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Electrochemically controlled solid-phase microextraction (EC-SPME) based on overoxidized sulfonated polypyrrole

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Abstract

A method for the extraction and selective determination of cations is proposed using electro-synthesized overoxidized sulfonated polypyrrole film. The polymer film is used for the selective extraction of trace levels of nickel and cadmium ions by solid-phase microextraction (SPME). The cation uptake and release properties of the overoxidized sulfonated polypyrrole film electrode were examined under both open circuit and controlled potential conditions for prospective applications in electrochemically controlled solid-phase microextraction. Increased extraction efficiency and selectivity toward cations were achieved in high saline content of water. Simple preparation of film coatings on a platinum wire was possible using a constant potential method. Applied positive and negative potentials facilitated the extraction and desorption of cations, respectively. Nickel and cadmium ions were desorbed into sample aliquot and determined by electrothermal atomic absorption spectrometry (ETAAS). The cation uptake and release mechanism is affected both by the cation exchange at the negative sulfonate and carboxylate moiety on the film and the altered solution pH occurring at the counter electrode caused by the applied potential. The method was validated using a standard reference material and tested for the determination of cadmium ion in commercial table salt samples.
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1. Introduction

Solid-phase microextraction (SPME) is based on the partitioning of the analyte between the extracting phase and the analyte matrix (water, air, etc.), In applying this method steps are often necessary in analysis of complex matrix samples to reduce the influence of interferences [1]. SPME has advantages of simplicity, low cost, ease of use and rapid preconcentration and extraction of analytes that exist in low concentrations. Extensive usage of organic solvents during the extraction step of traditional analytical procedures, the complexity of each individual matrices, and the limited availability of an analyte in confined finite volumes stimulated the use of SPME techniques [2]. In this respect, several studies demonstrated the successful application of SPME for the determination of ionic compounds using preconcentration cartridges [3], and fibers [4], polyurethane foams [5], C_{18} sorbents [6] and C_8/C_{18} polytetraethoxysilane/polydimethylsiloxane-coated fibers [7–9].

Electronically conducting polymers are of great interest not only because of their remarkable stability [10] but also for their growing usage in different analytical devices [11]. The electrochemical doping/undoping features of certain conducting organic polymer electrodes could be advantageous as SPME films for preconcentration and

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matrix separation of anionic [12,13], cationic [13–15] and neutral analytes [16,17]. Polypyrrole (PPy) and its derivatives, have attracted great interest in the development of electrochemically controlled solid-phase microextraction as ion exchange material for charged species [13,14,18]. 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.

Recent studies have proposed the use of overoxidized polypyrrole (OPPy) films for enhancing the selectivity towards cationics [19–21]. The overoxidized film works as a porous electrode coating, which has cation exchange and molecular sieve properties. It has been reported that, during overoxidation, polypyrrole loses most of its electroactivity due to ejection of dopant, and oxygen-containing groups such as carbonyl and carboxylate are introduced into the pyrrole unit [22–32]. The accumulative properties of the film for cationic species such as metal ions [33–35] and drugs [36,37] might also be attributed to the introduction of sulfonate moieties prior to overoxidation.

Preparation and characterization of the overoxidized sulfonated polypyrrole (OSPPy) film as solid-phase microextraction device was extensively described in a recent work from our laboratory [38]. This work describes a method for the use of electrochemical control of overoxidized sulfonated polypyrrole film to obtain rapid extraction and selective determination of trace levels of nickel and cadmium ions by electrothermal atomic absorption spectrometry (ETAAS). The cation exchange and anion exclusion properties of the overoxidized sulfonated polypyrrole are used for imparting higher selectivity to measurements of cations in the presence of high saline content of water. Sulfonation and overoxidation in the pyrrole ring lead to effective rejection of the anionic species and preferential collection of the cationic species. OSPPy film thus offers better discrimination against high saline content than overoxidized polypyrrole films alone. The developed method is straightforward and suitable for the extraction and analysis of cationic species in aqueous samples that contain elevated chloride concentration.

2. Experimental

2.1. Chemicals and reagents

Pyrrole (99%) was obtained from Aldrich (Milwaukee, WI, USA) and distilled before use. Fluorosulfonic acid (HSO_3F) was obtained from Aldrich (Milwaukee, WI, USA). Tetrabutylammonium tetrafluoroborate, sodium borohydride, sodium chloride, and other chemicals were purchased from Merck (Darmstadt, Germany) and were used as received. The ranges of concentration from standard cadmium and nickel solution (Titrisol Merck, 1000 mg/L) were prepared by appropriate dilution. All the chemicals used in this study were of analytical reagent or HPLC grade. All solutions were prepared by appropriate dilution from stock solutions using pre-distilled 18 MΩ deionized water produced by a Barnstead/Thermolyne water purification system (Dubuque, IA, USA).

2.2. Instrumentation and analytical conditions

All the electrochemical experiments were carried out on a potentiastat/galvanostat (model 362, EG&G Princeton Applied Research from Ireland). Polymer film formation was achieved in a conventional one-compartment three-electrode cell. Nitrogen pre-purged solution containing 0.1 M pyrrole monomer in 0.01 M $TBABF_4$/acetonitrile and 40 mM HSO_3F as sulfonation reagent. The sulfonated polypyrrole films were deposited on platinum working electrodes, (0.2 mm i.d. × 2.0 cm platinum wire) by applying a constant deposition potential. Growth of the films was controlled based on the amount of charge passed ($7\,C\,cm^{-2}$ resulting in a film of 300 μm thickness) [39]. Sulfonated films were overoxidized in 0.01 M aqueous NaCl solution applying a constant potential of 1.5 V for 30 min versus the reference electrode used. The overoxidation process was monitored by following current decay and continued until the current was leveled off.

A platinum wire (0.2 mm i.d. × 2.0 cm) was used as the counter electrodes and a pseudo Ag/AgCl electrode was employed as the reference electrode. The distance between the working and counter electrode was 3 mm. All data points reported in this work represent the average of three replicates. All experiments were run at room temperature. Table 1 summarizes the experimental conditions for the EC-SPME method presented in this work for Cd(II) and Ni(II) determination.

Determination of the released cation species was carried out by electrothermal atomic absorption spectrometry. An ATI Unicam 939 model atomic absorption spectrophotometer (Cambridge, UK) equipped with a UNICAM GF 90 electrothermal atomizer with FS 90 Plus autosampler and pyrolytic graphite-coated graphite tubes were used for the ETAAS measurements. UNICAM data-coded nickel and cadmium hollow cathode lamps were operated at 10 mA with a 0.2 and 0.5 nm spectral band pass, respectively. Deuterium background correction was used. The furnace temperature programs used are as follows. For nickel; drying with $10\,^{\circ}C\,s^{-1}$ ramp up to 120 °C and holding for 30 s, pyrolysis with $50\,^{\circ}C\,s^{-1}$ ramp up to 1000 °C and holding for

Table 1
Optimized operating conditions for SPME for Cd(II) and Ni(II) determination

SPME[a]	
Film formation	+1.5 V in ACN
Overoxidation	+1.5 V in 0.01 M NaCl
Uptake potential	+1.5 V
Uptake time	60 s for Cd(II), 180 s for Ni(II)
Release potential	−0.5 V in 0.01 M NaCl
Release time	60 s

[a] All applied potential is constant potential vs. pseudo Ag/AgCI reference electrode.

20 s, atomization at 2500 °C, for 3 s and cleaning at 2700 °C for 3 s. For cadmium; drying with 10 °C s^{-1} ramp up to 120 °C and holding for 30 s, pyrolysis with 50 °C s^{-1} ramp to 300 °C and holding for 20 s, atomization at 900 °C, for 3 s and cleaning step at 1200 °C for 3 s. The peak area of the signal was considered for the analysis using ETAAS.

Cadmium in commercial table salt samples was determined using flow injection cold vapor AAS as a comparison method.

2.2.1. EC-SPME of cations

To extract cations with overoxidized sulfonated film, the film was first washed with 0.01 M NaCl solution and water. It was then transferred to 10 mL sample of aqueous target solutions with high saline content for extraction, by applying a positive potential under stirred conditions (1 min for Cd and 3 min for Ni, respectively). After extraction, the electrode was washed with the 0.01 M NaCl solution and water, and then transferred to a small volume-vial (2 mL) containing 1 mL of 0.01 M NaCl solution where the analyte was released negative potential versus reference electrode for 60 s. Uptake and release potentials were 1.5 and −0.5 V, respectively. The influence of carryover of the sample solution was reduced by washing the coating with 0.01 M NaCl solution and pure water after each extraction process, and then immersing it in 1 mL of 0.01 M NaCl solution for desorption. The effect of the solution pH, the uptake and release of the cations was investigated by adjusting the SSpH with Britton–Robinson buffer solutions.

2.2.2. Procedure of cold vapor AAS

Two parallel solutions, 20% (w/v) from each table salt, were dissolved in deionized water. A series of standard addition solution were prepared by adding 8 mL of sample solution, appropriate amount of cadmium standards and 0.7 M HCl. Then final solution was diluted to 10 mL. Two hundred and fifty microlitres of the sample or the standard was injected into the carrier stream. Peak height of the signal was used for quantitation.

3. Result and discussion

In a previous work, electrochemically overoxidized and sulfonated polypyrrole films were prepared and characterized [38]. Rapid accumulation and/or release were achieved by the applied positive and negative potentials, respectively. Cationic exchangeability of this film was found to be influenced by the applied uptake and release potentials and the solution pH during uptake and release processes. The existence of the negatively charged sulfur-containing groups was proven by EDAX spectra. The surface morphologies of OSPPy and PPy films were compared by SEM measurements. It was concluded that sulfonation followed by overoxidation led to the formation of more compact surface morphology. These films were more robust and adherent after sulfonation followed by overoxidation. The negatively charged and covalently bounded carboxylate and sulfonate groups were responsible for rapid accumulation of cationic species such as Ni(II) and Cd(II) ions. The cation uptake capacity of this film was enhanced considerably when a positive potential was applied during the extraction step.

The pH value of the solution which is determined by the production of either OH^- or H^+ ions at the auxiliary electrode during accumulation and release of cationic species also was a critical factor in the use of the film as cationic permselective device. Decreasing pH results in the exchange of H^+ ions with the accumulated cations causing a rapid release of the latter. Similar behavior was observed in the ion exchange electrochemical deionization system constructed by anion-exchangeable and cation-exchangeable polypyrrole electrodes as proposed by Shimidzu et al. [40]. It is interesting to note that non-sulfonated overoxidized polypyrrole film did not accumulate the cations at all from aqueous solutions with high salinity under the same experimental conditions. It must also be emphasized that the non-sulfonated overoxidized polypyrrole film is very fragile and has powdery characteristics which is not suitable for the accumulation purpose. Sulfonated non-overoxidized polypyrrole film on the other hand, is very compact and but has non-porous structure which limits the surface area.

The conductivity and electroactivity of the overoxidized film decrease considerably. Nevertheless the remaining electroactivity is apparently sufficient to be operative for the cation uptake.

3.1. Effect of uptake/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 SPME/ETAAS [7,41]. Simplicity of preparation and convenience of the use make SPME a better analytical method for micro- and sub-micromolar matrices. Therefore, the transition of a specific analyte from the matrix 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.

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. Fig. 1 shows the effect of the polymer thickness on the extracted amounts of Ni(II) and Cd(II) ions. The polymer film thickness influences the extraction efficiency due to the increased surface area. The thickness is highly effective on the surface area up to a certain value due to the porous structure of the film. After a certain thickness value diffusion limitation starts to limit the extraction amount.

It is clear that as the film thickness increases, the sensitivity will also increase. Thicker coatings have, therefore, higher

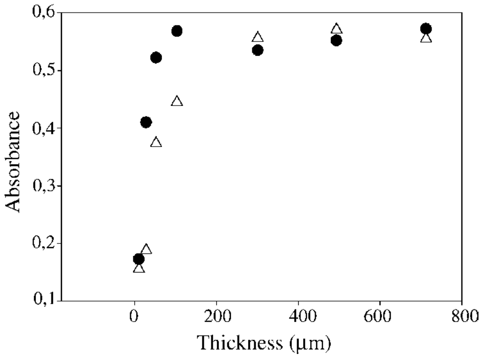

Fig. 1. Effect of changing the polymer film thickness on the ET-AAS signal intensity (●) 70 ng mL^{-1} of Cd(II) and (△) 300 ng mL^{-1} of Ni(II) ion.

ion exchange capacity and result in larger dynamic range before the coating becomes saturated. The polymer coatings used in this study (300 μm) are significantly thicker than the poly(3-methylthiophene) film used by Gbatu et al. [12] and polypyrrole/*p*-toluenesulfonic acid film used by Liljegren et al. [18].

Thicker polymer coatings would also be little affected by an irreversible loss of some of the ion exchange sites upon successive extraction and desorption, which could improve the reproducibility of the extractions. The single film reproducibility of the EC-SPME analysis for Cd(II) ions was calculated over ten analysis and yielded a %R.S.D. of 4.74. This level of reproducibility was a great improvement compared to a previously evaluated conductive film, which showed conformational and extraction efficiency changes over several extraction and release cycles [12,13,18].

The fraction of the polymer involved in the extraction and release steps depends on the mobility of the ions within the polymer, as well as the time scale of the experiments. During all experiments, 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/release time profiles of 50 ng mL^{-1} of Cd(II) and 240 ng mL^{-1} of Ni(II) at OSPPy films are given in Fig. 2. From the data depicted in Fig. 2A, the optimum time used for Cd(II) and Ni(II) uptake was 60 and 180 s, respectively. The extraction time used in this work was 60 s for Cd(II) ions and 180 s for Ni(II) ions, respectively. Fig. 2B shows that the optimum time to be used for release of Cd(II) and Ni(II) was 60 s. The film used in this study as SPME coatings, showed remarkably short equilibration time (within minutes) for the analyte uptake and release. Furthermore, it is worth noting here that these extremely short uptake and release times were attained by the applied potential because of the changing solution pH.

3.2. Interference effects

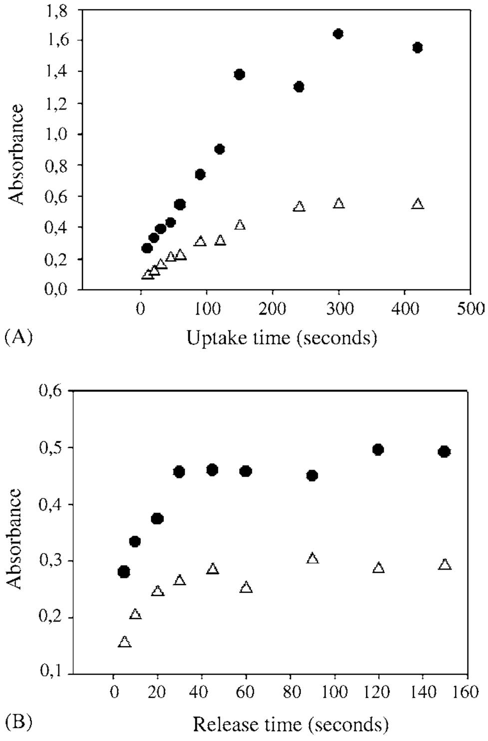

Fig. 2. (A) Uptake time profiles of 70 ng mL^{-1} of (●) Cd(II) and 300 ng mL^{-1} of (△) Ni(II) at OSPPy films (60 s release time were used in both cations). (B) Release time profiles of 70 ng mL^{-1} of (●) Cd(II) and 300 ng mL^{-1} of (△) Ni(II) at OSPPy films (uptake times for Cd(II) and Ni(II) are 60 and 180 s, respectively).

It is important to differentiate between two types of interference events, the first during the uptake step and the second during the ETAAS measurement. The performance of the polymer film studied in this work was evaluated in presence of some potential-interfering cations and anions. For instance analysis of sea water and dialysis concentrates cannot be directly carried out by ETAAS due to the high saline composition of the matrix, which produces a high background signal. The usual practice of diluting sample aggravates the problems and leads to poor results. Even modern AAS instruments, including the Zeeman background correction system or the transversely heated graphite atomizer, do not overcome the problems caused by the presence of elevated chloride concentration and therefore do not eliminate the necessity of sample pretreatment. An important conclusion for this part of the present work is the possible determination of cations directly from water in the presence of high concentration of chloride. On the other hand, cationic interferences during the uptake step may be more pronounced when compared to the determination step. In this respect, we investigated the possible interferences for Cd(II) and Ni(II) ions determination by Cl^{-} from NaCl, and by NO_3^{-} from KNO_3. The interference effects are illustrated in Fig. 3. As could be noted from the Fig. 3, ETAAS signals of Cd(II) and Ni(II) ions remain constant throughout a wide range of concentrations of NaCl up to 1.5 M NaCl. The decrease of the signal after this concentration is apparently caused by competition of Na^{+} cations resulting in a lower uptake efficiency for Cd(II) and Ni(II) ions. Similar behavior is observed in KNO_3 matrix. These

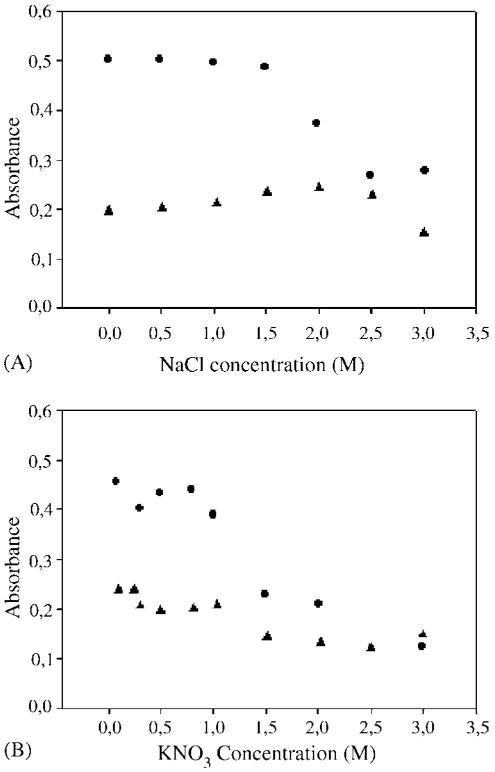

Fig. 3. The effect of various matrices on (●) 70 ng mL^{-1} of Cd(II) and (▲) 300 ng mL^{-1} of Ni(II) ET-AAS signal. Uptake potential: +1.5 V; release potential: −0.5 V; uptake and release time: 60 s. Matrix used (A) NaCl and (B) KNO$_3$.

Table 3
Amount of cations extracted using the OSPPy film

Cation[a]	Amount of cation extracted (ng)	R.S.D. (%)
Cadmium	2.33	7.49
Nickel	4.49	8.71

[a] Cation concentration in the sample: cadmium (10 ng mL^{-1}), nickel (40 ng mL^{-1}) in 0.5 M NaCl solution ($n = 5$). Uptake volume 10 mL and release volume 1 mL.

Table 4
Recovery studies of cadmium ion

Cadmium content (ng mL^{-1}) in 0.5 M NaCl		
Added	Found	% Recovery
10	11.4	105 ± 9
10	11.3	
10	9.6	
10	9.4	
10	10.7	

results were achieved in matrices far more concentrated than conventional ETAAS can handle. The direct determination of trace metals in sea water by using chemical modification (to stabilize the analytes and to remove the matrix from the sea water) and background correction is a possibility to be considered at only relatively low salt concentrations [42].

Calibration curves (constructed by spiking of Cd and Ni to the extraction matrice) for OSPPy and their corresponding figures of merit are listed in Table 2. From these results we concluded that OSPPy could reliably be used as an SPME element for cations such as Ni(II) and Cd(II). The detection limits in this work are those of ETAAS. Furthermore these values were those obtained with aqueous samples with high salinity for which ETAAS detections are limited due to interferences.

The extracted amounts of cations are given in Table 3, for an extraction potential of +1.5 V versus pseudo Ag/AgCl reference electrode. These amounts can be compared to the 210 pg of arsenate previously extracted from a 0.1 ppm solution by Gbatu et al. [12] using a poly(3-metylthiophene) coating and 0.02 μg of Cd, Co, Zn extracted from 1 ppm solution by Liljegren et al. [18] using polypyrrole doped with *p*-toluenesulfonic acid. 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 higher extraction efficiency found in the present work could be explained by the fact that Liljegren et al. used a much thinner polymer film with less efficient mass transport during the accumulation step [43] or by different properties of the electro-polymerized polypyrrole film doped with *p*-toluenesulfonic acid.

Recovery studies on the proposed method were performed by analyzing spiking sample of the different concentration of high saline content water with appropriate amount of the stock solution of Ni(II) and Cd(II) ions as shown in Tables 4 and 5. The large scatter in the recovery values in Tables 4 and 5 are arranged randomly and were obtained with different film coatings. They are not repetitive values obtained with the same coating.

3.3. Analysis of standard reference material

We evaluated the performance of coated polymer material (SOPPy) in the waste water standard reference material (EU-L1 waste water, SCP-Canada) containing cadmium

Table 2
Figures of merit for EC-SPME, ETAAS of calibration curves for OSPPy as coating

Figure of merit	Linear range[a] (ng mL^{-1})	Slope	Intercept	R^2	%R.S.D.[b]	Limit of detection[c] (ng mL^{-1})
Nickel	30–300	1.76×10^{-3}	−0.0126	0.9916	7.95	3.1
Cadmium	7–80	20.0×10^{-3}	−0.0231	0.9929	6.03	0.74

All data points represent the average of five replicates.

[a] Based on linear plot of concentration vs. ETAAS signal.

[b] %R.S.D. calculated from five separate experiments.

[c] Three times of the standard deviation of blank measurements.

Table 5
Recovery studies of nickel ion

Nickel content (ng mL^{-1}) in 0.5 M NaCl		
Added	Found	% Recovery
40	40.9	
40	46.0	
40	42.7	103 ± 8
40	38.2	
40	38.0	

Table 6
Comparison and analysis results of commercial table salt samples by EC-SPME–ETAAS and cold vapor AAS

Cadmium content (ng g^{-1}) in commercial table salt samples		
	EC-SPME–ETAAS	Cold vapor AAS
Sample A	2.8 ± 0.3	2.4 ± 0.3
Sample B	2.5 ± 0.3	2.8 ± 0.1

and nickel ions. The certified metal ions contents in this material were 60 ± 2 and 200 ± 4 ng mL^{-1} for cadmium and nickel ions, respectively. Other metal ions present in the 30–10000 ng mL^{-1} range included Al, As, B, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, P, Pb, Sb, Se, Sr, Tl, V, and Zn. To avoid adsorption and complexation of organic species arising from the waste water matrix, reference waste water sample was boiled in concentrated nitric acid to destroy the organic species in the sample. After appropriate dilution, EC-SPME procedure was carried out and ETAAS signals were recorded under the same experimental conditions and calibration plots were attained. The concentrations of Cd(II) and Ni(II) ions in the standard waste water reference material were observed as 62.64 ± 5.42 and 188.89 ± 17.09 ng mL^{-1}, respectively. The obtained values showed good agreement with the certified values with good precision.

3.4. Analysis of commercial table salt samples

Cadmium ion was determined in two different commercial table salt samples using both EC-SPME–ETAAS and cold vapor AAS methods according to the procedure given in Section 2. However, 120 s uptake time was employed to obtain the required quantitation for cadmium ion in 3% (w/v) commercial table salt samples. Detection limit was achieved as 4 pg for 120 s uptake time of cadmium ion. Table 6 compares the results of cadmium found in commercial table salt samples by standard addition method using both EC-SPME–ETAAS and cold vapor AAS methods. The values obtained with EC-SPME–ETAAS method were in good agreement with those obtained by cold vapor AAS method.

4. Conclusion

The results of the present study clearly show that overoxidized sulfonated polypyrrole films seem to be a promising SPME system, possessing high selectivity for cations as well as straightforward synthetic procedures, irrespective of the degraded nature of an overoxidized sulfonated polypyrrole as a coating material. As the present technique allows potential controlled steps from the extraction step to the release step the described approach offers increased control over the whole extraction procedure. We have also demonstrated that increasing the electrostatic character of overoxidized polypyrrole films provides higher selectivity in analysis of cations in the presence of excess chloride ion. The selectivity of the method toward cations in the presence of anionic species is explained in terms of the change in the negatively charged nature of the film during sulfonation and overoxidation processes.

In conclusion, the electrochemical control of the potential applied to the polymer coating such as OSPPy, containing solfonate and carboxylate groups, does accelerate the rate of the uptake and release of cations, like Ni(II) and Cd(II). Thus, potential switching should be adaptable to the microfiber polymer films for future designing of the EC-SPME devices.

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