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Extraction of arsenic as the diethyl dithiophosphate complex with supercritical fluid and quantitation by cathodic stripping voltammetry

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Abstract

The separation of arsenic based on in situ chelation with ammonium diethyl dithiophosphate (ADDTP) has been carried out using methanol-modified supercritical CO_2. Aliquots of extract were added to an electroanalytical cell and arsenic was determined by square wave cathodic stripping voltammetry (SWCSV) at a hanging mercury drop electrode (HMDE). Quantitative extractions of $As(DDTP)_3$ were achieved when the experiments were carried out at a pressure of 2500 psi, a temperature of 90 °C, 2.0 mL of methanol, 20.0 min of static extraction and 5.0 min of dynamic extraction in the presence of 18 mg of ADDTP. Analysis of arsenic was made using 150 mg L^{-1} of Cu(II) in 1 M HCl solution as supporting electrolyte in the presence of ADDTP as ligand. Preconcentration was carried out by deposition at a potential of −0.50 V and the intermetallic compound Cu_xAs_y was reduced at a potential of −0.77 to −0.82 V, depending on ligand concentration. The results showed that the presence of ligand plays an important role, increasing the method's sensitivity and preventing the oxidation of As(III). The calibration graph of the $As(DDTP)_3$ solution was linear from 0.8 to 12.5 μg L^{-1} of arsenic (LOD 0.5 μg L^{-1}, $R = 0.9992$, $t_{acc} = 60$ s). The method was validated using carrot pulp spiked with arsenic solution. This method was applied to the determination of arsenic in samples of carrots, beets and irrigation water. Arsenic in beets was: skin 4.10 ± 0.18 mg kg^{-1}; pulp 3.83 ± 0.19 mg kg^{-1} and juice 0.71 ± 0.09 mg L^{-1}; arsenic in carrots was: skin 2.15 ± 0.09 mg kg^{-1}; pulp 0.59 ± 0.11 mg kg^{-1} and juice 0.71 ± 0.03 mg L^{-1}. Arsenic in water were: Chiu-Chiu 0.08 mg L^{-1}, Inacaliri 1.12 mg L^{-1}, and Salado river 0.17 ± 0.07 mg L^{-1}.

Keywords: Supercritical fluid extraction; Cathodic stripping voltammetry; Arsenic; Diethyl dithiophosphate

1. Introduction

Arsenic is one of the most toxic elements found in nature, and it constitutes one of the main concerns in relation to human health. Arsenic is second only to lead as the main inorganic contaminant in the original US Environmental Protection Agency's (EPA) National Priority List (NPL) of Superfund sites. Arsenic can be found in drinking water, in the air as volatile arsines, and in soil, where it can concentrate if absorbed on soil components. Consumption of water with high concentrations of this nonmetal over an extended period of time causes serious diseases, including development of cardiovascular and peripheral vascular disease anomalies, neurological and neurobehavioral disorders, diabetes, hearing loss, portal fibrosis of the liver, lung fibrosis, hematological disorders, and carcinoma, especially in rural and semi-urban areas where water irrigates food or drinking water is often used without treatment [1–5]. This problem has been reported in many countries of the world, especially in Chile, Argentina, Mexico, China, Taiwan, Bangladesh, Poland, Canada, Japan and India. Arsenic enrichment in water in the Antofagasta Region of Chile is well known. Here the streams are characterized by a high As content (100–1000 mg L^{-1}), mainly associated with the quaternary volcanic and present-day geothermal activity in the Andes

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mountains [6–9]. The current maximum contaminant level for all forms of arsenic in groundwater is $50\,\mu g\,L^{-1}$, set by the EPA in 1975 based on a Public Health Service standard originally established in 1942. On 22 January 2001, the EPA adopted a new standard for arsenic in drinking water of $10\,\mu g\,L^{-1}$, to be enforced by January 2006.

A wide variety of methods exist for extracting this element from environmental solid samples. Variation of the results is generally ascribed to loss of volatile arsenic during extraction. Microwave methods are often recommended because there is little or no loss by volatility, and less time and less acid are needed to carry out the extraction [10–12]. Due to their low concentration in numerous solid and liquid samples there is crucial need for the preconcentration of arsenic before analysis. In the last years solid phase extraction (SPE) has been successfully used for the preconcentration, separation and determination of metal ions. The mechanism of retention depends on the nature of the sorbent and may include simple adsorption, chelation, ion-pair formation, or ion exchange. The most common sorbent of this type is octadecyl-bonded silica (C-18-silica). The chelating agent may be added directly to the sample or to introduce the functional chelating group into de sorbent [13–16].

Supercritical fluid carbon dioxide alone or with a modifier is an alternative to the extraction of metal ions as complexes from environmental samples. A suitable chelating agent that has reasonable solubility in supercritical solvents and forms stable and extractable chelates is necessary. One family of ligands which has been used extensively for complexation–extraction with immiscible organic solvents or extraction with sorbents is that of the derivatives of dithiocarbamic acid. However, they are unstable in acid media and tend to decompose in supercritical CO_2 extraction systems [17–20]. The ammonium salt of *O*,*O*-diethyl dithiophosphate (ADDTP) forms stable complexes with arsenic, weak complexes with some metal ions like Ni(II) and Co(II), is stable in acid solutions due to its resistance to hydrolysis, allowing extraction and complexation at low pH, does not react with alkali and alkaline earth metals, and is very soluble in methanol [21–23]. According to the literature, the presence of phosphorus compounds increases the efficiency of extraction of inorganic arsenic. Arsenic forms complexes having a 1:3 metal:ligand stoichiometry, and $As(DDTP)_3$ has a stability constant $K_f = 2.5 \times 10^9\ M^{-1}$ [17].

Several analytical techniques have been used for arsenic determination at trace levels, such as atomic absorption spectrometry, atomic fluorescence spectrometry, ICP mass spectrometry, UV–vis spectrometry, hydride generation, graphite furnace, potentiometry, gas or liquid chromatography with different detectors, and prior conversion of inorganic and methylated arsenic compounds into their diethyl dithiocarbamate complexes or trimethylsilyl derivatives [24–26]. Among these methods, electrochemical techniques have the advantage of being sensitive and of low cost, and they can be used to determine As(III) and As(V) without previous separation. Arsenite can be reduced to the element in acidic solution, deposited onto a solid electrode such as gold, platinum or copper, and then stripped off using anodic stripping voltammetry (ASV) [27–29]. As(III) is not amenable to determination by stripping voltammetry at a hanging mercury electrode because of the insolubility of arsenic in mercury. In the presence of copper an electrochemical–chemical reaction occurs and an intermetallic compound, Cu_xAs_y, is formed which can be preconcentrated on the mercury electrode and then stripped cathodically. There are two possible reaction mechanisms depending on deposition potential and acid concentration. One of them is that As^{III} is reduced to As^o and Cu^{II} is reduced to Cu(Hg). The As^o and Cu(Hg) deposited on the electrode surface could then form intermetallic compounds with different Cu:As ratios. On the other hand, chloride plays an important role in the process of deposition of Cu_xAs_y, probably through stabilization of the Cu^I formed at the HMDE which could react with As^o forming Cu_3As [30]. At a potential of about −0.70 to −0.80 V, the intermetallic compound is reduced, resulting in arsine and Cu(Hg). If copper and acid concentrations are constant, the peak current is a function of arsenic concentration. However, it was found that the arsenic peak decreased upon repeated scanning, probably due to reaction between mercuric ion and As^{III}, since mercury can dissolve in acidic media. $HgCl_2$ solution was added to the electroanalytical cell, causing the disappearance of the reduction peak, which indicated such an oxidation may have occurred [30]. In an attempt to stabilize the peak current, the effect of reducing reagents such as iodide, ascorbic acid and hydrazine had been investigated. These reagents can reduce mercuric ions or combine with them to prevent them from reacting with As^{III}. As a result, the peak current of As^{III} was constant during repeated scans. These reducing agents and others such as hydroxylamine, oxalic acid, potassium disulfite, sodium sulfite, sodium metabisulfite/sodium thiosulfate, and sodium dithionite have been used to reduce As(V) to As(III) [30–33]. Another possibility is adsorptive stripping voltammetry, in which arsenic(III) is accumulated on the mercury electrode surface in the form of a complex such as pyrrolidine dithiocarbamate [34].

One objective of this study was to find the optimum conditions for performing the extraction of As(III) with methanol-modified supercritical CO_2 using ammonium diethyl dithiophosphate as ligand for in situ complexation. A second objective was to find a method that would allow direct quantitation of the small methanolic extract volume obtained without further treatment. Cathodic stripping voltammetry in the presence of ADDTP was an adequate quantitation method which improved the sensitivity of the Cu–As intermetallic compound method. The procedure was then validated using uncontaminated carrot pulp and applied to the analysis of real samples of carrots, beets and irrigation water from the Calama area of Chile.

2. Experimental

2.1. Reagents

Standard solutions of arsenic were prepared by diluting a commercial standard solution containing 9630 μg mL^{-1} (ICP/DCP standard in 4 wt.% HNO_3, Aldrich, St. Louis, MO). Diethyl dithiophosphate, ammonium salt, 95% (ADDTP, Aldrich). HPLC-grade methanol was purchased from Fisher Scientific (Pittsburgh, PA). Stock solutions of ADDTP in methanol were stable for several months. Copper standard solution containing 1000 μg mL^{-1} (E. Merck, Darmstadt) 37% fuming hydrochloric acid (Merck), and hexadistilled metallic mercury (Radiometer Analytical, Lyon) were used for the electroanalytical measurements. Deionized water from a Millipore (Milford, MA) MilliQ system was used for preparing the aqueous solutions. Cellulose filter paper (Whatman 42, purchased from Merck) was used as inert support for liquid samples in the extractor. SFE-grade carbon dioxide (Indura, Santiago, Chile) was used in this study. Carbon dioxide modified with methanol is not commercially available; for that reason the modifier was added directly to the extraction cell.

2.2. Apparatus

All the extractions were performed with an SFE-400 extractor (Supelco, Bellefonte, PA). A 20-mL stainless steel vessel obtained from Supelco was used for the extraction. Fused-silica tubing (12–15 cm × 50 mm i.d.) was used as a restrictor. The flow rate of the extraction fluid was approximately 0.5 mL min^{-1} (as a liquid).

Square wave cathodic stripping voltammetry (SWCSV) was carried out with an MDE 150 polarographic stand (Radiometer Analytical, Lyon, France). The MDE 150 was controlled with TraceMaster 5 PC software. A 5-mL capacity measuring cell was equipped with a hanging mercury drop electrode (HMDE), a reference electrode ($Ag/AgCl/KCl_{3M}$), an auxiliary platinum electrode, a mechanical mini-stirrer, and a capillary to supply an inert gas. All experiments were carried out in an argon atmosphere. All potentials are quoted relative to the reference electrode.

2.3. Procedures

2.3.1. Extraction parameters with synthetic solutions

1.0 mL of 9.63 μg mL^{-1} arsenic solution was spiked onto circles (125 mm diameters) of filter paper and dried at room temperature in a hood with circulating air. The filter paper with the arsenic was cut into small pieces and placed in the extraction vessel. Ammonium diethyldithiophosphate (ADDTP) and methanol as modifier were added. The system was closed and the CO_2 inlet valve was opened, allowing the CO_2-methanol mixture to homogenize. Studies were made as functions of temperature (50–160 °C), pressure (1000–3000 psi), extraction time (10–60 min), amount of methanol (1.0–4.0 mL) and amount of ligand (10.0–50.0 mg). The extracts were received in empty 10.0 or 5.0 mL volumetric flasks. The system was cooled, then about 3.0 mL of methanol were added to the extraction vessel, and this washing solvent was received in the same flask. When the best extraction parameters had been found, the method was validated using 5.0 g aliquots of uncontaminated carrots spiked with 100 μL aliquots of 96.3 μg mL^{-1} arsenic solution. The spiked carrots were placed in a freezer at −20 °C for hours, days and weeks. These extracts were analyzed by square wave cathodic stripping voltammetry.

2.3.2. Determination of arsenic from carrots, beets and irrigation water

The skin, dry pulp and juice of carrots and beets were separated. Two to four milliliter aliquots of the liquid samples (carrot and beet juice, and irrigation water) were placed on filter paper and dried at room temperature in a hood. Subsequently, the filter paper with the liquid samples or 5.0 g of solid samples was placed in the extraction vessel, and 18 mg of ADDTP ligand and 2.0 mL of methanol were added. The best extraction parameters were set in the extractor. The extracts of the samples were received in empty 5.0 mL volumetric flasks. Arsenic in the extracts were analyzed by SWCSV using standard addition method.

2.3.3. Square wave cathodic stripping voltammetry

Studies of ligand, copper and acid concentration, methanol effect, electrolysis time and potential, step and amplitude, pulse duration, scan rate and saturation the mercury drop, were made to select the best conditions to ensure the highest possible sensitivity and precision.

The general procedure used to obtain voltammograms was the following: 3.0-mL of solution containing 150 mg L^{-1} of Cu in 1 M HCl was pipetted into a 5.0 mL voltammetric cell. Hundred microliter aliquots of the solution containing arsenic complex and free ligand in methanol were added. The solution was purged with water-saturated argon (5 min) to remove dissolved oxygen. Subsequently, five mercury drops were discarded and the accumulation was carried out for 60 s at −0.500 V with a stirring speed of 400 rpm. After a 5 s quiescent period, the potential was scanned between −0.500 and −1.100 V using square wave modulation with 0.005 V step amplitude, 0.025 V pulse amplitude, and 0.04 s step duration. The calibration curves were drawn and linear regression and limits of detection (LOD) were determined. Arsenic was quantified by the standard addition method.

2.4. Limits of detection (LOD) and quantitation (LOQ)

The LOD was calculated from $y_{DL} = a + 3S_{x/y}$ and $y_{DL} = a + bx_{DL}$, where a is the intercept, $S_{x/y}$ is the random error in x and y, and b is the slope. The LOQ was calculated from $y_{DL} = a + 10S_{x/y}$ [35].

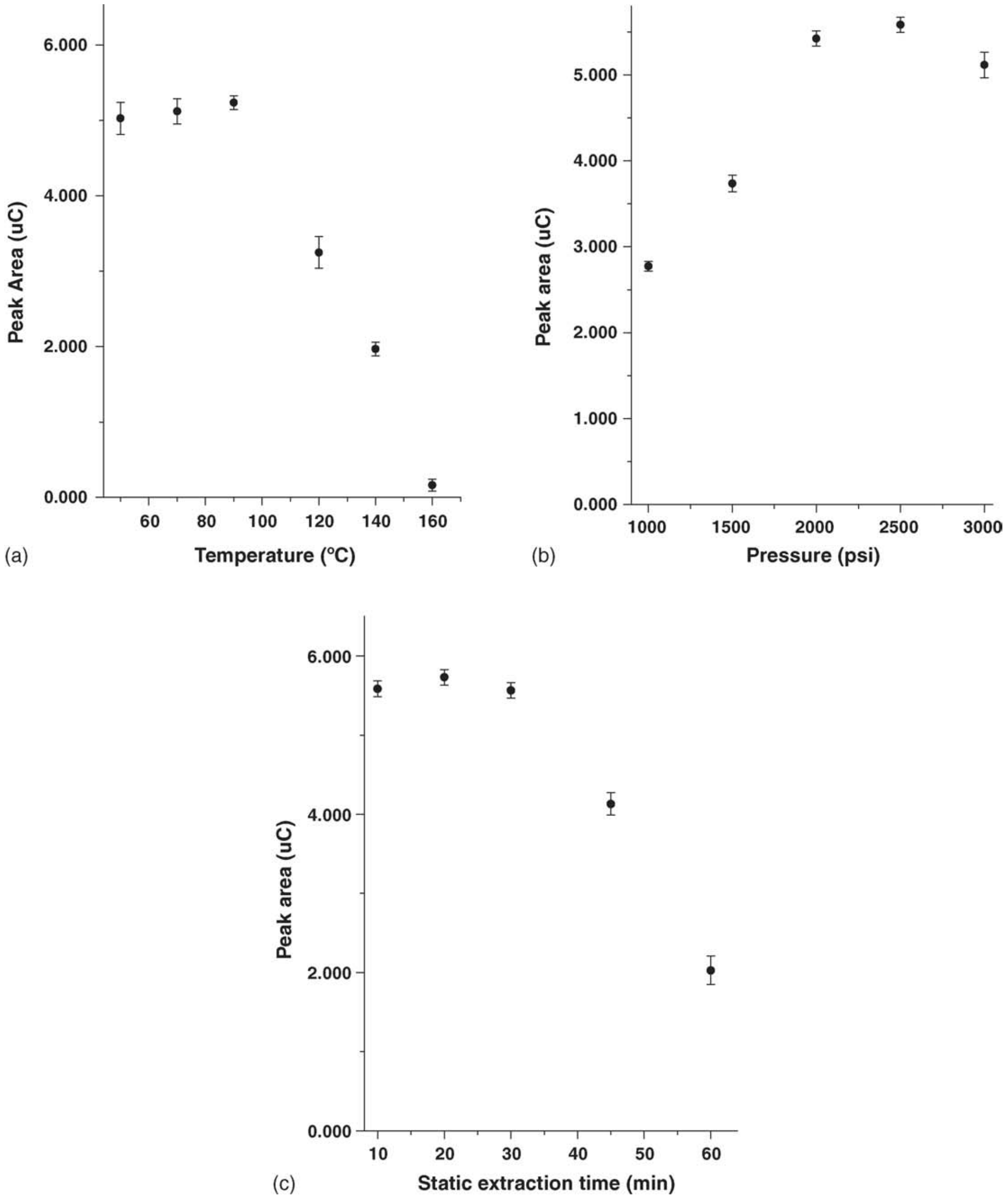

Fig. 1. (a) Recovery of As(ADDTP)$_3$ complex as a function of oven temperature (50, 70, 90; 120, 140 and 160 °C). Conditions: 96.3 μg of arsenic; 10 mg of ADDTP ligand; 2.0 mL of methanol; pressure 2000 psi, restrictor temperature 50 °C, and 10 min in static mode followed by 5 min in dynamic mode. (b) Recovery of As(ADDTP)$_3$ complex as a function of system pressure (1000, 1500, 2000, 2500 and 3000 psi). Conditions: 96.3 μg of arsenic; 10 mg of ADDTP ligand; 2.0 mL of methanol; temperature 90 °C, restrictor temperature 50 °C, and 10 min in static mode followed by 5 min in dynamic mode. (c) Recovery of As(ADDTP)$_3$ complex as a function of static extraction time (10, 20, 30, 45 and 60 min) followed by 5 min in dynamic mode. Conditions: 96.3 μg of arsenic; 10 mg of ADDTP ligand; 2.0 mL of methanol; temperature 90 °C, pressure 2500 psi, and restrictor temperature 50 °C.

3. Results and discussion

3.1. Extraction parameters

The effect of temperature (50, 70, 90, 120, 140 and 160 °C), pressure (1000, 1500, 2000, 2500 and 3000 psi) and extraction time (10, 20, 30, 45 and 60 s) are shown in Fig. 1a–c. These values are related to the averages of three measurements under the same conditions. Recovery was achieved by adding 96.3 μg of As(III), 10 mg of ADDTP and 2.0 ml of methanol in the extractor for 10.0 min of static extraction and 5.0 min of dynamic extraction. From the variable temperature study it is seen that at high values recovery decreases, probably due to decomposition. The optimum temperature was 90 °C, and it was used in all later measurements. From the variable pressure study it was found that the greatest recovery occurred at 2500 psi, but at 3000 psi it decreased slightly. Later extractions were made at a pressure of 2500 psi and a temperature of 90 °C, and extraction time was varied from 10 to 60 min. The results are shown in Fig. 1c. When extraction time was increased from 10 to 20 min, recovery increased; however, longer times were not adequate because recovery decreased, perhaps because of slow decomposition of the ligand or the complex. These measurements were repeated many times because it was expected that recovery as a function of time should increase or reach a steady state. All the measurements were carried out with 2.0 mL of methanol. Subsequently, 1.0, 2.0, 3.0 or 4.0 mL of methanol were added to the extraction vessel, but the highest recovery was obtained with 2.0 mL. When acetonitrile was added to the extraction cell as modifier, the recovery of arsenic as DDTP complex was lower than that with methanol. With the purpose of increasing the recovery of arsenic complex, small aliquots of water (50–100 μL) were added to the inert support or to the real sample, but the yield increased only slightly. The study of the extraction parameters was made with larger amounts of arsenic (96.3 μg) because we wanted to know the tendency of the curves as a function of temperature, pressure, extraction time, and amount and type of modifier and the maximum amount extracted. When the optimum experimental parameters were achieved and extraction was only 95.3%, we made extractions with smaller amounts of arsenic in the vessel, changing the amount of ligand. Quantitative recoveries were achieved when the amount of arsenic was less than or equal to 9.63 μg adding 18 mg instead 10 mg of ADDTP. The method was validated using 5.0 g of carrot pulp samples spiked with 100 μL of 96.3 $\mu g\,mL^{-1}$ arsenic solution. Six extractions were made (temperature 90 °C, pressure 2500 psi, 18 mg of ADDTP ligand, 2 mL of methanol as modifier, 20 min static extraction and 10 min dynamic extraction) and the recovery was 9.58 ± 0.08 μg.

3.2. Quantitation of arsenic by SWCSV

Cathodic stripping voltammetry of As^{III} with formation of the intermetallic compound Cu_xAs_y using HMDE has been well described in the literature. However, our solutions contained $As(DDTP)_3$, ADDTP and methanol. For that reason, and to achieve maximum sensitivity in the voltammetric response, it was necessary to carry out studies as a function of copper and ligand concentration, electrolysis time and potential, stirring rate during deposition, step and pulse amplitude, and scan rate.

The effect of changes of the electrolysis potential on the peak currents was studied over the 0.10 to −0.60 V range versus Ag/AgCl with 10.0 $\mu g\,L^{-1}$ As(III) and 0.09 $mg\,mL^{-1}$ ADDTP solution (Cu(II) 150 $mg\,L^{-1}$, 1 M HCl as supporting electrolyte) with an accumulation time of 60 s. High and reproducible values of peak current were obtained when the accumulation potential was −0.35 to −0.50 V. On the other hand, peak current increased linearly with accumulation time up to 360 s. Longer times were not studied.

High acid concentration is necessary for the reduction of Cu_xAs_y compound. However when higher concentration of 1 M HCl solution were used, peak current due to H^+ reduction increased and covered the arsenic peak. Due to the presence of DDTP ligand, a much higher amount of copper than that used by other authors was necessary. To obtain the optimum copper concentration, it was varied between 0 and 400 $mg\,L^{-1}$ with two different concentrations of As^{III} and ADDTP ligand. Voltammograms were obtained with 5.0 $\mu g\,L^{-1}$ (or 10.0 $\mu g\,L^{-1}$) of As^{III} and 0.10 $mg\,mL^{-1}$ (or 0.20 $mg\,L^{-1}$) of ADDTP ligand in 1 M HCl solution, and aliquots of copper(II) solution were added. Fig. 2 shows a plot peak current as a function of copper concentration. In this figure it is seen that maximum sensitivity is obtained with about 150 $mg\,L^{-1}$ of copper(II). Higher copper concentrations saturate the mercury drop. With the first additions of copper a peak to −0.46 V is seen which corresponds to the Cu complex; when the copper concentration is higher than that of ligand, a peak at −0.15 V is seen which corresponds to free copper or copper in chloride medium. If the Cu:L ratio is 1:2, copper complex is precipitated and the arsenic peak potential is close to the reduction of H^+.

Later, voltammograms for various ligand concentrations in the presence of 150 $mg\,L^{-1}$ of copper in 1 M HCl were recorded using an accumulation potential $E_{acc} = -0.50$ V with a time of 60 s (Fig. 3). This solution contained 32.2 $\mu g\,L^{-1}$ of As^{III}. Aliquots of 3 $mg\,mL^{-1}$ ADDTP ligand in methanol solution were added (curves 3–11), with solution concentration ranging from 0.019 to 0.358 $mg\,mL^{-1}$. In these voltammograms it is seen that the current peak obtained in the presence of ligand are higher than those obtained without ADDTP. The peak reduction potential of Cu_xAs_y shifts slightly towards more negative values with increasing ADDTP concentration.

Voltammograms for various arsenic concentrations with constant concentration of the ADDTP ligand using these conditions were recorded. The corresponding calibration graph followed the linear equation $y = 8 \times 10^{-4} + 0.076x$

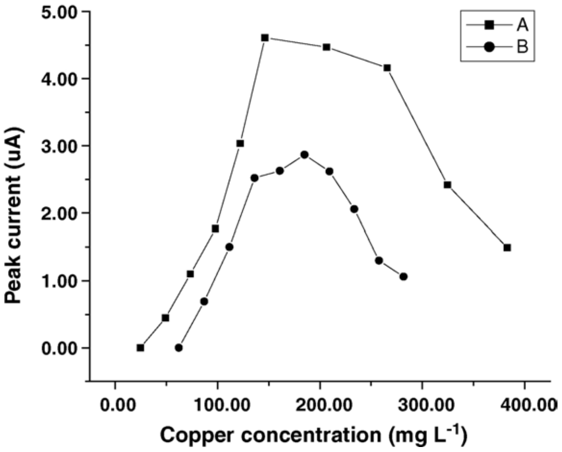

Fig. 2. Effect of copper concentration on the arsenic peak current. (A) As^{III} 10.0 $\mu g\,L^{-1}$, ADDTP 0.20 $mg\,mL^{-1}$ in HCL 1 M. (B) As^{III} 5.0 $\mu g\,L^{-1}$, ADDTP 0.10 $mg\,mL^{-1}$ in 1 M HCl. Accumulation potential (E_{acc}) −0.50 V, accumulation time (t_{acc}) 60 s.

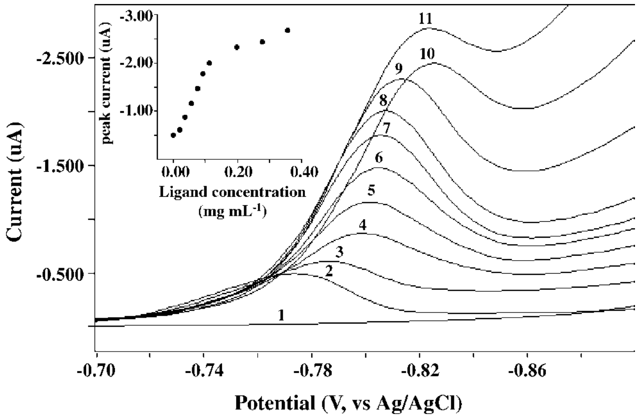

Fig. 3. Square wave cathodic stripping voltammetry of arsenic solution in the presence of different ligand concentrations. Accumulation potential (E_{acc}) −0.50 V, accumulation time (t_{acc}) 60 s; scan from −0.50 to −1.10 V. Curve 1: blank (3.0 mL of supporting electrolyte, 150 mg L^{-1} Cu(II), 1 M HCl); curve 2: adding 100 μL As(III) 1 μg mL^{-1}; curves 3–11 in the presence of 20, 40, 60, 80, 100, 120, 220, 320 and 420 μL of 3 mg mL^{-1} ADDTP ligand methanol solution.

($r = 0.9992$, $n = 8$). The linear calibration plot extends up to a concentration of 12.5 μg L^{-1}. At higher concentrations the linearity remains, but the slope of the calibration curve is lower. The LOD was found to be 0.5 μg L^{-1}, while the LOQ was calculated to be 1.8 μg L^{-1} at an accumulation time of 60 s. For increasing sensitivity of the method, longer accumulation times must be used.

3.3. Analysis of samples

In a first step, the extracts were quantified by HPLC using a C-18 stationary reverse phase (25 cm, ID 4 cm, 5 μm column) and UV detection at 270 nm (methanol:water 85:15, pH 2.0 as mobile phase). One high area peak (tr = 18.65 min) and one small peak (tr = 21.66 min) were obtained, and calibration curves were linear considering individual areas or the sum of the areas of two peaks. However, when extracts from real samples were analyzed, a high peak corresponding to the Fe(DDTP)$_3$ complex was obtained, with retention time very near to that of the As(DDTP)$_3$ complex peak. We tried to eliminate this interference, but other ligands which react with iron had absorbance at 270 nm and the signals were very wide. Then an electroanalytical technique was used.

Hundred microliter aliquots of the extracts containing the complex and free ADDTP ligand were placed in an electroanalytical cell that contained supporting electrolyte (150 mg L^{-1} Cu(II), 1 M HCl) until an adequate peak was obtained. Depending on the arsenic concentration in the samples, the extracts were concentrated to 1–2 mL under reduced pressure. Fifty microliter aliquots of standard arsenic solution were added and the standard addition method was applied. Ten samples of carrots, beet and irrigation water were analyzed in triplicate. The following results were obtained: arsenic in beets, skin 4.10 ± 0.18 mg kg^{-1}; pulp 3.83 ± 0.19 mg kg^{-1} and juice 0.71 ± 0.09 mg L^{-1}; arsenic in carrots, skin 2.15 ± 0.09 mg kg^{-1}; pulp 0.59 ± 0.11 mg kg^{-1} and juice 0.71 ± 0.03 mg L^{-1}. Arsenic in irrigation water were: Chiu-Chiu 0.08 mg L^{-1}; Inacaliri 1.12 mg L^{-1} and Salado river 0.17 ± 0.07 mg L^{-1}. These arsenic levels in food are very high, because according to the WHO, an intake of 1.0 mg of inorganic arsenic per day may give rise to skin lesions within a few years. Our interest was centered in the analysis of As(III) since it is the most toxic, and a reduction agent for the determination of total arsenic was not used. Using this procedure, arsenic concentrations as low as 0.8 μg L^{-1} could readily be determined in a complex matrix (food, vegetables, soil, etc.) using a short time of 60 s as deposition time prior to extraction for 20 min with supercritical methanol-modified CO$_2$. Excess methanol-free ligand and metal ions present in the samples that could be extracted with the arsenic complex, such as iron, lead, zinc, chromium and copper, do not interfere with peak current. Hydrochloric acid concentration cannot be greater than 1 M because the proton reduction signal would rise and cover the arsenic peak. The method of intermetallic compound Cu$_x$As$_y$ in the presence of ADDTP ligand was more sensitive and reproducible, a reducing agent to avoid reaction between mercuric ions and As^{III} was not necessary, and the standard and sample solutions of the extracts were stable for several months to 4 °C. In the determination of arsenic in the extracts obtained from the samples, ligand and copper concentration were almost constant due to the use of the standard addition method.

The search for the conditions for extraction and quantitation may be slower than with other methodologies, but after getting them the method is sensitive, reproducible and fast. The advantages of this method are those inherent to voltammetric techniques, which allow high sensitivity analysis with an instrument of lower cost and maintenance than spectrometric techniques such as those that use a graphite oven and plasma.

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