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Talanta 65 (2005) 613–620
Talanta
www.elsevier.com/locate/talanta

Review

Analysis and speciation of arsenic by stripping potentiometry: a review

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Received 20 April 2004; received in revised form 8 June 2004; accepted 23 July 2004
Available online 12 October 2004

Abstract

This paper provides a review that summarizes several examples of the literature from 1980 to 2003, to illustrate the applications of stripping potentiometry for the determination and speciation of arsenic in several samples. A discussion on the main advantages of stripping potentiometry in comparison with other electrochemical methods employed for arsenic determination is presented. Special attention is devoted to stripping modes (constant current or chemical stripping) and to issues related to the choice of working electrodes and supporting electrolyte. This approach has been also applied at arsenic determination in flow systems. A section is dedicated to speciation of arsenic and total arsenic determination and other to analytical characteristic of method and their interferences. An extensive compilation, organize by experimental and analytical parameters and real sample studied is presented.

Keywords: Arsenic; Determination; Speciation; Stripping potentiometry; Potentiometric stripping analysis; Constant current stripping analysis

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doi:10.1016/j.talanta.2004.07.034

1. Introduction

Arsenic is the 20th most abundant element in the earth's crust, 14th in the seawater and 12th in the human body [1]. This element occurs naturally in a wide range of minerals, which, together with a once widespread use in pigments, insecticides and herbicides, represent the major sources of arsenic in natural waters. The others uses of arsenic and arsenic compounds are in wood preservatives, glass manufacture, alloys, electronics, catalysts, feed additives and veterinary chemicals [2]. The growing interest of environmental scientists and analytical chemists for this element can be appraised in various recent reviews [1–9].

Arsenic has been identified as a public health problem because it has serious toxic effects even at low exposure levels and is widespread in the environment [10]. The US Environmental Protection Agency (EPA) has reduced public health risks from arsenic in the drinking water in January 2001 [11]. The agency has establishing a new arsenic standard at 10 $\mu g\,L^{-1}$ down from the current 50 $\mu g\,L^{-1}$ level.

Arsenic contamination in natural water is a worldwide problem and has become a challenge for the scientists. It has been reported in recent years form several parts of the world like USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India [9,12,13]. Knowledge of the speciation of arsenic in natural water is important because the bioavailability and physiological and toxicological effects of arsenic depend on its chemical form.

Speciation analysis involves the use of analytical methods that can provide information about the concentration of the different physico-chemical forms of the element [14] and its total concentration in the sample [15]. Speciation of arsenic in environmental samples is gaining increasing importance, as the toxic effects of arsenic are related to its oxidation state. The arsenic occur in the environment in different oxidation states [16]: As(V), As(III), As(0) and As(−III). As(III) is reported to be 25–60 times more toxic than As(V), and several hundred times as toxic as organic arsenicals (at least in the case of the mono and dimethylated forms) [3,5,17]. These facts indicate why it would be of priority interest to develop methods for the selective determination of As(III).

A wide variety of methods to determine arsenic have been used [2,3,6,18]: ultraviolet spectrometry; atomic absorption spectrometric methods (AAS), mainly coupled to hydride generation (HG-AAS); electrothermal-AAS in graphite furnace (ETAAS); atomic fluorescence spectrometry (AFS); atomic emission spectrometry (AES), generally with inductively coupled plasma (ICP-AES); inductively coupled plasma-mass spectrometry (ICP-MS); X-ray spectrometry; neutron-activation analysis (NAA); and capillary electrophoresis. Methods based on these techniques require expensive instrumentation, complicated procedures and special sample pre-treatment. Besides, most of these methods are essentially sensitive to total arsenic.

In general, electrochemical methods offer possibilities to determine arsenic and arsenic compounds at low concentrations [16]. These techniques offer the different advantages: simple instrumentation and operation, low cost, high sensitivity and excellent selectivity which allows diversifying the oxidation states of arsenic featuring different level of toxicity. However, simple direct measurements are possible only in simple solutions. In solutions with a complex matrix, the arsenic determination is only possible after separation from the interfering matrix.

Potentiometric methods have rarely been used to determine arsenic compounds. The few investigations aimed at the development of arsenate-selective electrodes produced no practically significant results.

Among the dynamic techniques, potentiostatic measurements are the most important for electro-analytical purposes. Chronoamperometric provide information about electrode reactions. The chronocoulometry has seldom been used for arsenic determinations, but is important for establishing the number of electrons involved in the electrode processes. Voltammetry and polarography (voltammetry with dropping mercury electrodes) are the most widely used electroanalytical techniques for the determination and speciation of arsenic [8,15]. In direct-current polarography (DCP), the detection limit for arsenite is approximately 0.7 $mg\,L^{-1}$. The detection limit decrease considerably by using differential pulse polarography, the most frequently used polarographic technique used today. Cyclic voltammetry is mainly used to investigate the reversibility and kinetic aspects of electrode reactions.

Generally, stripping analysis is better suited than direct polarography for trace determination in real samples because the substance of interest is pre-concentrated on the working electrode. The stripping techniques are suited to automated determinations or to fieldwork. Voltammetry stripping analysis is frequently used to determine traces of arsenic.

The principle of potentiostatic techniques is also realized in amperometric detectors for determining arsenic by flow injection or after gas chromatographic separation. Chronopotentiometry, a galvanostatic technique, is also employed. Concentrations of analytes in solution are obtained from potential–time curves recorded at constant currents.

Recently stripping potentiometry has been also used. This technique has been shown to possess advantages in sensitivity and selectivity over the voltammetric techniques [19–26]. In this way, the most important difference between potentiometric and voltammetric stripping is that in potentiometric no current passes through the working electrode during stripping. This makes the technique insensitive to interferences from electro-active substances present in the sample. In voltammetric stripping, such substances give rise to background currents that overlap the current stripping peaks. On the other hand, the time is the physical parameter measured in potentiometric stripping that can be measured with higher accuracy, precision and resolution than currents used in voltammetric methods [21].

This paper presents an overview of the stripping potentiometry for the determination of arsenic that has not been extensive studied.

2. Stripping potentiometry of arsenic

Stripping potentiometry has developed rapidly as a practical technique in both batch and flow systems. This method is based on the potentiostatic enrichment of analytes on an electrode surface and the subsequent re-oxidation or re-reduction of the analytes by means of either spontaneous chemical reactions or by a combination of such reactions and an applied constant current [27].

The two most common enrichment (electrolysis) procedures in anodic stripping potentiometry for arsenic determination are based on potentiostatic analyte reduction and simultaneous dissolution in gold on a working electrode surface [28–34], schematically:

$$\mathrm{As(III)} + 3\mathrm{e}^- \rightarrow \mathrm{As(Au)}$$

or

$$\mathrm{As(V)} + 5\mathrm{e}^- \rightarrow \mathrm{As(Au)}$$

Several authors have realized the pre-electrolysis step by electrochemical reduction of arsenic from a solution contained Au(III). In this way, elemental gold has been co-deposited with arsenic on the working electrode [27,35–39], schematically:

$$\mathrm{As(III)} + q\mathrm{Au(III)} + (3+3q)\mathrm{e}^- \rightarrow \mathrm{As(Au)} + q\mathrm{Au}$$

or

$$\mathrm{As(V)} + q\mathrm{Au(III)} + (5+3q)\mathrm{e}^- \rightarrow \mathrm{As(Au)} + q\mathrm{Au}$$

The molar excess gold(III), q, is in the order to avoid saturation by the reduced analyte in the gold film formed on the working electrode surface. In order to make the electrolysis as efficient as possible, this step is normally performed under convective conditions, e.g., electrode rotation, sample rotation or electrode vibration. In the subsequent oxidation (stripping) step, where the working electrode potential, E, is monitored versus time, t, the reduced arsenic is re-oxidized (stripped), either solely by oxidants present in the sample, for example Au(III) [27,35–37,39–41], or by an applied constant current, i_{ox}, [28–34,38,42] or by a combination of both [27,37,39], schematically:

$$\mathrm{As(Au)} + \mathrm{Au(III)} \rightarrow \mathrm{As(III)} + \mathrm{Au}$$

$$\mathrm{As(Au)} + i_{ox} \rightarrow \mathrm{As(III)} + 3\mathrm{e}^-$$

$$\mathrm{As(Au)} + \mathrm{Au(III)} + i_{ox} \rightarrow \mathrm{As(III)} + \mathrm{Au}$$

These are the two fundamental versions of technique applied to the arsenic determination: potentiometric stripping analysis (PSA) with chemical re-oxidation and constant current stripping analysis (CCSA) with current re-oxidation. The most common oxidants are dissolved oxygen and unreduced gold(III) ions. The relative contributions from the two-oxidation sources; chemical oxidants and i_{ox}, depend on the magnitude of the applied current, the concentrations of oxidants in the sample, the diffusion layer thickness during oxidation and the diffusion coefficients of the oxidants. In order to decrease the chemical contribution, caused by diffusion of chemical oxidant to the electrode surface, stripping is normally performed under quiescent conditions, i.e., convection is stopped 10–15 s prior to commencement of the stripping process.

In the determination of arsenic has been also used the cathodic stripping potentiometry (CSP) on a glassy carbon mercury film electrode in the presence of copper(II) ions [43]. The electro-deposition step involves the formation of a copper amalgam, which subsequently reacts with arsenic to form copper arsenide as given below [44]:

$$2\mathrm{As(III)} + 3\mathrm{Hg(Cu)} + 6\mathrm{e}^- \rightarrow \mathrm{Cu_3As_2} + 3\mathrm{Hg}$$

The reduction of the deposited copper arsenide to arsine is achieved by the application of a constant reductive current during the stripping step. The proposed electrode process during the stripping step involves the reduction of the copper arsenide as given below [44]:

$$\mathrm{Cu_3As_2} + 3\mathrm{Hg} + 12\mathrm{H}^+ + 12\mathrm{e}^- \rightarrow 2\mathrm{AsH_3} + 3\mathrm{H_2} + 3\mathrm{Hg(Cu)}$$

On the other hand, the stripping potentiometry for arsenic determination has been also used in flow cell and flow systems [28,30,34,36,37,40,42]. Incorporating a stripping potentiometric detector in an automated on-line flow analysis system yields some advantages [42] that include: higher throughput of sample, improved precision by minimizing the opportunities for human error, lower risk of contamination, lower consumption of sample and reagents, and the straightforward ability to exchange of the electrolytic medium between the electrodeposition and the stripping steps.

Table 1 contains a summary of several methods collected from literature of the last 23 years, in which it has been possible to determine arsenic by stripping potentiometry. The principles of the method just as the experimental conditions are summarized in this table.

3. Working electrode materials

In the electroanalytical determination of arsenic by stripping techniques, the use of gold electrodes, either a solid gold electrode or either gold plated electrode in anodic stripping [45–61], or mercury and mercury film electrodes in cathodic stripping [44,58,60,62–67], have been recommended.

Anodic stripping potentiometry for the determination of arsenic on gold [30,40,42] or gold-film [27–29,31–39,68] electrodes was described in various applications. Gold is the most suitable electrode for the determination of arsenic by stripping potentiometry. The hydrogen overpotential is greater than that for platinum, which reduces the problem

Table 1

Arsenic form	Technique[a] (measuring mode, arrangement)	Working electrode[b] (type, configuration)	Method principles[c]	Experimental parameters (oxidant, supporting electrolyte)	Analytical parameters (linearity, detection limit, specified levels of interfering ions and species[d])	Sample(s)	Reference
As(III)	PSA: co-deposition: $E_d = -0.05$ V, $t_d = 120$ s with the working electrode rotating; stripping: Au(III) used of oxidant with the working electrode rotating	Au(GCE)	A: $E_p = 0.15$ V vs. SCE	Au(III) serving also for co-depositing Au-film; 7 M HCl + 0.4 mM Au(III)	0.015–0.05 μM, 0.05–0.5 μM; 0.5–50 μM; 4.3 nM; Sb(III), Bi(III), Cu(II), Hg(II), Ag(I)	Model solution	[35]
As(III)	GSA: deposition: $E_d = -0.35$ V, $t_d = 100$ s with stirring; stripping: $i_{ox} = 12$ μA in quiescent solution	Au(GCE)	B: $E_p = 0.12$ V vs. Ag/AgCl	Positive current; 7 M HCl + 2.5×10^{-4} M Au(III)	0.005–0.15 μg/mL, 0.05–2 μg/mL; 8 ng/L; –	Steels, reference materials	[38]
As(III)	CCSA: deposition: $E_d = -0.5/-0.6$ V, $t_d = 120$ s; stripping: $i_{ox} = 7.5$ μA	Au(GCE)	C	Positive current; 0.5–2.5 M HCl + 2.5 M $CaCl_2$	1–50 ppb, 50–250 ppb; 1 ppb; Sn(II), Sn(IV), Pb(II)	–	[32]
As(III)	CCSA-flow system: deposition: $E_d = -1.05$ V, $t_d = 180$ s; stripping: $i_{ox} = 0.1$ μA	AuDiE	D: $E_p = -0.48$ V vs. Ag/AgCl	Positive current; NaOH solution at pH = 12	0.5–100 ppb, 0.1–50 ppb; 0.21 ppb; Bi(III), Pb(II), Sb(III)	Environmental samples	[42]
As(III)	CCCSP: deposition: $E_d = -0.5$ V, $t_d = 240$ s; stripping: $i_{ox} = 5$ μA	Au(GCE)	E: $E_p = 0.2$ V vs. Ag/AgCl	Positive current; 3 M HCl + 10 mg/L Au(III)	0.01–2 mg/L; 10 ppb	Model sample	[39]
As(III)	CCSA: deposition: $E_d = -0.9$ V, $t_d = 21$ s, stripping: $i_{ox} = 14$ μA	Au(GCE)	C: $E_p = 0.15$ V vs. SCE	Positive current; 5 M HCl	–, 0.1 ppb; Cu, Ni, Zn, Pb, Cd; surfactants such CTMAB, TX-100 and SDS	Fish, water and solid samples, reference material	[33]
As(III)	PSA-flow cell: co-deposition: $E_d = -0.1$ V, $t_d = 60$ s, $v_{flow} = 0.59$ mL/min; stripping: Au(III) used of oxidant with $v_{flow} = 0.59$ mL/min	Au(GCE)	A: $E_p = 0.2$ V vs. Ag/AgCl	Au(III) serving also for co-depositing Au-film; 1.2 M HCl + 160 mg/L Au(III)	5–20 ppb, 5–50 ppb, 50–500 ppb; 0.55 ppb; Cu(II), Se(IV), Sb(III), Bi(III), Hg(II), Pb(II)	Model solutions, tap water sample	[36]
As(III)	PSA-flow system	AuE	–	Au(III); HCl/Au(III) solution	10–1000 ppb	–	[40]
As(III)	PSA: deposition: $E_d = -0.4$ V, $t_d = 100$ s; stripping: –	AuFE	–	–; 1.5 M HCl	– 0.6 ppb	Food, Natural water	[68]
As(V)	CCSA: deposition: $E_d = -1$V, $t_d = 10$ s with stirring; stripping: $i_{ox} = 1.5$ μA without stirring	Au(Pt)	F: $E_p = 0.15$ V vs. SCE	Positive current; 2 M HCl	–; <0.1 ppb; Cu(II), Sn(IV)	Model solutions	[31]
As(III); As(V); As_{TOT}	CCSA-flow system: deposition: $E_d = -0.3$ V, $t_d = 240$ s, $v_{flow} = 1$ mL/min; stripping: $i_{ox} = 2.5$ μA, $v_{flow} = 2.2$ mL/min	AuFiE	Pre-reduction: As(V) + $2I^- \rightarrow$ As(III) + I_2; C: $E_p = 0.16$ V vs. SCE	Positive current and Au(III); 5 M HCl and 5 M HCl + 100 mg/L Au(III)	1–10 ppb; 0.15 ppb; Cu(II)	Sea water	[30]
As(III); As(V); As_{TOT}	CCSA-flow system: deposition: $E_d = -1.8$ V, $t_d = 60$ s, $v_{flow} = 1$ mL/min (As(V) and As_{TOT}) or $E_d = -1.6$ V, $t_d = 30$ s, $v_{flow} = 1$ mL/min (As(V)) and $E_d = -0.4$ V, $t_d = 60$ s, $v_{flow} = 1$ mL/min (As(III)); stripping: $i_{ox} = 0.5$ μA, $v_{flow} = 1$ mL/min	Au(PtFi)	Pre-oxidation: As(III) + HNO_3 or $HMnO_4$ or Hg(II) nitrate → As(V); F: $E_p = 0.2$ V vs. Ag/AgCl	Positive current and Au(III); 4 M HCl + 2.5 M $CaCl_2$ and 4 M HCl + 5 mg/L Au(III))	–; 0.1 ppb; Hg(II), Cu(II)	Sea water, urine	[28]
As(III); As(V); As_{TOT}	CCCSP: deposition: $E_d = -1$ V, $t_d = 240$ s; stripping: $i_{ox} = 40$ μA	Au(GCE)	Pre-oxidation: As(III) + Au(III) → As(V); G: $E_p = 0.2$ V vs. Ag/AgCl	Positive current; 1 M HCl + 250 mg/L Au(III)	–; 0.26 ppb	Model solutions	[27]
As(III); As(V); As_{TOT}	CPS: deposition: $E_d = -0.6$ V, $t_d = 30$ s with stirring; stripping: $i_{RED} = -1.5$ μA without stirring	MFE	Pre-reduction: As(V) + 2R-SH → As(III)+R–S–S–R + $2H^+$; H: $E_p = -0.75$ V vs. Ag/AgCl	Negative current; 1 M HCl + 5 mg/L Cu(II)	10–200 ppb; 2 ppb; Cd, Pb, Zn	Water, bobine liver, dogfish muscle samples	[43]
As(III); As(V); As_{TOT}	CCCSP-flow cell: Potentiostatic deposition: $E_d = -1.2$ or −1.5 V or galvanostatic deposition: $i_d = -3$ mA; stripping: $i_{ox} = 200$ μA	Au(PoE)	Pre-reduction: As_{TOT} + $N_2H_4 \cdot 2HCl \rightarrow$ As(III); C: $E_p = 0.2$ V vs. Ag/AgCl	Positive current; 0.1 M HCl	0.5–100 ppb,1–1000 ppb, 9–10000 ppb (As(III)); 0.15 ppb; Cu, Bi, Sb, Pb	Tap water, mineral water seawater and waste water samples, reference material, soil extract	[34]
As(III); As(V); As_{TOT}	CCSA: deposition: $E_d = -0.4$ V (As(III) and As(V)), $t_d = 15$ s (As(III)) or $t_d = 60$ s (As(V)) with stirring; stripping: $i_{ox} = 5$ μA, quiet solution (As(III) and As(V))	Au(C/SO)	Pre-reduction: $H_2AsO_4^-$ + 2R-SH → $H_2AsO_3^-$ + R–S–S–R + H_2O; C: $E_p = 0.18$ V vs. SCE (As(III)) or 0.25–0.38 V vs. SCE (As(V))	Positive current; 1 M $HClO_4$ + 0.2 M HCl	5–15 ppb, 10–50 ppb, 20–100 ppb, 100–300 ppb (according to t_d); 2 ppb As(III) and 0.5 ppb $As(V)_{RED}$; Hg(II), Ag(I), Se(IV), Cu(II)	Polluted river water, model samples	[29]
–	dPSA	–	–	–	–	Rice	[41]
As(III); As(V); As_{TOT}	PSA-flow cell: co-deposition: $E_d = -0.1$ V, $t_d = 60$ s, $v_{flow} = 0.59$ mL/min (As(III)) or $E_d = -0.7$ V, $t_d = 45$ s, $v_{flow} = 0.67$ mL/min (As(V)); stripping: Au(III) used of oxidant with $v_{flow} = 0.59$ mL/min	Au(GCE)	A and G: $E_p = 0.2$ V vs. Ag/AgCl	Au(III) serving also for co-depositing Au-film; 1.2 M HCl + 160 mg/L Au(III)	2.5–12.5 ppb, 10–50 ppb, 50–500 ppb; 0.55 ppb (As(III)) and 0.79 ppb (As(V))	Model solutions, polluted water samples	[37]

A: co-deposition: As(III) + qAu(III) + $(3 + 3q)e^- \rightarrow$ As(Au) + qAu, stripping: As(Au) + Au(III) → As(III) + Au; B: co-deposition: As(III) + qAu(III) + $(3 + 3q)e^- \rightarrow$ As(Au) + qAu, stripping: As(Au) + $i_{ox} \rightarrow$ As(III) + $3e^-$; C: deposition: As(III) + $3e^- \rightarrow$ As(0) stripping: As(0) + $i_{ox} \rightarrow$ As(III) + $3e^-$; D: deposition and stripping: $AsO_2^- + 2H_2O + 3e^- \rightarrow As + 4OH^-$; E: co-deposition: As(III) + qAu(III) + $(3 + 3q)e^- \rightarrow$ As(Au) + qAu; stripping: As(Au) + Au(III) + $i_{ox} \rightarrow$ As(III) + Au; F: deposition: As(V) + $5e^- \rightarrow$ As(0), stripping: As(0) + $i_{ox} \rightarrow$ As(III) + $3e^-$; G: co-deposition: As(V) + qAu(III) + $(5 + 3q)e^- \rightarrow$ As(Au) + qAu, stripping: As(Au) + Au(III) + $i_{ox} \rightarrow$ As(III) + Au; H: deposition: 2As(III) + 3Hg(Cu) + $6e^- \rightarrow Cu_3As_2 + 3Hg$, stripping: $Cu_3As_2 + 3Hg + 12H^+ + 12e^- \rightarrow 2AsH_3 + 3H_2 + 3Hg(Cu)$ and (–) denotes unspecified.

[a] PSA, potentiometric stripping analysis; GSA, galvanostatic stripping analysis; CCSA: constant current stripping analysis; CCCSP: constant current coulometric stripping potentiometry; CPS: cathodic stripping potentiometry; and dPSA: differential potentiometric stripping analysis.

[b] Au(GCE): gold-film plated glassy carbon electrode; AuDiE: gold disk electrode; AuE: gold electrode; AuFE: gold film electrode; Au(Pt): gold plated platinum disk; AuFiE: gold fibre electrode; Au(PtFi): gold plated platinum-fibre electrode; MFE: mercury film electrode; Au(PoE): gold plated porous electrode; Au(C/SO): Silicone oil-based carbon paste plated with gold.

[c] R–SH: SH–CH_2–CH(–NH_2)–COOH cysteine; R–S–S–R: HOOC–CH–(–NH_2)–CH_2–S–S–CH_2–CH(–NH_2)–COOH cystine.

[d] CTMAB: cetyltrimethyl ammonium bromide; TX-100: triton X-100; SDS: sodium dodecyl sulphate.

of simultaneous evolution of hydrogen [55] while depositing arsenic. Besides, gold displays better reversibility of the electrode reactions for arsenic in both the plating and stripping step [55], which results in higher and sharper oxidation peaks [51,55]. However, the response of gold electrode is very strongly dependent on the past history, pre-treatment and the oxide films formation [51]. The solid gold electrodes have high costs and require permanent control and care of the quality of their surface [68]. From time to time, special treatment procedures such as polishing, activating or regeneration of the electrode surface are necessary to avoid possible oxidation of the electrode surface and its memory effects [44]. Besides, elemental arsenic is not electrically conductive, and once deposited at an active electrode side, it passivates the location to further deposition of electro-active species [53,55,57], including more arsenic. Such troubles can be overcome by using the so-called gold-film electrodes. In this case, gold is deposited electrolytically in a form of thin metallic layer [69] on the surface of a suitable electrode support (graphite, platinum or gold itself). More recently, it has been shown that carbon paste electrodes can also be used as convenient supports for gold film electrodes [69,70]. On the other hand, the favourable effect of gold(III) ions presents in the supporting electrolyte on the sensibility of the determination of arsenic has been explained [53] as due to simultaneous deposition of gold and arsenic on the support; this prevents complete coverage of the support by elemental arsenic, which would decrease the efficiency of the pre-electrolysis on account of the low-electrical conductance of arsenic. Few authors [35–37,40] proposed a potentiometric stripping determination employing chemical oxidation of elemental arsenic on the electrode surface by gold(III) ions present in the supporting electrolyte. Some authors [27,35–39] used the co-deposition of arsenic and gold.

In contrast, cathodic stripping analysis of arsenic on mercury film electrodes is not usually employed due to relatively poor sensitivity of arsenic on mercury electrodes [35,53,65] and also because of interferences from some ions [55]. The methods based on the co-deposition of arsenic and other metal ions as intermetallic compounds on a hanging mercury drop electrode (HMDE) have been reported [44,65]. However, cathodic stripping potentiometry has been explored for arsenic determination on a glassy carbon mercury film electrode in the presence of copper(II) ions [43].

4. Supporting electrolyte

In anodic stripping determinations of arsenic, the stripping medium must be acidic in order to avoid the formation of hydrolysed species during stripping step [35,38,44,46,48,53,55].

It follows from the literature [35,50,51,53,56,71–73] that hydrochloric acid is the most suitable and widely used supporting electrolyte for the electrochemical stripping determination of arsenic. This acid provided good sensitivity and the stripping peaks were also narrow which indicated that the charge-transfer reaction was fast and reversible [48,51,53,74,75]. Various authors have concluded that the use of higher concentration of hydrochloric acid increases the arsenic stripping signal [18,51,75]. The presence of chloride in the samples is therefore interpreted as being necessary to provide well-defined stripping reactions for arsenic [31,56] because of the chlorine ions strongly complex arsenic to form $AsCl_3$ [51,76]. According to Arnold [77], the As(III) species in aqueous solutions contained hydrochloric acid at increasing concentration are found to be consistent with the existence of the following species: H_3AsO_3, $As(OH)_2^+$, $As(OH)_2Cl$, $As(OH)Cl_2$, and $AsCl_3$

Since $As(OH)_2Cl$ and $As(OH)Cl_2$ are thought to be the actual species, which take part in the electron-transfer reaction on the electrode [75], the deposition efficiency of As(III) become higher as the amount of $As(OH)_2Cl$ and $As(OH)Cl_2$ increases with increasing hydrochloric acid concentration. Moreover, it is noteworthy that more chloride ions tightly bound in double layer around the electrode act as a bridge between the arsenic ion and the electrode, which makes the redox reaction more reversible [75,78]. From above descriptions, the conversion of As(III) species and the occurrence of chloride ion-bridge may explain the corresponding positive shift of peak potential and increasing arsenic signal.

In arsenic determination by stripping potentiometry, the stripping plateaus are also better defined in media containing hydrochloric acid [27–40,43,68]. However, higher concentrations of hydrochloric acid have been avoided because it offered no significant increase in arsenic signal and there was also more irreproducibility that may be due to adsorbed chloride on the gold substrate [76]. Besides, it was also advised that prolonged exposure to hydrochloric acid concentrations be avoided as it could destroy the working electrode [35,72]. And on the other hand, it is necessary to minimize the amount of acidic waste generated. It was previously found that when arsenic was determined in a hydrochloric acid matrix, chlorine was generated at the auxiliary electrode concurrent with arsenic deposition at the working electrode. The chlorine would then diffuse to the working electrode where it would readily oxidise the gold electrode surface, thereby making it inactive [42]. This problem was solved by using a flow cell [34,37] or a flow system [28,30,40,42]. In this way only the solution from the jet reached the working electrode surface; thus, the chlorine could not diffuse to it. It has also been postulated that the gold film was oxidised in the presence of a high chlorine concentration to the $AuCl_4^-$ complex. This would decrease the active gold surface area and result in poor reproducibility [51]. In these systems, the flow approach making it possible to pre-condition the electrode in one solution and clean it in another between consecutive runs.

Aldstadt and Martin [42] explored the determination of arsenic by stripping potentiometry in alkaline media as an alternative to the published methods for arsenic determination

under acid conditions. The optimum pH level was found to be 12. A flow injection method that avoided the use of chlorides is designed. The method is applicable to arsenic compounds that can be base hydrolysed to yield arsenious acid.

5. Speciation of arsenic and total arsenic determination

Environmental samples, such as freshwater, seawater, animal tissues and soils, may contain inorganic and organic arsenic compounds. To determine total arsenic by electrochemical methods, the various arsenic compounds must be converted to arsenate, As(V) or preferably arsenite, As(III) [16]. Solid samples and samples containing organic arsenic compounds must be mineralized. The oxidative environment during these digestions (HNO_3, H_2SO_4, and $HClO_4$) assures that all of the arsenic present is converted to arsenate. Aqueous samples or extracts that do not contain organic compounds need not be digested, unless the organic matrix interferes with the determination. Differentiating between inorganic and organic arsenic compounds is carried out by two steps [16]. First, total inorganic arsenic is determined by the electrochemical method proposed. In a second step, all compounds are converted to arsenate by oxidative mineralization followed by repeated measurement of total arsenic.

As(III) and As(V) exhibit different electrochemical behavior. Conventionally, As(III) is electrochemical reduci to the element, while As(V) is generally considered to be electrochemically inert under normal conditions [28,30,55,60,65,79]. This means that for the determination of total arsenic content, it is necessary to reduce As(V) to As(III). Some chemical reductants recommended were Na_2SO_3 [55], N_2H_4 + HCl + HBr [44], NaBr + N_2H_4 + H_2SO_4 [65], gaseous SO_2 [51,57], KI [58], KI + ascorbic acid [79], cysteine [29,73] and mannitol [63]. So, the differentiation and determination of As(III) and As(V) can be achieved by simply quantifying the difference between the total inorganic arsenic, i.e., As(III) + As(V), after applying the chemical pre-reduction step [73] and the original content of As(III). However, the reducing step is not a simple one and quite often there are problems including the additional treatment time and possible contamination of the sample due to the possible interference from an excess of reducing agent [55,73] or the products of the reduction reaction. In fact, in some cases, the solution has to be heated to complete the conversion of As(V) into As(III) and the results are inaccurate and not precise owing to losses of volatile compounds containing arsenic [80].

On the other hand, it is know that As(V) can be directly electroreduced to As(0) and their concentration can be directly determined without prior chemical reduction to As(III) by applying a potential sufficiently cathodic [18,59–61,81] using a gold film electrode or a gold electrode.

Most of stripping potentiometric methods were based on the chemical reduction of As(V) to As(III) with cysteine [29,43], KI [30] or hydrazine hydrochloride [34], prior to electrochemical reduction to As(0) and subsequent potentiometric stripping measurements. It was also shown that As(V) can be electrochemically reduced directly to As(0) by the use of low reduction potentials [31,37]. Some authors [27,28] carry out a pre-oxidation step to convert the As(III) to As(V) and afterwards, to reduce electrochemically the As(V) to As(0). The speciation is achieved to make the difference between the total arsenic and original As(III) or As(V) to find in the sample. The concentration of each species is determined in most instances by standard addition procedure.

Advantages of flow applied at stripping potentiometry have been described in the text. Between these advantages it is important to emphasize that stripping step can be applied in a medium containing no reducing agents and where the arsenic stripping peak is well separated from that of others.

6. Analytical characteristic of method and interferences

Compared to the voltammetric approach, the method utilizing stripping potentiometry for arsenic determination offers a more rapid procedure with improved analytical characteristics such as reproducibility [29,35] or reduce detection limit [27–30,33,35,43]. The lowest detectable amount decreases with increasing electrolysis time. The sensitivity of the arsenic response increased with increasing electrolysis time, like this the method is able to operate reliably even at low ppb levels (Table 1). However, the linear concentration range was limited by the saturation of electrode surface at longer electrolysis time and with higher concentration of analyte [29,30,36]. This relatively higher mean deviation observed may be associated with increased hydrogen evolution. Hence, to avoid problems that may arise from excessive hydrogen evolution, it is recommended to use short electrolysis times [33,34,36].

Possible interferents in the arsenic determination by stripping potentiometry are the ion metals, which can be reduced at the gold electrode or at the some electro-deposition potential than arsenic: Sb(III), Bi(III), Hg(II), Pb(II) and Cu(II) [36]. The stripping peak potentials for other gold-soluble elements, which are oxidized at potentials close to that of arsenic, can be separated simply by varying the chloride concentration in the stripping medium with calcium chloride and hydrochloric acid [28].

Special attention was paid to Cu(II) and Se(IV) ions whose interference due to the capability to form binary intermetallic compounds with arsenic such as Cu_3As_2 and As_2Se_3 and represent the most problematic point in the potentiometric procedure [36]. The most serious interferent in the potentiometric stripping determination of arsenic is Cu(II) [35,36]. The potentiometric method requires that the samples do not contain a too high content of Cu(II). In samples with an excess of Cu(II) versus arsenic, it should be necessary to modify the method with an additional step such as ion-exchange

separation in order to eliminate Cu(II) effectively from the sample prior to analysis [29]. Other authors avoided this interference by a completely re-oxidation of copper, prior to stripping of arsenic, at a potential different than potential of arsenic [30].

Inorganic and organic interferences were overcome either by decomposition prior to the analysis by ultraviolet irradiation [33] or acid digestion [43], and/or by use of standard addition for quantification of arsenic in samples [33,43].

Partial least-squares (PLS) regression calibration can overcome many of the problems encountered in stripping potentiometry applications [31] such as stripping peak overloads, formation of intermetallic compounds, reagent interferences, non-linearity in response and high-stripping curve backgrounds. One of the quality of the PLS calibrations approach is the possibility of detecting outliers, i.e., samples with deviating sample matrices, which can be invaluable in cases where no directly apparent interferences are at hand.

On the other hand, the basic method for arsenic determination [42] possesses advantages over other methods performed under acidic conditions, in that the effect of interfering metals can be eliminated. In this approach, the medium exchange solution is simpler as only fresh carrier enters the flow cell. Medium exchange allows the analyst to control the selectivity of the experiment because the stripping solution can be designed to complex an interfering species, to separate the peak potentials of overlapping analytes or to eliminate electro-active interferences.

Table 1 contains linear ranges, detection limit and interferences of the potentiometric methods for arsenic determination.

7. Analysis of real samples by stripping potentiometry

The possibilities of the optimized method are demonstrated by determinations of As(III), As(V) and total arsenic in samples of polluted river water, seawater, tap water, organic tissues, soils, food, etc. Besides, the adequacy of the potentiometric method was also verified by use of some reference samples.

The degradation of naturally dissolved organic matter or other organic compounds in water or effluent samples evidently can be obtained by traditional digestion methods. The determination of arsenic in solid samples and biological material require dissolution and, in some cases, decomposition of organic matrix prior potentiometric measurements by digestion or ultraviolet irradiation [28,33,43]. The determination of trace arsenic levels has been also carried out in a material of industrial interest steel. In the analysis of steel, the arsenic must first be separated by selective extraction of As(III) bromide into toluene and back-extraction into the supporting electrolyte [38].

Table 1 contains several examples of real samples studied by stripping potentiometry.

8. Conclusions

Arsenic contamination is a worldwide problem and has become a challenge for the world scientists. The toxic effects of arsenic are related to its oxidation state, resulting in increasing interests in the quantitative determination of individual species. Various approaches have been developed for determination and speciation of arsenic with its own advantages and limitations. Hydride generation-atomic absorption spectrometry is the most widely accepted method that determines arsenic at microgram per liter level.

Stripping potentiometry has been used during the past 23 years for the determination and speciation of arsenic in several samples. This method is a simple and viable low cost instrumental technique for arsenic determination at microgram per liter concentration. Gold and gold-film plated electrodes and HCl as support electrolyte have been widely used. The availability of electrodes might guide the selection towards diverse measuring modes of this technique. In the speciation studies, As(III) has been reduce electrochemical to the element, while As(V) has been chemically or electrochemically reduced at As(III). The flow systems have been also used with stripping potentiometry for arsenic determination. This method has been successfully applied to determine arsenic in real samples.

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