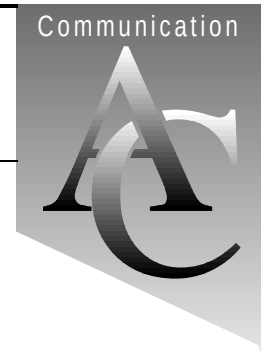
Electrochemical control of solid phase micro-extraction using unique conducting polymer coated fibers



Thompson P. Gbatu,[a] Ozcan Ceylan,[a] Karen L. Sutton,[a] Judith F. Rubinson,[a] Ahmed Galal,[b] Joseph A. Caruso[a] and Harry B. Mark, Jr*[a]

[a]*Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, OH, 45221-0172, USA*
[b] *Department of Chemistry, Faculty of Science, United Arab Emirates University, P.O. Box 17551, Al-Ain, United Arab Emirates*

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The use of a solid phase micro-extraction (SPME) method with poly(3-methylthiophene) coated platinum micro-fiber electrodes to extract arsenate ions from aqueous solutions without derivatization is described. The fibers were fabricated by cycling the working electrode between −0.20 and +1.7 V (*vs.* Ag/AgCl) in an acetonitrile solution containing 50 mM 3-methylthiophene monomer and 75 mM tetrabutylammonium tetrafluoroborate (TBATFB) electrolyte. All electrochemical procedures (extraction and expulsion) were conducted in a three-electrode system. After fabrication, the conducting polymer film was immersed in the sample solution and converted to its oxidized, positively charged form by applying a constant potential of +1.2 V with respect to Ag/AgCl reference electrode. Arsenate ions migrated into the film to maintain electroneutrality. Upon subsequent reversal of the potential to −0.60 V *vs.* Ag/AgCl, the polymer film was converted to its reduced, neutral form and the arsenate ions were expelled into a smaller volume (200 μL) of de-ionized water for analysis using flow injection with inductively coupled plasma mass spectrometric (ICP-MS) detection.

Introduction

Chemical speciation becomes important for trace metal analysis since, from a risk assessment perspective, it is not sufficient to quantitate the total elemental content of samples to define toxicities. For example, the determination of different forms of arsenic in the environment is critical because of the different levels of toxicity. Arsenate (AsO_4^{3-}) and arsenite (AsO_2^-) are present in surface waters, in ground waters, in soils, in plant tissues, and in animal tissues[1] and are highly toxic.

In general, the principal analyzed compounds for the speciation of arsenic are arsenite, arsenate, monomethylarsonic acid (MMA) ($CH_3AsO_3H_2$), dimethylarsenic acid (DMA) [$(CH_3)_2AsO_2H$], arsenobetaine [$(CH_3)_3As^+CH_2COO^-$] and arsenocholine [$(CH_3)_3As^+CH_2CH_2OH,Br^-$] and these have varying toxicities.[2,3] Therefore, for concise evaluation of the risks associated with the exposure of biological systems to arsenic, precise and accurate methods for the identification and quantitation of arsenic compounds must be evaluated. Among the many methods available for determining inorganic and organic arsenic compounds are liquid chromatography,[2–4] gas chromatography[5–11] and capillary zone electrophoresis.[12–14] Even though these methods give good sensitivities when coupled to element-specific spectrometric detectors such as ICP-AES and ICP-MS, they usually include difficult and time consuming sample preparation steps involving extraction and pre-concentration. A more efficient method is necessary for the extraction/preconcentration step of the analysis.

Recently, solid phase micro-extraction (SPME)[15–18] using silica and bonded phase fiber membranes[19–21] as well as crown ethers[22] has been the subject of investigations by a number of groups for extraction and pre-concentration of ionic and non-ionic organometals and metal ions from aqueous solutions. Although these techniques have proven useful for the extraction of non-ionic organometals, there are several disadvantages when performing extractions of ionic organometals and metal ions. These include the need for derivatization of the species or the fiber surface to enhance the coating/water or coating/air partition coefficient of the ionic organometals,[21, 23] the need for using highly selective and expensive crown ethers for metal ions,[22] the length of time needed for both extraction and desorption (release) of the species from the coating when non-thermal desorption techniques such as HPLC solvents are used, and the possibilities of fouling the coating surface by matrix components.

Even though derivatization methods in conjunction with SPME have considerably reduced the sample preparation time for these compounds compared to previously used classical liquid/liquid and other forms of extractions,[21] they still have major drawbacks. Foremost is the need for expensive and sometimes toxic reagents and solvents. Also, side reactions involving the derivatizing reagents and matrix components such as metals, ions, ligands, and other hydrophobic compounds found in environmental samples tend to complicate derivatization. Another problem associated with derivatization is its effect on sensitivity. For example, $NaBH_4$ volatilizes inorganic As(III) and As(V) by formation of arsine (AsH_3), and methylarsenic acids by the formation of methylarsenic(III) hydrides.[24] However, different arsenic compounds have different optimum pH values for derivatization. The result is a difference in sensitivity when derivatization reactions are carried out at constant pH. In fact, this is a common problem in the simultaneous derivatization of several compounds.

Conducting polymers are a class of polymers that have electronic conductivity. The types, methods of preparation and applications are discussed elsewhere.[25–31] Conducting polymer films such as poly(3-methylthiophene) (P3MT), may be doped when exposed to an aqueous solution containing an analyte anion at a particular oxidizing potential. The dopant may be expelled when the polymer film is reduced to its neutral form by applying a constant reduction potential for a set period of time. This paper presents preliminary results for the improvement of extraction and pre-concentration, without derivatization, of arsenate ions from aqueous solutions using such conducting polymers.

Experimental

Preparation of conducting polymer micro-fiber electrode

Prior to the polymerization of 3-methylthiophene (3-MT), the micro-fiber electrode surface was conditioned (micro-fiber

electrode: 200 μm × 1.5 cm Pt wire; reference electrode: Ag/AgCl; and auxiliary electrode: 2 × 2 cm² platinum sheet) in a10 mM aqueous H_2SO_4 solution. The conditioning process was performed with a Model 173 potentiostat/galvanostat (EG & G, Princeton Applied Research, Princeton, NJ) with an applied potential of −1.6 V *vs.* Ag/AgCl for 2 min. After conditioning of the platinum micro-fiber electrode, 3-methylthiophene was polymerized on the surface to P3MT by repeatedly cycling the electrode (100 mV scan^{-1}) between −0.20 and +1.75 V[32] in an acetonitrile solution containing 50 mM 3-MT and 75 mM tetrabutylammonium tetrafluoroborate (TBATFB) electrolyte using a BAS-100 electrochemical analyzer (BAS, West Lafayette, IN).

Typical cyclic voltammetric conditions for the electropolymerization of 3-MT included the following: working electrode, 200 μm × 1.5 cm Pt wire; reference electrode, Ag/AgCl; auxiliary electrode, 2 × 2 cm² Pt sheet; scan rate, 100 mV scan^{-1}; CV cycle, −0.2 V to +1.7 V. The following conclusions, which are in agreement with the work of Galal[32] may be drawn:

(i) 3-MT is oxidized at +1.65 V to form the corresponding polymer.
(ii) Upon reversing the direction of the sweep from the first oxidation wave, a corresponding cathodic wave for the reduction of the polymer film is observed in the region from +0.20 to +0.60 V.
(iii) The subsequent anodic sweeps revealed the growth of the polymer film at a lower potential (~E_{pa} +1.6 V). The anodic peak potential occurring at ~ +1.20 V is attributed to the oxidation of the polymer film deposited during subsequent cycles.

The formation of a polymer layer over the substrate was indicated by an increase of the current at a potential of ~ +1.65 V, the oxidation potential of the monomer.[33]

Flow injection ICP-MS

A reciprocating pump (Dionex Corporation, Sunnyvale, CA) and a 6-port Rheodyne injector (Rheodyne, Cotati, CA) with a 10 μL loop were connected to an ELAN 6000 ICP-MS (Perkin-Elmer Sciex, Toronto, Canada) by means of a 46 cm long PEEK tube (0.01 in id). A cross flow nebulizer (Perkin-Elmer Sciex) with a Scott type spray chamber (Perkin-Elmer Sciex) was used.

Reagents

3-MT (99+% purity, Acros Organics, Bridgewater, NJ), TBATFB (99% purity, Acros Organics), acetonitrile (HPLC grade, Fisher Scientific, Fairlawn, NJ), sulfuric acid (96% pure, Fisher Scientific) and dibasic sodium arsenate ($Na_2AsO_4 \cdot 7H_2O$) (Matheson, Coleman and Bell, Cincinnati, OH) were used as purchased.

Results and discussion

Preparation of conducting polymer micro-electrode fiber

Fig. 1 is a scanning electron micrograph (SEM) of the polymer film on the platinum after polymerization. The surface of the ~5 μm thick polymer film has a 'bumpy' appearance. This is in agreement with other investigators[32] who found that when P3MT films were grafted as thin films (10^2–10^3 Å) on the electrode, the surface was very homogenous, but when the polymer thickness was increased to a few microns, a 'bumpy' deposit rather than a smooth film was obtained. These morphological changes may be explained in terms of structural defects, such as cross-linking, β- *versus* α-coupling of the thiophene units, and the reticulation associated with it.[32,34]

Flow injection ICP-MS

After the fabrication of the conducting polymer film on the platinum micro-fiber electrode, it was rinsed with de-ionized water and dried under a stream of N_2 gas for a few seconds. Afterwards, it was immersed in 20 mL of a 100 μg L^{-1} aqueous solution of AsO_4^{3-} and converted to its positively charged form by application of a potential of +1.2 V *vs.* Ag/AgCl. Arsenate ions (AsO_4^{3-}) migrated into the polymer film to maintain electro-neutrality. Upon reversal of the potential to −0.6 V *vs.* Ag/AgCl, the polymer was converted back to its neutral hydrophobic form and the arsenate ions were expelled into a smaller volume (200 μL) of de-ionized water. 10 μL aliquots were injected *via* flow injection into the ICP-MS, using de-ionized water as the carrier solvent. It was determined that for a 10 min extraction period, approximately 210.4 ± 2.3 pg As was extracted from the 100 μg L^{-1} aqueous solution into the film. This figure was obtained from consideration of the first extraction of three films fabricated in very similar fashion. Attempts to determine the linear dynamic range of the film proved difficult because of a decrease in the film uptake ability during successive extractions. This phenomenon is explained below.

Fig. 2 is a chronoamperometric plot of the expulsion of the arsenate ions from the polymer film when a potential of −0.60 V *vs.* Ag/AgCl was applied. It may be seen that the expulsion is completed in a very short period of time; approximately 10 s in an aqueous matrix. Previous electrochemical and X-ray photoelectron spectroscopy (XPS) studies have shown that less than 5% of doping anions remain in the polymer matrix on reduction.[32] Shortening of this expulsion time further can

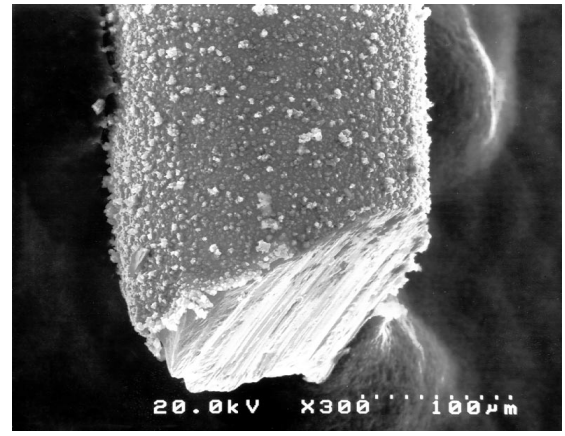

Fig. 1 Scanning electron micrograph (SEM) of poly(3-methylthiophene) film fabricated by cyclic voltammetry (working electrode: 200 μm × 1.5 cm Pt wire; reference electrode: Ag/AgCl; auxiliary electrode: 2 × 2 cm² Pt sheet); scan rate: 100 mV scan^{-1}; CV cycle: −0.2 to +1.7 V.

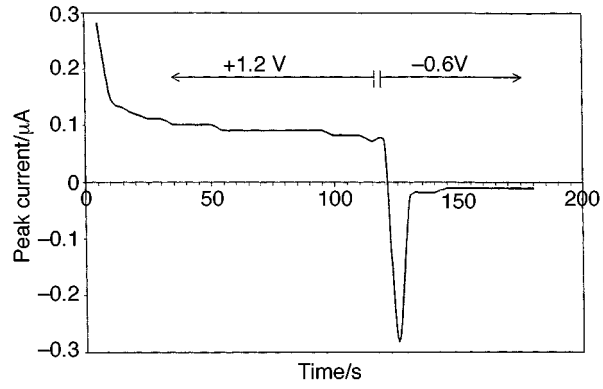

Fig. 2 Chronoamperometry of the doping and undoping of poly(3-methylthiophene) film with AsO_4^{3-}. Doping potential: +1.2 V; undoping potential: −0.6 V.

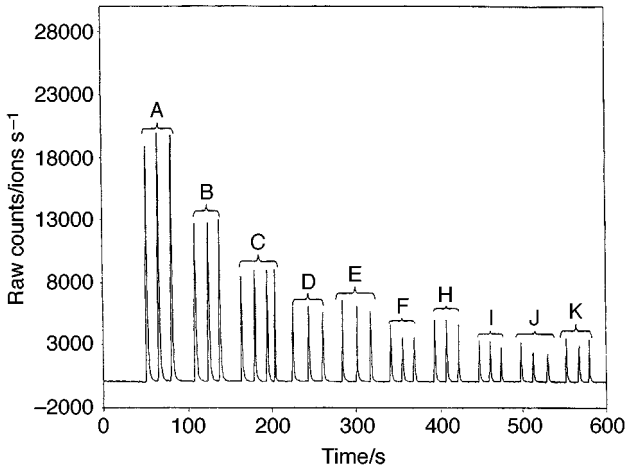

Fig. 3 Flow injection (FI)-ICP-MS plot of undoped AsO_4^{3-} in de-ionized water. Injection loop: 10 μL; carrier stream: de-ionized water; flow rate: 1.0 mL min^{-1}.

probably be obtained by more extensive optimization of the synthesis conditions and is the subject of current studies.

Typical flow injection peaks obtained from ICP-MS analysis of aliquots of the expelled arsenate are shown in Fig. 3. At least three injections of aliquots from each extract were carried out as shown. A closer look at the flow injection peaks (A–K) of Fig. 3 shows a decrease in the amount of arsenate (AsO_4^{3-}) taken up during successive extractions. Considering the uptake and expulsion cycle of each film, it seems that the morphology of the film changes during each cycle. This trend was observed in three polymer films fabricated under similar conditions. Even though it has been shown that electrochemically synthesized polythiophenes showed high stability and doping/undoping reversibility in aqueous medium,[32,35] it is known that, in the case of poly(methylthiophenes) (PMT), the film expands and contracts when doped and undoped, resulting in conformational changes during each cycle. This change is attributed to the loss of the fibrillar nature of the outer layer of the film[36] where the bulk of the doping occurs. Therefore, it is postulated that the decreasing doping ability of the film may be attributed to these factors. Efforts to increase the reproducibility on multiple extractions by optimization of the synthesis conditions[37] are presently underway. These include variation in film thickness and conditioning protocols before each extraction, among others.

As the uptake and expulsion process involve a redox process in the polymer, there is a definite possibility of valence change of redox analytes, such as the various arsenic species, during these processes. This would eliminate the speciation capability in the analyses. This effect is being investigated. However, because of the availability of polymers with a wide range of redox potentials, it is very likely that such problems could be circumvented.

Conclusions

The potential use of poly(3-methylthiophene) film to extract and pre-concentrate anionic species such as arsenate from aqueous solutions without derivatization, and desorb or expel directly into an HPLC or flow injection system for analysis, has been demonstrated. There are several advantages of such an extraction and pre-concentration technique over previously established methods. First of all, it eliminates the need for expensive and sometimes toxic reagents and solvents. Second, by eliminating the derivatization step, the problem of sensitivity encountered when the species that are being simultaneously derivatized have different reaction rates at a particular pH or temperature is removed. Finally, extraction and pre-concentration of these species from aqueous solutions, without derivatization ultimately greatly reduces analysis time.

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