME step, an aliquot of final extraction were injected into the IC system. Finally, according to the obtained amounts of anions the extraction efficiency was calculated. The percentage of the extraction yields was given in Tables II and III. Nitrate was detected in both of two water samples. However nitrite was not detected in the water samples. Organic and/or inorganic molecules in water samples may make an interference and competition with analyte ions at PPy film. However, polypyrrole film has the potential to be employed as material for the EC-SPME purposes.

CONCLUSIONS

In conclusion, our preliminary fundamental results show that the use of electrochemically controlled polypyrrole film to obtain rapid (less than 5 min) extraction and determination of anions is suitable for

TABLE II
The IC Analysis of Porsuk River by PPy Film with and without EC-SPME

Anion	Amount of anion extracted on PPy ^a (ng mL^{-1})	Amount of anion ^a (without extraction) (ng mL^{-1})	Extraction yield (%)
Chloride	6.30	7.64	82.46
Nitrite	n.d.	n.d.	–
Nitrate	2.25	4.09	54.40

n.d.: not detected.

^a The relative standard deviations (R.S.D.) are between 2.7 and 4.5% ($n = 3$).

TABLE III
The IC Analysis of Tap Water by PPy Film with and without EC-SPME

Anion	Amount of anion extracted on PPy ^a (ng mL ⁻¹)	Amount of anion ^a (without extraction) (ng mL ⁻¹)	Extraction yield (%)
Chloride	7.90	11.78	67.06
Nitrite	n.d	n.d	–
Nitrate	2.42	9.86	24.54

n.d.: not detected.

^a The relative standard deviations (R.S.D.) are between 2.7 and 4.5% ($n = 3$).

future designing of the EC-SPME devices. The anion-exchange properties of the polypyrrole are used for imparting higher selectivity to measurements of anions in water samples. Further studies on the variations of polymer synthesis conditions, film thickness, linearity of response, and quantitative kinetics of uptake and release, etc. are underway. The developed method is straightforward and suitable for the extraction and analysis of anionic species in aqueous samples. This polymer film is a suitable device which has potential for EC-SPME applications.

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