



Determination of arsenic in the presence of copper by adsorptive stripping voltammetry using pyrrolidine dithiocarbamate or diethyl dithiophosphate as chelating-adsorbent agents. Effect of CPB on the sensitivity of the method☆



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ABSTRACT

A sensitive method for the determination of arsenic based on the formation of their complexes with ammonium pyrrolidine dithiocarbamate (APDTC) or ammonium diethyl dithiophosphate (ADDTP) prior to the formation of the intermetallic compound (Cu_xAs_y) whose reduction is directly related to As(III) concentration is presented. The effects of various operational parameters such as HCl, Cu(II) and ligand concentrations (C_{HCl} , $C_{\text{Cu(II)}}$, C_{APDTC} , C_{ADDTP}); accumulation potential and time (E_{ads} , t_{ads}) were optimized. The optimum experimental conditions chosen were C_{HCl} : 1.25 and 2.00 mol L^{-1} ; $C_{\text{Cu(II)}}$: 60 and 40 mg L^{-1} ; E_{ads} : -0.40 and -0.30 V; and t_{ads} : 80 and 60 s for APDTC and ADDTP, respectively. On the other hand, the optimum ligand concentrations were 0.20 and 1.50 $\mu\text{mol L}^{-1}$ for APDTC and ADDTP, respectively ($C_{\text{As(III)}}$: 15.00 $\mu\text{g L}^{-1}$). It was found that in the presence of cetylpyridinium bromide (CPB) the peak current of the arsenic signal is higher than in the absence of this cationic surfactant, and these values attained a maximum at 7.8 and 2.6 $\mu\text{mol L}^{-1}$ for APDTC and ADDTP, respectively. Under these conditions, the reduction signals of Cu_xAs_y are found at -0.82 V and -0.64 V for APDTC and ADDTP, respectively. The relationship between peak current and As(III) concentration is linear in the 0.50–3.00 $\mu\text{g L}^{-1}$ (APDTC) and 2.50–15.00 $\mu\text{g L}^{-1}$ (ADDTP) range. The detection limits (DLs) were found to be 0.08 and 0.27 $\mu\text{g L}^{-1}$ for APDTC and ADDTP, respectively (t_{ads} : 30 s). The relative standard deviations for 30 replicate measurements at the lowest level of each method, 0.10 $\mu\text{g L}^{-1}$ for APDTC and 2.00 $\mu\text{g L}^{-1}$ for ADDTP, were 3.9 and 25.2%, respectively. The results showed that the presence of ligand plays an important role, improving the signal current of As(III) and preventing the oxidation of As(III) to As(V), achieving the best sensitivity and repeatability when APDTC was used. Finally, the method was validated using synthetic drinking water spiked with As(III) and was applied to the determination of total arsenic in water from the Loa River (North of Chile) with satisfactory results.

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1. Introduction

The toxicity of arsenic on human health is well known. The adverse effects depend on chemical form (organic and inorganic arsenic) and oxidation states (-3 , 0 , 3 , and 5) that occur in the environment. In fact, As(III) is about 100 times more toxic than As(V), and methylated compounds which contain trivalent arsenic are more cytotoxic and genotoxic than arsenite [1–3]. The most common form of exposure is by consumption of contaminated drinking water, especially in rural and semi-urban areas where water irrigates food crops, or drinking

water is often used without treatment. Prolonged exposure causes serious diseases, including arsenical dermatosis, hyperkeratosis, and arsenicosis, besides neurological and neurobehavioral disorders, cardiovascular and peripheral vascular disease anomalies, diabetes, hearing loss, portal fibrosis of the liver, lung fibrosis, hematological disorders and carcinoma [2,4–6].

The occurrence of natural arsenic contamination is fairly usual, because this nonmetal can be mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions, and in various countries of the world (Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, Vietnam and many parts of the USA) problems with high levels of arsenic have been identified. In 1962 arsenic enrichment in drinking water triggered in the Second Region of Chile an intake of this metalloid at concentrations greater than 500 $\mu\text{g L}^{-1}$ [2]. It has been estimated that 7% of all deaths occurring in Antofagasta between 1989 and 1993 were due to

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past exposure to arsenic in drinking water. Currently, although the Chilean standard, in order to abide by the WHO recommendations, established since 2005 a permissible concentration of $10 \mu\text{g L}^{-1}$ of arsenic in drinking water, it is still a problem because water availability is dramatically scarce [7,8]. The region is extremely arid; the only permanent superficial water is the Loa River which provides water for cities, mining activity, and agricultural development in the area. The quality of water from the Loa River is poor due to high salinity and high dissolved arsenic and boron, because its main tributary (El Salado) has its origin in the geothermal field of El Tatio [6]. Therefore, arsenic detection is critical to the health care of the population in these areas.

The traditional methods used for arsenic determination are spectrometric techniques like hydride generation atomic absorption spectrometry (HG–AAS), hydride generation atomic fluorescence spectrometry (HG–AFS), electrothermal absorption spectrometry (ET–AAS); inductively coupled plasma (ICP) with atomic emission and mass spectrometry (ICP–AES; ICP–MS) as detectors; high performance liquid chromatography (HPLC) coupled with several detectors; and neutron activation analysis (NAA) [9–12]. On the other hand, electroanalytical techniques, mainly stripping voltammetry, 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). However, arsenic does not form amalgams with mercury. In these cases adsorptive stripping voltammetry (AdSV) is the adequate technique for its determination in a variety of matrices. AdSV requires the presence of a ligand with adsorptive properties, the complexes must be formed quantitatively and quickly in solution, and they must be adsorbed on the electrode's surface. The only study reported involves the use of pyrrolidine dithiocarbamate as complexing and adsorbing agent [13]. On the other hand, As(III) can react with copper or selenium [14] to form intermetallic complexes such as Cu_xAs_y or Se_xAs_y , which can be preconcentrated on the working electrode and then stripped cathodically. This method makes it possible to obtain low detection limits. However, due to the instability of the As(III) the use of reducing agents, such as hydroquinone or hydroxylamine, to avoid oxidation of As(III) to As(V) has been necessary. With the same purpose, complexing agents such as diethyl dithiophosphate (DDTP) [5] and diethyl dithiocarbamate (DDTC) have been used [15]. In addition, the sensitivity and selectivity of AdSV depend on the choice of a suitable ligand as well as the working electrode. Despite the toxicity of mercury, the hanging mercury drop electrode (HMDE) is a nearly ideal electrode, especially for cathodic processes and mainly due to good adsorptive properties. On the other hand, the presence of a ligand with adsorptive properties can form a complex not only with arsenic but also with other metal ions which form intermetallic compounds with arsenic, such as Cu or Se (M_xAs_y) allowing the accumulation of arsenic in the previous step [16].

Another possible way of enhancing the adsorptive process and the sensitivity of the method is the use of surfactants, whose beneficial effects are unpredictable, as they tend to interfere by competitive adsorption. Cationic surfactants can be adsorbed on the mercury electrode by hydrophobic and electrostatic attraction. Neutral metal complexes in the solution can be attracted by the positively charged surfactant to form stable compounds and be transported consequently to the electrode surface in the accumulation step [17].

The main objective of the present work was to study and compare the sensitivity of the AdSV method using ammonium pyrrolidine dithiocarbamate (APDTC) or ammonium diethyl dithiophosphate (ADDTP) in the presence of Cu(II) and the effect of the presence of cetylpyridinium bromide (CPB) on the arsenic determination. The study made by Arancibia et al. [5] showed the positive influence of DDTP and Cu(II), but did not go into the effect of CPB, while Zima et al. [15] showed only the positive influence of PDTC and did not report studies in the presence of Cu(II) or CPB. The method was validated using a synthetic

drinking water matrix spiked with As(III) and was applied to the determination of total arsenic in river water from the Calama area in the North of Chile.

2. Experimental

2.1. Apparatus and equipment

Stripping voltammetry measurements were made with a Metrohm 797 VA Computrace Stand with a hanging mercury drop electrode (HMDE). The reference electrode was Ag/AgCl/KCl 3 mol L^{-1} , and the auxiliary electrode was a platinum wire. Solutions were stirred during the purging and deposition steps with a rotating PTFE rod. The solutions were deaerated using high-purity nitrogen. pH was measured with an Orion model 430 pH meter.

2.2. Chemicals and samples

Standard solutions of arsenic were prepared by diluting a stock solution of $1000 \text{ mg L}^{-1} \text{ As}_2\text{O}_3$ (TraceCert, Fluka Analytical, CAS 39436). Standard solutions of Cu(II) containing 1000 mg L^{-1} (Titrisol CuCl_2 , Merck, CAS 744739–4) and 37% fuming hydrochloric acid (Emsure Merck, CAS 7647-01-0) were used as supporting electrolyte. Standard solutions of ammonium pyrrolidine dithiocarbamate (APDTC, Sigma, CAS 5108-96-3) and ammonium diethyl dithiophosphate (ADDTP, Sigma, CAS 1068-2200) were prepared in methanol, while cetylpyridinium bromide hydrate (CPB, Sigma, CAS 202869-92-9) and sodium dodecyl sulfate (SDS, Sigma, CAS 202869-92-9) were prepared in water. Interference studies were made by diluting standard solutions (1000 mg L^{-1} CertiPUR, Merck) of Cd, Ni, Li, Al, Co, Mg, Be, Se, Fe, Sb, Mo, Ca, Zn, Tl, Mn, K, Bi, and Pb. The method was validated by determining arsenic in spiked synthetic drinking water and was applied to the determination of total arsenic in drinking water and river water from the arsenic rich zone in the north of Chile (city of Calama). The measurements were performed subsequent to the addition of 1.0 mL of $6 \text{ mol L}^{-1} \text{ HCl}$ solution and $80 \mu\text{L}$ of $0.40 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ solutions for every 5.0 mL of the sample. All solutions were prepared with deionized water (LiChrosolv, Merck CAS: 7732-18-5). Synthetic drinking water was prepared with reference to the maximum levels of some metals in drinking water recommended by WHO and the Chilean standard (Sb 20; Ba 100; Cd 3; Pb 10; Hg 6; Ni 70; Se 40; Cr 50; Fe 100; Mg 100; Mn 100; and Zn $100 \mu\text{g L}^{-1}$).

2.3. Adsorptive stripping voltammograms

Voltammetric measurements were made using the following procedure: 0.08–2.40 mL of HCl solution (12.5 mol L^{-1}), 0.0–2.0 mL of Cu(II) solution (1000 mg L^{-1}), aliquots of APDTC or ADDTP solution ($50.0 \mu\text{mol L}^{-1}$), and deionized water 10.0 mL were pipetted into the voltammetric cell. The experimental conditions were: drop size = 0.5 mm^2 , initial purge = 60 s, stirring speed = 2000 rpm, $E_{\text{ads}} = -0.20$ to -0.80 V and $t_{\text{ads}} = 10$ to 160 s. After an equilibration time of 10 s, the adsorptive voltammograms were recorded with the potential scanned from -0.30 to -1.00 V using differential pulse (DP), (modulation amplitude, 10 to 600 mV; interval time, 40 ms; potential step, 5 mV, resulting in a scan rate of 10 mV s^{-1}). Each scan was repeated three times. The calibration curves were obtained and linear regression and detection limits were calculated. In order to eliminate matrix effects the standard addition method was used.

2.4. Limits of detection (DL) and quantitation (QL)

The DL was calculated from $y_{\text{DL}} = a + 3\sigma_{x/y}$ and $y_{\text{DL}} = a + b x_{\text{DL}}$, where a is the intercept, $\sigma_{x/y}$ is the random error in x and y , and b is the slope. The QL was calculated from $y_{\text{DL}} = a + 10\sigma_{x/y}$ [18].

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