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Electrochemically Aided Control of Solid Phase Micro-Extraction (EASPME) Using Conducting Polymer-Coated Solid Substrates Applicable to Neutral Analytes

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Abstract. A method for the extraction and selective determination of the neutral species arsenobetaine (AsB) is proposed using electro-synthesized organic conducting polymer (OCP) films. The polymer films are used as solid phase micro-extraction (SPME) elements for the direct and specific extraction of trace levels of AsB. The separation and detection of the arsenic (As) species is attained using an HPLC-ICP-MS interfaced system. The selectivity of the method towards neutral AsB in the presence of other anionic As-species is explained in terms of the change in the hydrophobic nature of the film during the doping/undoping processes. The type of OCP, the thickness of the film, the applied potential during uptake and release of AsB are among the factors studied for the method. The uptake and release time/potential profiles are given, and a thermodynamic model is proposed. The performance of poly(3-octylthiophene), poly(3-dodecylthiophene), and poly(3-hexadecylthiophene) films were compared, with the best results obtained using poly(3-octylthiophene). The detection limit and linear dynamic range using this method are 14 ng mL^{-1} and 70–1200 ng mL^{-1}, respectively. The method was validated using a standard reference material and tested for the determination of AsB in artificial environmental soil samples.

Key words: Solid phase micro-extraction; arsenic; arsenobetaine; speciation; organic conducting polymers; trace-analysis; HPLC-ICP-MS.

Interest in the speciation and determination of arsenic-species in different sample matrices, namely marine organisms [1], soil [2], sewage sludge [3], drinking water [4], mine waste-influenced emergent wetlands [5], and natural waters [6] has been growing in the last few years. Concerns have also arisen regarding the bioavailability and transformations of As in these matrices. For instance, the influence of As compounds (as total As concentration) contained in the soil on plant yield has been reported [7]. In addition, a considerable amount of sewage sludge (including incineration ash) is disposed of in landfills, and subsequently a fair amount of this material is then reused as fertilizers or construction materials [3]. Recent diet studies conducted in different locations around the world have shown a reasonable estimate of the mean dietary intake of total As for humans aged 12 and above to be 34–40 μg/day [8–10]. Arsenic is mobile in many groundwater environments, and the potential for transport of As from

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tailings impoundments into groundwater systems is also of environmental concern [11]. Among the analytical systems used for As speciation/determination are those adopting ion (-exclusion) chromatography [12] and micellar liquid chromatography [13]. Several detecting systems were also employed, such as inductively-coupled plasma/mass spectrometry (ICP-MS) [13], inductively-coupled plasma/atomic emission spectrometry (ICP-AES) [14], heated quartz-cell atomic absorption spectroscopy (AAS) [15], and electrochemistry [16]. Extensive usage of organic solvents during the extraction step of a given analytical procedure, the complexity of each individual matrix, and the limited availability of an analyte in a confined finite volume stimulated the use of SPME techniques [17]. In this respect, several studies demonstrated the successful application of SPME for the determination of As using anionic pre-concentration cartridges [18] and fibers [19], polyurethane foam [20], C_{18} sorbents [21], and C_8/C_{18} polytetraethoxysilane/polydimethylsiloxane coated fibers [22–24].

On the other hand, electrically conducting polymers continue to inspire scientists not only because of their remarkable stability [25] but also for their growing usage in different analytical devices [26]. However, it was demonstrated only recently that this class of synthetic polymers can be employed for ionic arsenic pre-concentration/speciation as SPME devices [27, 28]. In a recent preliminary publication [29] we proposed the use of poly(3-dodecylthiophene) for the electrochemically aided SPME of arsenobetaine. In the present follow-up work, we will address the following issues: (i) the selective determination of neutral arsenobetaine in the presence of other anionic arsenic species, (ii) the comparison of the performance of different ''long chain 3-alkyl substituted poly(thiophenes)'' as SPME devices, (iii) study of the different parameters, such as film thickness, uptake/release time of analyte, applied potential, percent recovery, interferences and figures of merit for the speciation method, (iv) the distribution of analyte between the sample matrix and the polymer film, and (v) validating the organic conducting polymer OCP/SPME method for AsB using a certified standard reference material.

Experimental

Instrumentation

A voltammetric analyzer CV-50W from Bioanalytical Systems Inc. (West Lafayette, IN) was used for the electro-synthesis and electrochemical characterization of the polymeric films, and also for the effect of applied potential on the analyte uptake experiment. An ISO-2000 isocratic HPLC pump from Chrom. Tech. Inc. (Apple Valley, MN), a Hamilton PRP-X100 anion exchange column (250×4.1 mm) and a Rheodyne injector with 200 µL injection loop were used for the separation of all the species studied. The chromatographic system was interfaced to a Perkin Elmer Elan 6000 ICP-MS for the detection of As species. Scanning electron micrographs were obtained by a Phillips XL30 from FEI Co. (Peabody, MA) using 5 kV beam energy. This instrument was equipped with an energy dispersive analyzer (EDAX) from Phoenix (Mahwah, NJ).

Chemicals, Solutions and Sample Preparation

Octyl-, dodecyl-, and hexadecyl-thiophene were purchased from Aldrich (Milwaukee, WI). All other chemicals used throughout this study were of analytical reagent grade. HPLC grade solvents were purchased from Fisher Scientific (Fairlawn, NJ) and used without further purification. Arsenobetaine was prepared by Mike Fricke (Department of Chemistry, University of Cincinnati, Cincinnati OH). All solutions were prepared by appropriate dilution from stock solutions using pre-distilled 18.2 MΩ de-ionized water produced by a Sybron/Barnstead system (Dubuque, IA). Purified nitrogen (99.998%) from Wright Brothers (Cincinnati, OH) was used for oxygen purging of solutions. Arsenobetaine stock solution had a concentration of 1000 mg L^{-1} in de-ionized water. Tap water samples were obtained from a lab at the University of Cincinnati. The uptake (accumulation) step consisted of dipping the polymer film in a 5.0 mL sample of aqueous arsenobetaine solution. The release was accomplished by placing the polymer film into a three-electrode cell containing 250 µL de-ionized water, a pseudo Ag reference electrode and a platinum wire auxiliary electrode. The potential measured during a long sequence of experiments using a pseudo Ag reference electrode does not change significantly and exhibits a 20–30 mV difference with respect to the Ag/AgCl electrode. A platinum wire ($2.0\,cm \times 0.20\,mm$, net dimensions) was used for polymer deposition and arsenobetaine extraction. A platinum sheet ($1.5 \times 1.5\,cm^2$) was also used as noted in the text for some polymer

Table 1. Operating conditions for SPME-HPLC-ICP/MS for AsB speciation and detection

SPME
- Film formed in 40 cycles, between +0.20 V and +2.00 V (100 mV/s).
- Uptake time: 60 s (with no potential applied)
- Release time: 60 s (with +1.50 V applied, vs. pseudo Ag reference) in H_2O.

HPLC
- Column: Hamilton PRP-X100 anion exchange (250×4.1 mm).
- Rheodyne injector with 200 µL injection loop.
- Mobile phase: 30 mM $(NH_4)_2CO_3$ (pH = 8.70).
- Pump flow rate: 1.10 mL min^{-1}

ICP/MS System
- Rf power: 1200 W
- Plasma gas flow rate: 10 L min^{-1}
- Auxiliary gas flow rate: 1.0 L min^{-1}
- Nebulizer gas flow rate: 900 mL min^{-1}
- Measurement mode: dual
- Replicate times/ms: 100
- Scan mode: peak hop

film deposition and examination with SEM. A 30 mM $(NH_4)_2CO_3$ solution (pH = 8.70) was used as the elution phase (flow rate = 1.10 mL/min) for the HPLC separation of arsenic species. All data points reported in this work represent the average of three replicates. Polymer film formation was achieved in a conventional one-compartment three-electrode system and a N_2 pre-purged solution containing monomer. The working platinum substrate was subjected to repeated cycles of potential $E_i = +200$ mV, $E_{max} = +2000$ mV at a scan rate of 100 mV/s. All potentials were reported versus Ag/AgCl unless otherwise stated. All experiments were run at room temperature (ca. 25 °C ± 0.1 °C). Table 1 summarizes the experimental conditions for the SPME, HPLC, ICP/MS methods presented in this work for AsB determination.

Results and Discussion

Poly(3-alkylthiophenes) are conducting polymers that are not ''conductive'' without doping [30]. In the doping process, charge carriers are introduced into the chain. For each charge transferred into the thiophene chain backbone, a counter ion ''inclusion'' to the polymer film guarantees overall charge neutrality [30] (c.f. Fig. 1).

On the other hand, the presence of a relatively long side chain within the polymer increases the hydrophobic property of the film. Moreover, poly(3-alkylthiophene) should be stable in both ''doped'' and neutral forms in aqueous media due to the fact that the oxidation and reduction potentials lie between those of O_2 reduction and H_2 oxidation values [31].

Polymer Film Formation

Typical repeated cyclic voltammograms (CVs) (ca. 40 cycles, scan rate 100 mV/s) of a platinum wire (1.0 cm × 200 μm) working electrode in 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) and 0.05 M 3-octylthiophene (OT)/acetonitrile (AcN) are given in Fig. 2. The relative increase in current values for the forward and reverse directions of the CV indicates film thickening. Apart from the first cycle, a trend is observed where the broad oxidation potential peak shifts to a less positive value while the reduction potential peak shifts to more negative value, showing characteristic behaviour of conducting polymers. This can be explained in terms of the catalytic property of the film during the first cycle, and upon which successive layers are added [32]. A similar procedure for film formation was also followed with 3-dodecylthiophene (DDT) and 3-hexadecylthiophene (HDT). It is very important to note that for all films the respective last scan always ended at a final potential value (E_f) of +0.20 V, thus ensuring that the film was left in the neutral reduced state prior to the extraction step.

System Optimization

HPLC and plasma parameters were tuned on a daily basis. For all As measurements, the base ion chosen for mass detection was m/z = 75. The parameters for optimization of mass detection conditions were adopted from previous work [27, 29], and a summary of these values is given in Table 1.

Effect of Changing Type of Polymer on the SPME Performance

The hydrophobic/hydrophilic character of the polymer film plays a key role in the uptake/release processes [29]. However, these processes are also influenced by the overall nature of the polymer, i.e. ionic exchangeability [28, 33], the surface morphology, the side chain on the monomer, and film thickness. The results of the influence of varying the type of polymer (i.e. chain length of the 3-alkyl substituent on the monomer) on the recovery data of AsB are presented in Table 2. Poly(3-octylthiophene) (POT), poly(3-dodecylthiophene) (PDDT), and poly(3-hexadecylthiophene) (PHDT) were formed as described in the above sections on the platinum wire. It is important to note that their corresponding SEM micrographs,

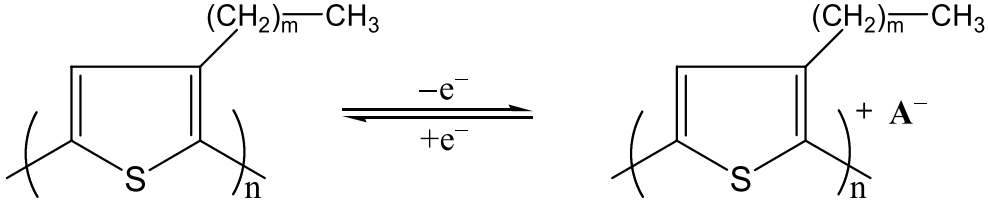

Fig. 1. Oxidation/reduction of poly(3-alkylthiophenes). m = 7, 11, 15 (octyl-, dodecyl-, hexadecyl-) A^-: counter anion

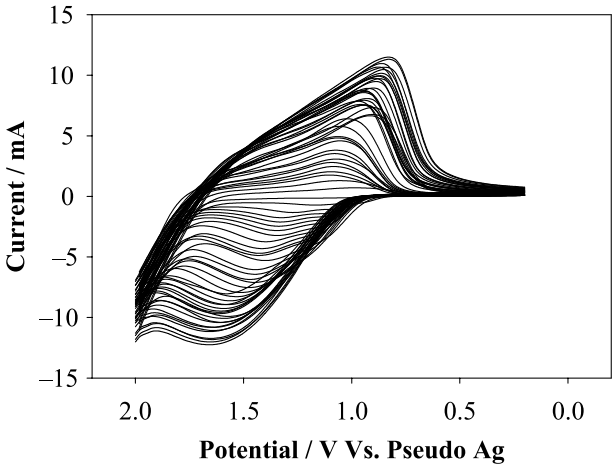

Fig. 2. Repeated cyclic voltammograms of 0.05 M OT, and 0.1 M TBATFB in AcN, and formation of polymeric film

depicted in Fig. 3a, b, and c, respectively, show an entirely different morphology, thickness, etc. for the 3 films. Inspection of the data in Table 2 reveals the following: (i) the average uptake of AsB from solution for the three polymers followed the order PHDT $\approx$ PDDT $>$ POT, with values of 108 ng μL^{-1}, 107 ng μL^{-1}, and 87 ng μL^{-1}, respectively; (ii) the lowest uptake % RSD of the three was obtained for POT. POT was chosen because the film was of greater mechanical stability. This could be attributed to the reproducibility in film formation of POT when compared to PDDT and PHDT. Comparison of the SEM of the three polymers, as presented in Fig. 3, revealed uneven and incomplete surface coverage of the platinum substrate in the case of PDDT and PHDT. However, the recovery data also showed a remarkable capacity for all the films studied in this work.

Effect of Uptake/Release Potential and Time on the Speciation of AsB

Uptake and release profiles of a given analyte to and from the coating element are critical factors, the values of which allow the extracting system to be used as an interface in an SPME/HPLC [22, 33]. Simplicity of preparation and convenience of use make SPME a better analytical solution for micro- and sub-micromolar matrix concentrations. 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 period of time. This is achieved when the distribution equilibrium is established for the analyte at the solution/film interface. Therefore, in a treatment analogous to that described by Mester et al. [17], a thermodynamic model can be devised for the polymer system under investigation. Thus, the total amount of analyte in the sample matrix phase is given by:

$$C_i V_m = C_c V_c + C_m V_m \tag{1}$$

where C_i is the initial concentration of analyte in the matrix, C_c and C_m are the equilibrium concentrations in the coating and matrix, respectively. V_m and V_c are the volumes of the coating and the matrix, respectively. The distribution coefficient of analyte at the coating/matrix interface, K_{cm}, is expressed by the following relation:

$$K_{cm} = \frac{C_c}{C_m} \tag{2}$$

and the amount of analyte extracted by the film coating is:

$$n_c = C_c V_c = C_i V_m - C_m V_m \tag{3}$$

Table 2. Effect of changing the type of polymer coating on the recovery data of AsB

Polymer[a]	Arsenobetaine/ng mL^{-1}				
	Added	Found	Average	Recovery %	% RSD (n = 3)
POT	100	84.20	87.47(±2.88)	84.20	3.52
	100	91.20		91.20	
	100	87.00		87.00	
PDDT	100	102.4	107.5(±6.30)	102.4	7.71
	100	116.4		116.4	
	100	103.8		103.8	
PHDT	100	58.33	108.1(±53.15)	58.33	65.1
	100	84.19		84.19	
	100	181.8		181.8	

[a] For each 100 ng addition, a new/freshly prepared polymer film was used.

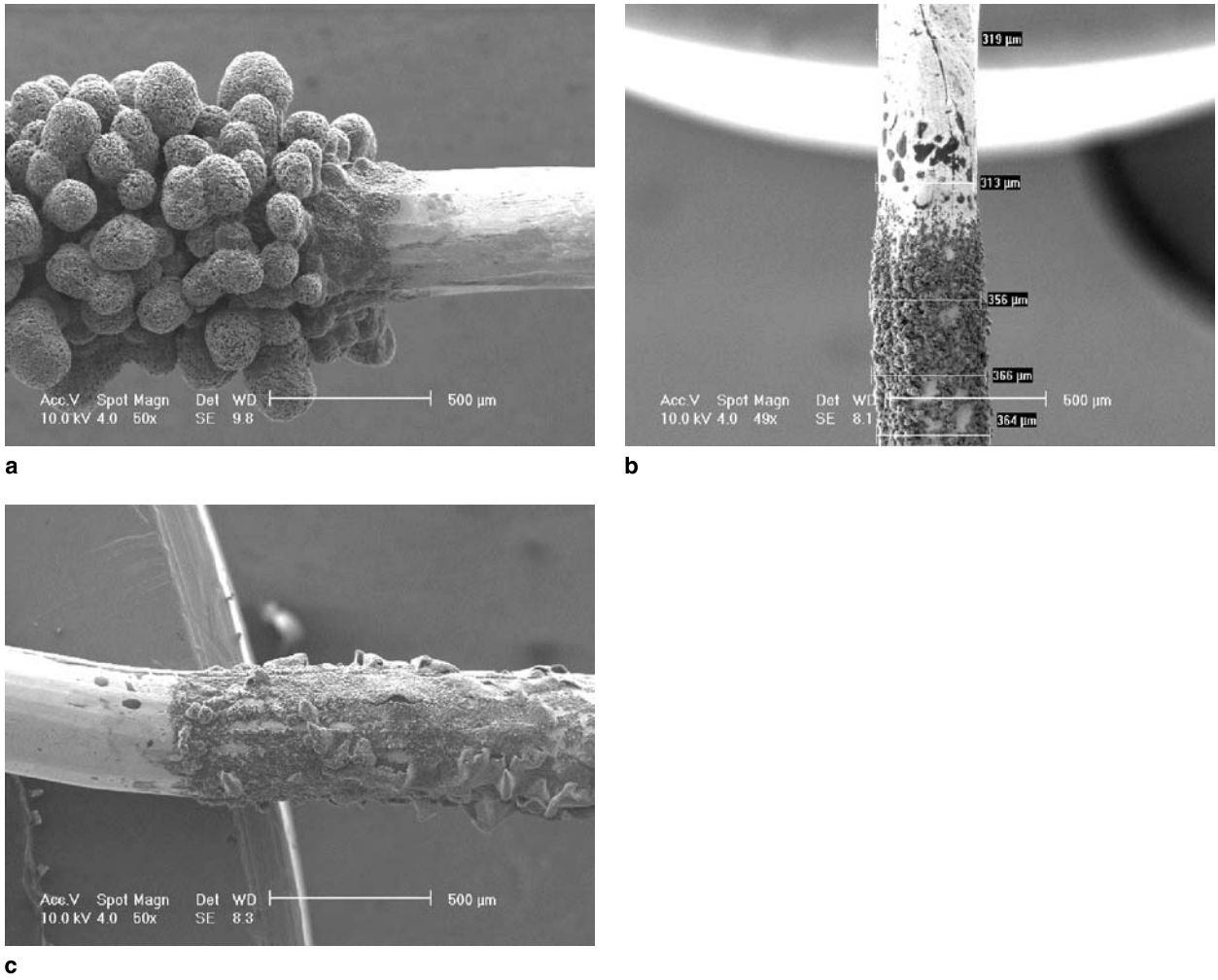

Fig. 3. SEM micrographs of POT (a), PDDT (b) and PHDT (c), formed on Pt wire (200 µm-diameter)

Using equations (1) and (2), equation (3) is rearranged to:

$$n_c = K_{cm} C_m V_c \tag{4}$$

It can be noted from equation (4) that the amount of analyte taken up on the film coating is a function of the distribution coefficient, concentration of analyte in matrix, and volume of coating (polymer film in this case). Equation (4) can be rewritten as:

$$n_c = K_{cm} \frac{V_c}{V_m} (C_i V_m - C_c V_c) \tag{5}$$

If we consider that the matrix volume is in most cases much larger than that of the coated polymer film, i.e. $V_m \gg V_c$, then equation (5) reduces to:

$$n_c = K_{cm} C_i V_c \tag{6}$$

An important conclusion is obtained from equation (6); that the amount of analyte extracted onto the polymer coating layer is independent of the matrix volume. It is also important to note here that the film thickness does not grow in a linear fashion with respect to the number of cycles in the CVs. On the other hand, the volume of the coating (accessible for analyte extraction) should be crucial to the thermodynamic limitation of the extraction process. The SEM pictures of Fig. 3a, b and c showed that surface regularity of the polymer film is in the order POT > PDDT > PHDT. The degree of regularity that the surface morphology possesses will affect the response behavior of the SPME determination of AsB. Figure 4 depicts the relationship of matrix volume of the film coating (V_c) to the amount extracted (n_c) for POT (cf. Fig. 4a) and PDDT (Fig. 4b), which, in agreement with the increase in film thickness, is represented by the increase in the number of cycles used during film formation (cf.

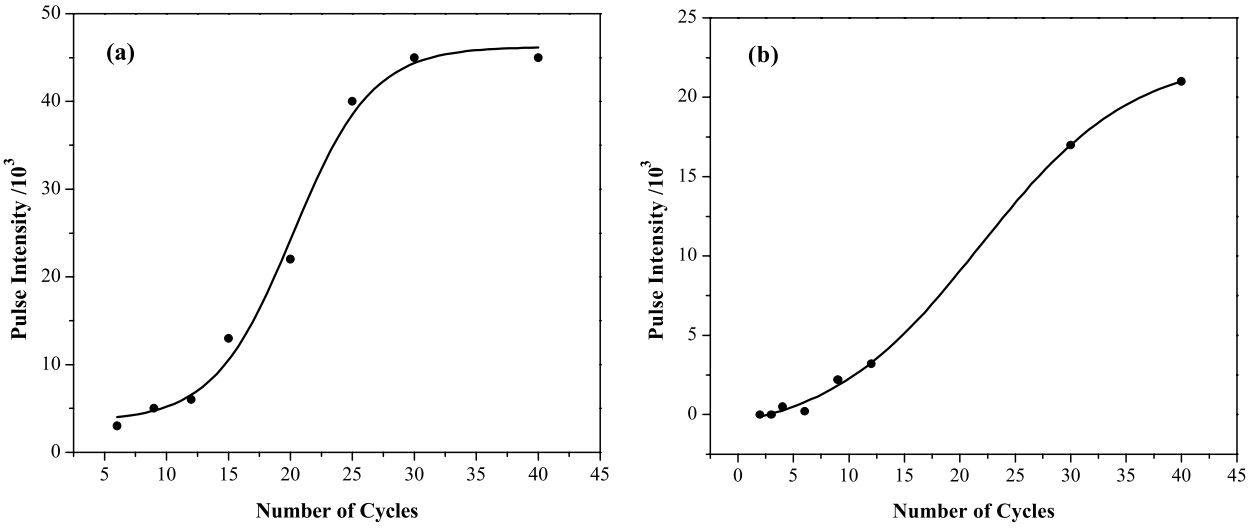

Fig. 4. Effect of changing the polymer film thickness (number of CV cycles during film formation) on the pulse intensity of As signal for POT (a) and PDDT (b)

x-axis of Fig. 4). An optimum film thickness formed using 40 cycles was used throughout the rest of this study. There may be a possible kinetic limitation with respect to increased film thickness based on previous findings of other researchers which show that the extraction time is inversely proportional to the diffusion coefficient of the analyte within the coating [17]. The extraction time t_e was kept constant (ca. 60 seconds) for 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 a. It should be noted, however, that the films used as SPME coatings in this study showed a remarkably short equilibration time for the analyte (AsB in this case) uptake and release (ca. 40 seconds). Moreover, the polymer films were used to coat a length of ca. 1.0 cm of the platinum wire with a nominal thickness, as estimated from SEM data, of 20 µm (±5.0 µm). These relatively small dimensions and fast equilibration time thus overcome the previously reported longer equilibration time and other inconveniences for the use of a commercial fiber SPME interface with HPLC-ICP systems for As speciation [28, 33]. The uptake/release time profiles of 100 ng mL^{-1} of AsB at POT and PDDT films are given in Figures 5a and b,

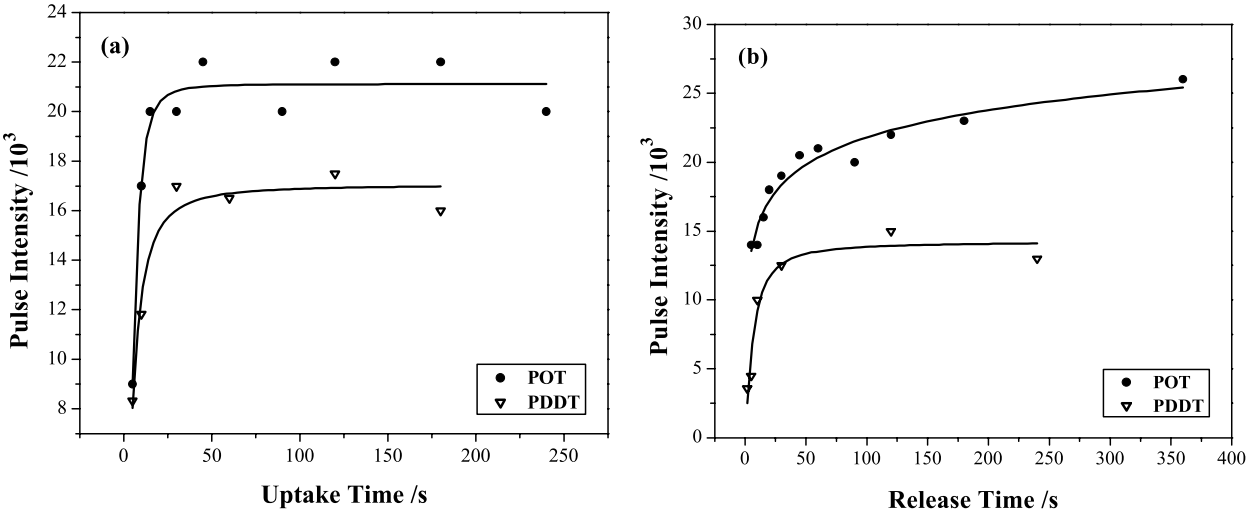

Fig. 5. Uptake (a) and release (b) time profiles of AsB at POT and PDDT films (no applied potential for uptake, and release potential is +1.5 V)

respectively. Film formation and extraction/release conditions were as follows: films were formed using 40 repeated cycles (CV), no potential was applied to the film during the uptake stage, and a +1.50 V (vs. pseudo Ag) potential was applied during the release of AsB from the coating. From the data depicted in Fig. 5, the "optimum" time used for uptake and release was 60 s. Also, the polymer films of OT and DDT display the valuable behavior of preferential uptake of the neutral species AsB in the presence of the charged AsO_2^- and AsO_4^{3-} species, as verified by the results of a combination of two experiments. First the effect of changing the uptake/release potentials on the analytical response signal (of the ICP measurement) towards AsB was examined. Figures 6a and b show that the maximum uptake of AsB occurs under the condition of no potential (open circuit) applied to the SPME coated film, and that maximum release (recovery) was obtained with an applied potential of +2.00 V (vs. a pseudo Ag reference electrode) during the release step. However, the figure shows that virtually *any applied potential* results in total release of AsB from POT. The second experiment was designed to confirm a previously reported explanation of the uptake/release mechanism [29] speculating that the driving force of uptake and release of AsB analyte

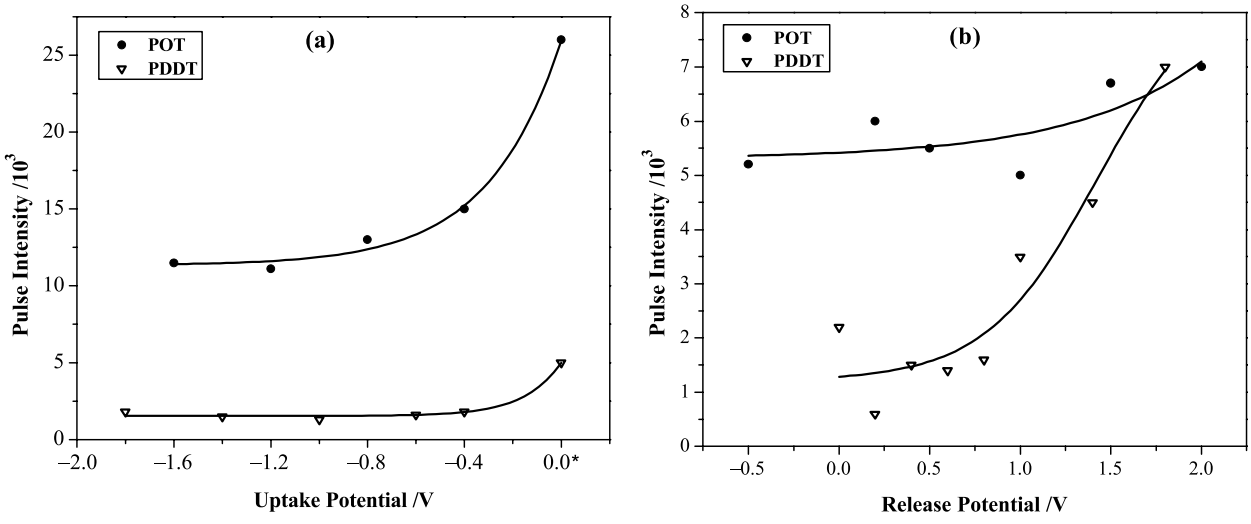

Fig. 6. Uptake (a) and release (b) potential profiles of AsB at POT and PDDT films (uptake and release times were 60 s, each). (*) No applied potential

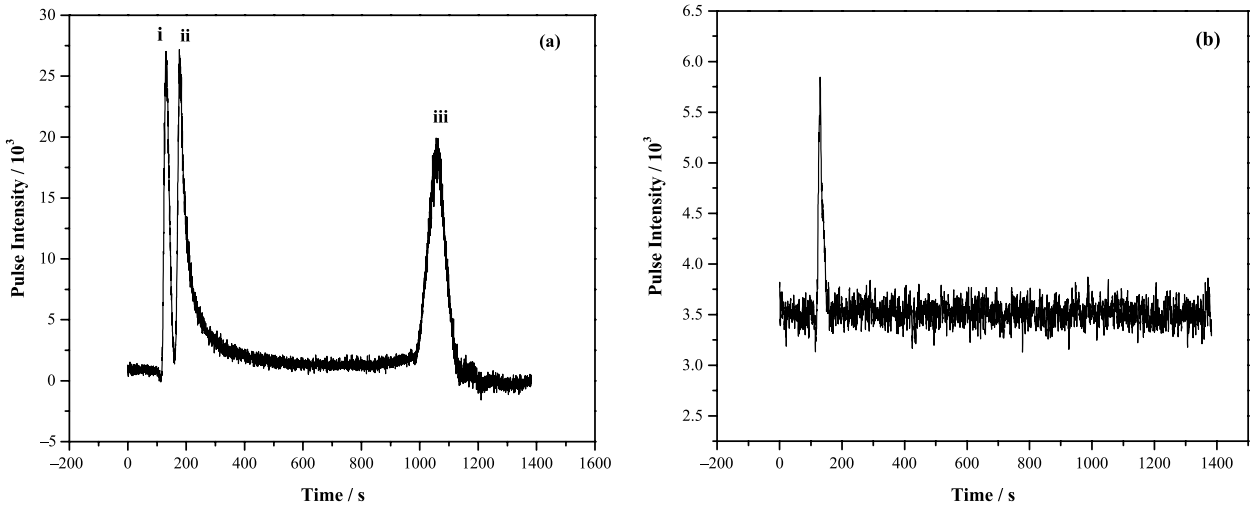

Fig. 7. Direct injection of AsB (i), AsO_2^- (ii) and AsO_2^{3-} (iii), 100 ng mL^{-1} each without speciation (a), and after extraction/release using POT/SPME (b)

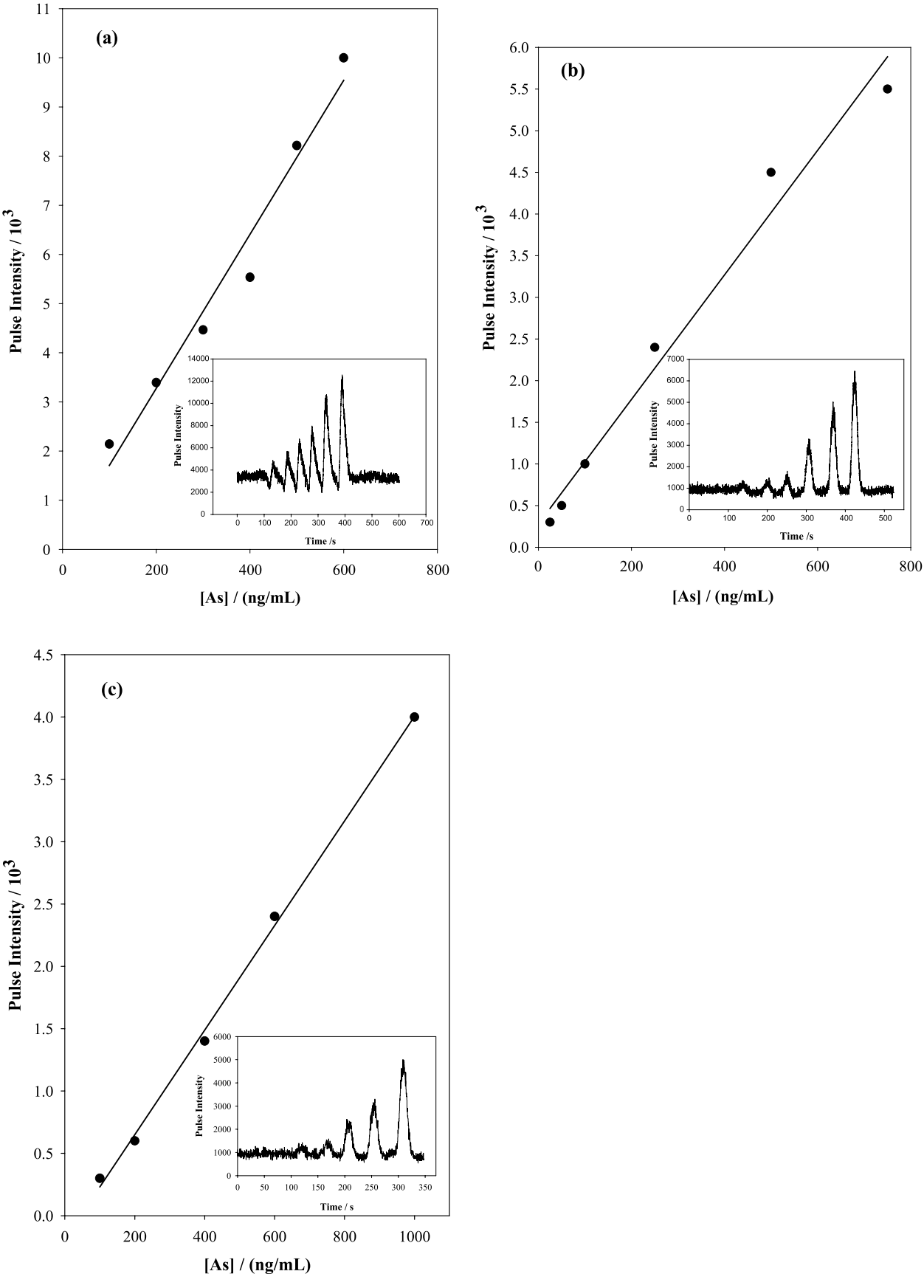

Fig. 8. Calibration curves of AsB using POT (a), PDDT (b) and PHDT (c) as the solid phase element

is based on the potential-driven ''switching'' of the hydrophilic/hydrophobic character of the film. As stated before, the polymer film is hydrophobic in its neutral ''undoped'' form and hydrophilic in the positively ''doped'' state. The HPLC-ICP chromatograms of Fig. 7a and b show the direct injection (no HPLC separation) of a mixture of 100 ng mL^{-1} each of AsB, AsO_2^- and AsO_4^{3-} and the same mixture after SPME using POT as the SPME extracting element, respectively. The data clearly shows the unique selectivity property of the polymer film towards AsB in the presence of two charged As-species and confirms that hydrophobic/hydrophilic ''switching'' is the driving force for uptake/release.

Figure 8 depicts the calibration curves (constructed by standard addition of AsB to the extraction matrix) for POT, PDDT, PHDT; their corresponding figures of merit are listed in Table 3. From these results we concluded that POT could reliably be used as an SPME element for the speciation of AsB in aqueous matrices containing a variety of charged As-species.

Table 3. Figures of merit for SPME, HPLC-ICP/MS of calibration curves using standard addition of 100 ng L^{-1} AsB for different polymers as coating element

Figures of merit	Polymer		
	POT	PDDT	PHDT
Linear range[a] [μg AsB L^{-1}]	70–1200	80–1000	350–1000
Slope [L (μg AsB) $^{-1}$]	17	9	3
Intercept	936	1036	234
R^2	0.998	0.999	0.988
% RSD[b]	0.931	1.45	3.25
Limit of detection[c] [μg AsB L^{-1}]	14	27	100

[a] Based on linear plot of concentration vs. mass spectrometry signal.
[b] A set of 3 replicate extractions and separations with standard addition method.
[c] Three times the standard deviation of three replicate extractions.

Interference Studies

In this work, the uptake step was completed prior to the on-line determination of the arsenic species. At this point, it is important to differentiate between two types of interferences: that occurring during the uptake step and that occurring in the on-line measurement. Thus, the performance of the polymer films studied in this work must be evaluated in the presence of some demonstrated interfering cations, anions and molecular species. For example, iron is a common element that is present at relatively high concentrations in several types of samples [34] including drinking water [35]. The presence of iron in the analysis matrix causes interference when using hydride generation/atomic absorption spectrometry as the means of on-line detection after sample extraction. On the other hand, some common anions such as Cl^- and SO_4^{-2} are interferents in the uptake step and more pronounced when compared to the determination step [34]. Therefore, we investigated possible interferences from Cl^- (NaCl), SO_4^{-2} (Na_2SO_4), Fe^{3+} ($FeCl_3$), and 1-octanol. The interference data is presented in Table 4. The data proved that the quantity of AsB thus accumulated during the uptake step at the polymer (POT) and its subsequent analysis is unaffected for both anionic species and Fe^{+3}. An important conclusion for this part of the present work is the possible determination of AsB directly from sea water in the presence of high anionic concentrations of chloride. In the case of presence of a neutral organic species such

Table 4. Effect of some interfering species on the recovery of AsB at POT SPME element

Interfering species[a]	Arsenobetaine/ng mL^{-1}				
	Added/ng	Found/ng	Average/ng	Recovery %	% RSD (n = 3)
Fe^{+3}	100	106.7	111.3(±4.6)	106.7	4.1
	100	115.9		115.9	
	100	117.9		117.9	
SO_4^{-2}	100	133.6	121.2(±10.9)	133.6	9.0
	100	107.0		107.0	
	100	122.9		122.9	
CI^-	100	87.5	86.2(±2.6)	87.5	3.0
	100	88.5		88.5	
	100	82.6		82.6	

[a] The concentration of each interfering species was 5.0 μg mL^{-1}.

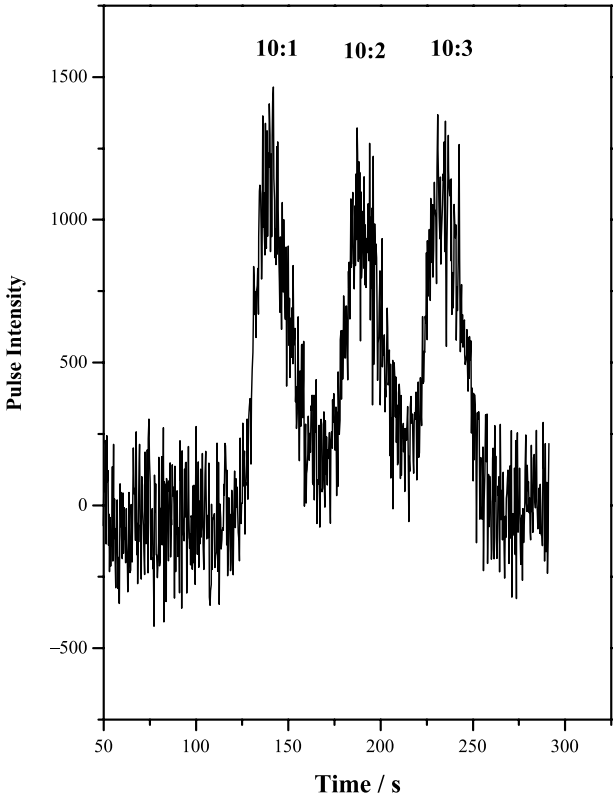

Fig. 9. Effect of addition of 1-octanol to the extracting medium on the speciation of the method towards 100 ng mL^{-1} AsB. Ratio shown is water/1-octanol (v/v)

as 1-octanol, the addition of higher total carbon in the aqueous solution should result in an improvement of the ionization efficiency of As in the plasma [36]. However, as could be noted from the typical ICP-MS signal of Fig. 9, addition of 1-octanol to the extracting matrix lowers the signal intensity values (see Fig. 7a and b for comparison). This effect does not appear to be proportional to the 1-octanol concentration. The addition of either ethanol or methanol has the same effect. Thus, it is true in general that neutrals in the analyte matrix compete for adsorption sites with the arsenobetaine and lower the uptake efficiency. This is a matrix effect that must be considered.

Analysis of Water and "Other" Environmental Samples

Tap water samples were spiked with different amounts of AsB and tested according to the procedure listed in Table 1. Table 5 compares the recoveries of AsB spiked in the tap water samples by standard addition method. It should be noted that no signals were detected for the non-spiked tap water, and recoveries were found to be

Table 5. Recovery of AsB in spiked water samples using POT as the SPME film element

Polymer	Arsenobetaine/ng mL^{-1}			
	Added	Found	Recovery %	% RSD (n = 3)
POT	200	197.7	98.9	4.1
	200	202.4	101.2	
	200	217.4	108.7	

205.08 ± 8.4 µg (99–109%) for 200 µg AsB spiked sample. The proposed method in this study would be adequate for monitoring drinking water standards both according to European (10 µg L^{-1} – 30 µg L^{-1}) and USA (50 µg L^{-1}) standards [37].

Two solid samples, silica- and clay-based, were received from the Department of Civil and Environmental Engineering of the University of Cincinnati. Each sample was spiked with 20 ng mL^{-1} to 200 ng mL^{-1} of AsB. Data for the recovery is 83%–106% for the silica-based samples but only 42%–65% for the clay-based samples. The relatively low recovery of AsB in the clay-based samples is not surprising, as clay is known as an anion exchanger and an absorber for neutrals such as AsB [38]. This high sorption ability thus competes with the polymer for the analyte, and the signal reduction is also a matrix effect in this case.

Analysis of a Certified AsB Sample

We evaluated the performance of the coated polymer material (POT) by analyzing a certified sample con-

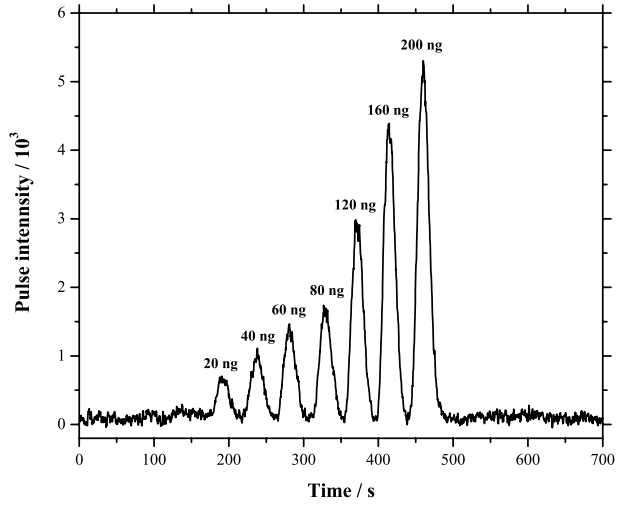

Fig. 10. Standard addition signals of AsB reference material using the SPME proposed method

taining AsB provided by the Food and Drug Administration (FDA) of Cincinnati, OH. Figure 10 shows the typical results of the standard addition analysis of the certified AsB sample using the present method. (Include summary of results.)

Conclusions

Organic conducting polymer films of 3-alkyl poly (thiophene) were used successfully as SPME element for the extraction and determination of trace amounts of AsB. Three alkyl substituted polymeric films were compared, and the best performance is in the order of POT > PDDT > PHDT. The extraction/analysis conditions were studied, and quantitative parameters are given. The presence of different common ionic interferents, which are troublesome in other methods, did not affect the analytical results for AsB. The presence of organic neutrals does, however, lower AsB uptake. The uptake (extraction) step of AsB into the film is mainly controlled by the interactions of the non-polar groups of the polymer with the organic based arsenic compound. On the other hand, the switching of the polymer film to the oxidized doped state resulted in an increase in the hydrophilic character of the polymer film and resulted in the release of AsB. The proposed method is simple and offers another application of organic conducting polymers in environmental determination of As-species. The method was successful in the determination of AsB in reference samples and some environmental matrices.

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