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REVIEW

Electrochemical methods for the determination of total arsenic and arsenic compounds

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The determination of total arsenic and of arsenic compounds in biological and inorganic samples is a task frequently encountered by analysts. Several electrochemical methods have been developed for the determination of total arsenic (generally after mineralization of the sample), arsenite, arsenate, methylarsonic acid and dimethylarsinic acid. The electrochemical behavior of several other organic arsenic compounds was also studied. This paper reviews these electrochemical methods, their application to environmental samples, and the problems encountered in the electrochemical determination of arsenic and arsenic compounds.

Keywords: Arsenic, arsenic compounds, electrochemical determination, polarography, stripping voltammetry

INTRODUCTION

The well-known toxicity and the likely essentiality of arsenic sustains the high interest of environmental scientists, toxicologists, and analytical chemists in this element. During the past 30 years, close to 2000 publications about environmental, biological and analytical aspects of arsenic and its compounds have appeared. This multidisciplinary approach is well expressed by the fact that arsenic-related publications can be found in several hundred different journals. A recent review about the determination of arsenic and arsenic compounds in environmental samples listed 445 reference.[1] The precise and accurate determination of total arsenic and of arsenic compounds in rocks, soils, fresh water, seawater, plant materials, animal tissues and human samples is a prerequisite for the proper evaluation of risks associated with exposure to arsenic compounds, for the clarification of the natural arsenic cycle,[2] for the establishment of cause–effect relationships, for the verification of the effectiveness of remedial actions and for the promulgation of recommendations of reasonable, safe and cost-effective maximal arsenic concentrations in soils, waters, air and food items.

Experimental results obtained during the past two decades clearly show that concentration measurements of total arsenic alone are inadequate for the evaluation of the impacts of arsenic on man, animals and plants.[3] The rich chemistry of arsenic makes it possible for inorganic and organic compounds of arsenic to be found in environmental samples. The various arsenic compounds differ with respect to their biological properties; some of the organic arsenic compounds are non-toxic, whereas others may have detrimental effects. Living organisms are capable of transforming arsenic compounds. For these reasons, analytical methods that allow the identification and quantification of inorganic and organic compounds of arsenic are needed.

Electrochemical methods are widely used in environmental analytical chemistry for the determination of inorganic and organic analytes. Although a considerable amount of literature exists about electrochemical determinations of total arsenic and of some arsenic compounds, the applications of these methods for environmental work are not overwhelming.

This review article summarizes the electrochemistry of arsenic compounds and describes the types of samples that have been analyzed for total arsenic and for arsenic compounds. This information should serve as a starting point for more applied work in the area of electrochemical identification and quantification of arsenic compounds

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in environmental samples, with emphasis on organic derivatives of arsenic.

All concentrations given in this review are in terms of arsenic unless stated otherwise.

ELECTROCHEMICAL TECHNIQUES

Some confusion about names of voltammetric techniques exists in the literature. In this article, the nomenclature suggested by IUPAC is used.[4]

Voltammetry, a technique popular not only for arsenic compounds, is based on the measurement of currents as a function of potential. Polarography is a special case of voltammetry characterized by the use of dropping mercury electrodes.

The measured currents consist of a faradaic current, which is proportional to the concentration of the electroactive species, and a capacitative current, which is caused by the formation of an electric double layer at the surface of the electrode. The capacitative current is an undesirable background current that decreases exponentially with time. In classical dc polarography both currents are normally measured. The detection limits for the determination of arsenite by dc polarography is approximately 0.7 mg dm^{-3}.[5,6]

Minimizing the influence of the capacitative current leads to lower detection limits. In modern electrochemistry, potential pulses are applied to the working electrode and the current is measured when the capacitative component is low. In this way the detection limits can be improved. A number of techniques differing with respect to the nature of the applied pulses are used: normal-pulse polarography (NPP), differential-pulse polarography (DPP), alternating-current polarography, and square-wave polarography. Differential-pulse polarography, the most frequently used polarographic technique today, allows the determination of arsenite in the concentration range 20 μg dm^{-3} to 50 mg dm^{-3}.[7] Figure 1 shows a differential-pulse polarogram of arsenite (10 mg dm^{-3}) in aqueous 1.0 mol dm^{-3} hydrochloric acid (HCl). Polarograms of arsenite obtained by sampled dc or linear-sweep polarography are presented in Fig. 2.

Another technique, mainly used for investigations of electrode processes, is linear-sweep voltammetry. In this method a linear potential sweep is applied to a solid electrode or to a single, hanging mercury drop. Linear-sweep voltammetry with a potential scan in one direction followed by a scan in the reverse direction is called cyclic voltammetry. This method is very often used for investigations of the reversibility of electrode reactions.

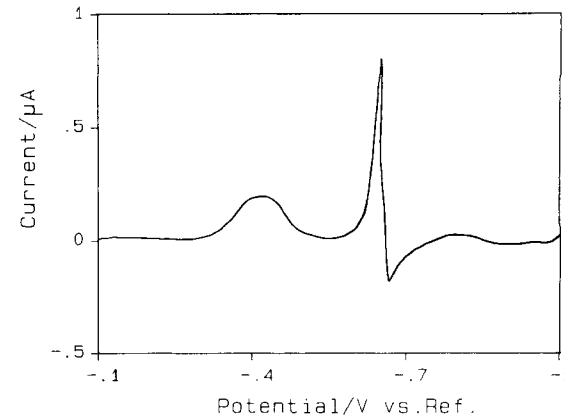

Fig. 1 Differential-pulse polarogram of 10 mg dm^{-3} arsenite in aqueous 1.0 mol dm^{-3} HCl.

An extensively used technique for the determination of traces of arsenic and heavy-metal ions is voltammetric stripping analysis. In this method the analyte is preconcentrated by electrolytic reduction into or onto the working electrode. After the preconcentration step the deposited analyte is determined by anodic oxidation (anodic stripping voltammetry, ASV) or further cathodic reduction (cathodic stripping voltammetry, CSV).

To obtain analytically usable signals, the duration of the preconcentration step (deposition time) will have to increase with decreasing concentration. For arsenic the following transformations occur at the electrodes:

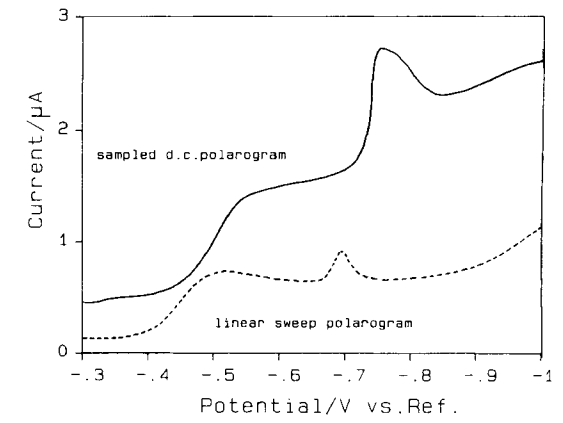

Fig. 2 Sampled dc and linear-sweep polarograms of arsenite solutions.

Preconcentration step: Arsenite → As(0)
Anodic stripping scan: As(0) → Arsenite (AsO_2^-)
Cathodic stripping scan: As(0) → AsH_3

The most widely used stripping mode is differential-pulse voltammetry, although other techniques such as conventional dc polarography and ac voltammetry are still in use.

In addition to the potentiostatic methods so far described for the determination of arsenic, galvanostatic techniques can be employed. Concentrations of analytes in solution are obtained from potential–time curves recorded at constant currents. Recently galvanostatic stripping modes were proposed.[8,9]

In another stripping technique, called potentiometric stripping analysis (PSA), arsenite is preconcentrated in the usual way. The elemental arsenic is, however, reoxidized chemically at a controlled rate. A suitable oxidizing reagent is Au(III), which is also used for codeposition with arsenic. The detection limit for arsenite—estimated from potential vs time curves—is given as $0.3\,\mu g\,dm^{-3}$.[10,11] More detailed information about stripping techniques is available in the literature.[12]

The concentration of arsenite (proportional to the current or potential) is determined in most instances by standard addition procedures. Assessment of the background under the current peak is necessary. A variant of the standard calibration procedure using two deposition times and two standard additions allows accurate determinations without additional baseline assessment.[13]

Generally, the instruments for voltammetric measurements are designed only for use in the laboratory. However, portable digital voltammeters have been developed for field explorations. The instruments employ solid electrodes in a novel cell design and allow the determination of a number of elements at $\mu g\,dm^{-3}$ levels.[14,15]

ELECTROCHEMISTRY OF ARSENITE

Anodic oxidation and cathodic reduction

The redox behavior of arsenite under conditions normally used in electrochemical measurements is described by Eqn [1]:

$$\text{Arsenate } (AsO_4^{3-}) \leftarrow \text{Arsenite } (AsO_2^-) \leftrightarrow \leftrightarrow As(0) \leftrightarrow AsH_3 \quad [1]$$

Polarograms of solutions of arsenite in dilute hydrochloric, sulfuric or perchloric acid consist of two waves that can be attributed to the reduction of arsenite to arsenic(0) and of arsenic(0) to arsine.

The half-wave potentials vs SCE corresponding to the two maxima occur at approximately -0.4 V and -0.8 V. A sharp current spike at -0.65 V is attributed to catalytic processes[6] and is observable only at concentrations higher than $300\,\mu g\,dm^{-3}$. The use of surfactants such as Triton X-100 or gelatine tends to suppress the spike but shifts maxima and increases the detection limits (i.e. makes them poorer).[5,16,17] The nature of the supporting electrolyte influences diffusion currents, shifts half-wave potentials and may cause additional waves.[5,6] Detailed information about these influences are given in the Tables.

In certain supporting electrolytes that contain traces of cobalt(II), iron(III), selenite or tellurite, the maximum at -0.8 V is split into two maxima. The appearance of these so-called catalytic maxima is associated with the catalytic evolution of hydrogen. This effect was used for the polarographic determination of arsenite in the range $1–15\,\mu g\,dm^{-3}$. For instance, in a system consisting of sulfuric acid–HCl–KBr–selenite, a catalytic wave appeared at -0.53 V.[18]

All methods described up to now are based on the reduction of arsenite to arsenic(0) and arsine with possible reoxidation to arsenite. Several attempts were made to use the oxidation of arsenite to arsenate for analytical purposes. In flow-injection analysis the anodic oxidation of arsenite would be the method of choice, because it is not troubled by the simultaneous reduction of dissolved oxygen during the cathodic reduction of arsenite. However, investigations of the anodic oxidation of arsenite on platinum electrodes in dilute perchloric acid showed that anodic currents (at 0.75 V) could be obtained only under special conditions.[19]

Electrochemical oxidations of arsenite were found to be highly irreversible at bare electrodes such as platinum and other noble metals. The irreversibility is probably caused by catalytic effects of noble-metal oxides on the surface of the electrodes.[20–24] Therefore, electrochemical oxidations cannot be used for analytical purposes under these conditions. A hanging mercury drop was suggested as an electrode for the anodic oxidation of arsenite to arsenate.[5,25]

Arsenite can be easily oxidized chemically in the presence of a catalyst. For instance, well-

known catalysts for the oxidation of arsenite with cerium(IV) are ruthenium(III), ruthenium(IV) or ruthenium(VIII). When mixed-valent ruthenium(II,III)-cyanide complexes are immobilized on an electrode surface, arsenite is catalytically oxidized by hexacyanoruthenate(III) as shown by cyclic voltammograms.[21]

Calibration curves are linear for the concentration range 0.2–90 mg As dm^{-3}. Other supporting electrolytes and modified redox couples for this catalytic oxidation lowered the detection limit of the method to 10 μg As dm^{-3}.[26,27]

Electrodes

For polarographic measurements, dropping mercury electrodes and hanging mercury drop electrodes are used. However, the low solubility of As(0) in mercury makes mercury electrodes less than ideal for stripping techniques.

Addition of selenite to arsenate-containing solutions eliminates these difficulties. Mercury forms mercury selenide through reduction of selenite. Arsenite reacts between -0.25 and -0.5 V with the deposited mercury selenide forming arsenic selenide, which is subsequently reduced to arsine at -0.72 V.[28,29] Similarly, copper(II) produces copper arsenide which dissolves in mercury and makes possible the use of a hanging mercury drop electrode for the determination of arsenite by stripping techniques.[30–32]

Anodic stripping voltammetry of arsenite with mercury as electrode material is not analytically useful. The oxidation of mercury interferes with the determination. Solid electrodes can be used in anodic and cathodic stripping techniques. Glassy carbon, gold or platinum electrodes form oxides at higher anodic potentials than mercury. Nevertheless, the coverage of electrode surfaces by oxide films influences the response of these solid electrodes. Furthermore, the electrode response depends on the pretreatment of the electrode.

Arsenite is incompletely reduced at pure glassy carbon electrodes. However, the reduction on glassy carbon electrodes is complete when the arsenite solution contains copper(II) or mercury. Under these conditions arsenite is reduced to arsine, which subsequently reacts with mercury to form a mercury arsenide.[33–36] Alternatively, the glassy carbon electrode can be copper-coated *in situ* before reduction of arsenite.[37] A mercury-coated copper electrode was used for the determination of 2 μg As dm^{-3} in solutions containing 30 mg Cu(II) dm^{-3}.[38] Another technique of high analytical interest uses *in situ* modified electrodes in stripping voltammetry. A glassy carbon electrode was coated with mercury by electrolysis of a Hg(II) solution at -0.9 V. Then the coated electrode was immersed into a solution containing (per dm^{-3}): 1.5 mol HCl, 0.4 mol KI, 0.0002 mol-mercury(II) nitrate and arsenite. A potential of -0.4 V was applied. During the electrolysis a layer of adsorbed iodide (I^-) and HgI_3^- is postulated to be formed first. Then arsenite as $As(OH)_2^+$ is probably concentrated in the I^-/HgI_3^--layer in the form of a binuclear complex. In the following cathodic scan the response of arsenic is recorded at -0.78 V. The detection limit of this method is 0.4 mg dm^{-3}.[39]

Concomitantly with the electrolytic deposition of arsenic(0) in stripping methods, hydrogen is formed. This hydrogen covers the surface of the electrode. When platinum electrodes are used, the large anodic waves from the oxidation of the hydrogen films on the electrode surface seriously interfere with the determination of arsenite in very dilute solutions. Gold has a higher overvoltage against hydrogen than platinum. Therefore, gold discs, gold wires, gold-plated glassy carbon and gold-plated graphite were used as electrodes.[40–49] Gold-plated glassy carbon electrodes were observed to function better when Au(III) was present in solution.[48]

An increasing electrode response to arsenite was observed when anodic stripping voltammetry was carried out with platinum electrodes in the presence of gold(III).[40] The deposition of arsenic(0) on an electrode surface increases the electric resistance of the electrode, decreases the current and increases the detection limit. Therefore, solid electrodes must be cleaned after each measurement. Unusual electrode materials such as copper, titanium and steel were used for investigations on the reduction mechanism of arsenic(III).[50]

A study was carried out to check whether or not oxygen should be removed from an arsenite solution in which arsenic is to be determined by anodic stripping voltammetry with gold electrodes in 1 mol dm^{-3} sulfuric acid. The presence of oxygen appears to increase the precision of the determination and to speed up the electrode reactions.[51]

Several attempts were made to electrolyse and strip anodically in non-aqueous solutions to prevent the reduction of hydrogen ions. Very

negative potentials between -2.5 V and -3.5 V can be applied to the reduction of arsenic(III) at platinum or gold electrodes.[52-55, 154]

ELECTROCHEMISTRY OF ARSENATE

Arsenate is electrochemically inactive under conditions used in the electrochemical determination of arsenite. Only when arsenate was dissolved in 11.5 mol HCl dm^{-3}, were polarographic signals obtained.[56] These signals became too complex to be useful for analytical work at arsenic concentrations above 0.004 mol dm^{-3}.

Arsenate becomes electroactive when phenols, such as catechol[57, 58] and pyrogallol,[5, 58] or aliphatic polyhydroxy compounds, such as D-mannitol, are added to 2 mol dm^{-3} perchloric acid solutions of arsenate.[59, 60] Under these conditions arsenate can be determined by polarographic techniques. The exact mechanism for this activation is not known. Ligation to or condensation of the hydroxyl groups with arsenic acid is a probable cause.

Arsenate can also be reduced to elemental arsenic on a freshly prepared gold-coated platinum-fiber electrode at electrolysis potentials below -1.6 V vs Ag/AgCl. Reoxidation at constant current leads to an arsenic stripping peak between -0.1 and $+0.15$ V.[9] Selective electrodes for monohydrogen arsenate ($HAsO_4^{2-}$) and hexafluoroarsenate (AsF_6^-) are mentioned in the literature.[61-63] However, high (i.e. poor) detection limits, bad reproducibility, and low selectivity make these electrodes unsuitable for analytical applications.

DETERMINATION OF ARSENITE

Conventional dc polarography is rarely used today for the determination of arsenite. This technique was used to study the effects of different supporting electrolytes, such as dilute acids, buffers, complexing agents and ε-caprolactam, on half-wave potentials and detection limits for arsenic.[16, 25, 64]

Most of the polarographic determinations of arsenite were carried out with the differential-pulse technique. Table 1 summarizes these methods and provides information about supporting electrolytes, types of samples and detection ranges. A majority of the investigated samples are aqueous solutions (seawater, fresh water, standard solutions) or solutions obtained through dissolution of alloys or particulates. Extracts from biological samples have so far not been investigated.

Not included in Table 1 are the galvanostatic stripping investigations. Galvanostatic stripping curves at a constant current of 2 μA were evaluated by chronopotentiometric techniques for the determination of arsenic in steel and raw copper.[65, 66]

A computerized potentiometric stripping method for the determination of arsenite in 7 mol dm^{-3} HCl containing 80 mg Au(III) dm^{-3} as oxidizing reagent had a detection limit of 0.4 μg dm^{-3}.[10]

Catalytic waves can be used for the polarographic determination of traces of arsenite in water samples,[67] minerals, rocks,[68] steel[69] and ores.[18] To avoid poisoning of the surface of the mercury electrode by elemental arsenic, gold(III) was added to the solutions. Arsenic was preconcentrated on a gold-plated glassy carbon electrode. In a supporting electrolyte of 0.5 mol dm^{-3} HCl, 2.5 mol dm^{-3} perchloric acid, and 0.0005 mol dm^{-3} tin(II) chloride, a catalytic peak appears at $+0.34$ V.[48] Table 2 summarizes the operating conditions and concentration ranges.

Anodic stripping voltammetry was used to determine arsenic(III) in non-aqueous solutions. A potential of -2.5 V was employed for the reduction of arsenic(III) at platinum electrodes,[52] and -3.5 V for the reduction at gold electrodes (electrolysis time between 5 and 50 s).[53] Lithium perchlorate in acetonitrile (0.1 mol dm^{-3}) served as supporting electrolyte. The extremely low detection limit of 0.3 ng dm^{-3} was reported to have been achieved in this non-aqueous system with gold electrodes.[54, 55]

DETERMINATION OF ARSENATE

For the direct electrochemical determination of arsenate a number of procedures are available.

In a 2 mol dm^{-3} perchloric acid solution containing D-mannitol, arsenate can be determined by differential-pulse polarography at a half-wave potential of -0.55 V in the concentration range from 20 μg dm^{-3} to 160 mg dm^{-3}. Figure 3 shows differential-pulse polarograms of arsenate alone

Table 1 Determination of arsenic(III) by different voltammetric methods

Method	Electrode	Supporting electrolyte (M = mol dm^{-3})	Potential (V)	Working range (μg As dm^{-3})	Sample containing arsenic(III)	References
DPCSV[a]	HMDE[f]	1 M-HCl/2 × 10^{-3} M-Cu^{2+}	−0.55 (−0.04)[h]	0.2–20	Prepared aqueous solutions and seawater	31, 70
DPCSV	HMDE	1 M-HCl	—	1–50	Environmental samples[k]	71, 72
LSASV[b]	Cu-coated carbon	2 M-HClO$_4$/10^{-4} M-Cu^{2+}	−0.6 (−0.14)[h]	3–24	Seawater	37
LSASV	Au disk	—	0.16	1–50	Waste water	73
ASV	Au	—	—	1–30	Natural water	74
ASV	Au, Pt	—	—	70–700	Prepared solutions with antimony and bismuth	75
ASV	Rot. glassy carbon	Presence of Cu(II)	— (−0.60)[h]	70–700	Lake water	76
ASV	Au-plated graphite	—	—	1–200	River water	77
ac CSV[c]	Cu-coated graphite	HCl/CuSO$_4$/KI/HgCl$_2$	—	—	Arsenic in indium after dissolution	78
ac ASV	Au-coated graphite	2 M-HCl	−0.5	0.8–3.5	Arsenic in nitric acid	79
DPP[d]	DME[g]	0.1 M-EDTA/1 M-acetate	−0.6	—	Air particulates after dissolution	80
DPP	DME	1 M-HCl	−0.6	30–300	Trap water in presence of thallium	81
DPP	DME	Buffer, pH 8.3	−1.66	90–300	Prepared solutions with tellurite and tellurate	82, 83
DPP	DME	—	—	0.1–50	Alloys and plating baths	84, 85
FSDPP[e]	DME	1.5 M-HCl/10^{-2} M-Br$^-$	−0.43	50–250	Alloys, simultaneously with antimony and tin	86

[a] Differential-pulse cathodic stripping voltammetry. [b] Linear-scan anodic stripping voltammetry. [c] Alternating current cathodic stripping voltammetry. [d] Differential-pulse polarography. [e] Fast-scan differential-pulse polarography. [f] Hanging mercury drop electrode. [g] Dropping mercury electrode. [h] Original literature was not available for more detailed description of the samples. [k] Determinations were carried out using a flow-through cell.

and a mixture of arsenate and arsenite in aqueous solutions containing D-mannitol and perchloric acid. Arsenite will interfere with the determination of arsenate under certain conditions. Oxidation of arsenite to arsenate with chlorine eliminates this interference and allows the determination of total inorganic arsenic as arsenate.[59, 60]

A computerized instrument for the determination of arsenate, by a flow potentiometric or constant-current stripping technique, employed the electrochemical reduction of arsenate on a gold-coated platinum-fiber electrode by electrolysis at −1.8 V vs Ag/AgCl in 4 mol dm^{-3} HCl/2.5 mol dm^{-3} calcium chloride solutions. Subsequent stripping at 0.5 μA produced a peak at −0.3 V. A detection limit of 0.1 μg dm^{-3} could be obtained.[9]

Indirect methods for the determination of arsenate are based on the formation of heteropolyacids with molybdenum and tungsten.[95] The heteropolyacids are separated by extraction, and molybdenum is determined by differential-pulse or dc polarography either in an organic solvent or after back-extraction in aqueous solution. The detection limit of this method which was used for the determination of arsenic in ores, is reported to be 1.9 mg dm^{-3}.[96] If the catalytic wave of molybdenum is used,[97] the detection limits are at low μg dm^{-3} levels.[98–100] A mixture of the ternary arsenic–bismuth–molybdate heteropolycomplex and sodium carboxymethylcellulose produces an

Table 2 Catalytic polarographic methods for the determination of arsenic(III)

Method	Electrode	Supporting electrolyte	Potential (V)	Working range ($\mu g\ dm^{-3}$)	Sample containing arsenic	References
ASV[a]	Au-plated carbon	$HCl/HClO_4/SnCl_2$	0.34 (-0.50)[g]	0.15–29	Natural water	48
DPP[b]	DME[f]	H_2SO_4/HCl/KBr/Se(IV)	-0.53	1–300	Ores	18
DPP	DME	H_2SO_4/phenanthroline/$CoSO_4$	1.25	0.4–20	Minerals	68
DPP	DME	H_2SO_4/citric acid/KI/Co^{2+}	-0.75	0.1–150	Water	67, 87
DCP[c]	DME	H_2SO_4/KI/Te(IV)	—	50–300	Steel	69
CRP[d]	Hg	H_2SO_4/NH_4I/Te(IV)	-0.6	1–130	Human hair	88
OSC[e]	Hg	Co(II)/KSCN/ascorbic acid	-0.75	—	Water	89, 90, 91
OSC	Hg	H_2SO_4/Te(IV)	-0.87	0.1–3	Water	92, 93
OSC	Hg	H_2SO_4/Te(IV)/KI	-0.73	1–900	Soy sauce	94

[a] Anodic stripping voltammetry. [b] Differential-pulse polarography. [c] Direct current polarography. [d] Cathode-ray polarography. [e] Oscillopolarography. [f] Dropping mercury electrode. [g] Pre-electrolysis potential.

adsorption wave on a dropping-mercury electrode at -0.47 V. The detection limit is 0.6 mg dm^{-3}.[101]

In a study aimed at the determination of alkali-metal arsenates with the help of a mercury electrode in an organic medium in the presence of tetrabutylammonium iodide, a potential of -1.6 to -2.8 V vs SCE was used.[102]

DETERMINATION OF TOTAL INORGANIC ARSENIC

Environmental samples, such as fresh water, seawater, soil solutions, plant materials, animal tissues, soils and rocks, may contain inorganic and organic arsenic compounds. For the determination of total arsenic by electrochemical methods, the various arsenic compounds must be converted to arsenate, or preferably arsenite. Solid samples and samples containing organic arsenic compounds must be mineralized. The oxidative environment during these digestions (HNO_3, H_2SO_4, $HClO_4$) assures that all arsenic is present in the digests as arsenate. Aqueous samples, or extracts that do not contain organic compounds, need not be digested. The digested samples should contain only arsenate. In such samples—after proper dilution and other necessary preparation procedures—total arsenic may be determined in the form of arsenate by differential-pulse polarography in the presence of D-mannitol (see 'Determination of arsenate'). Because of the reducibility of arsenite without additional reagents, the polarographic determination of total arsenic via arsenite might be preferable. Because the arsenate is present in the digests, the arsenate must be reduced to arsenite before the polarographic determination.

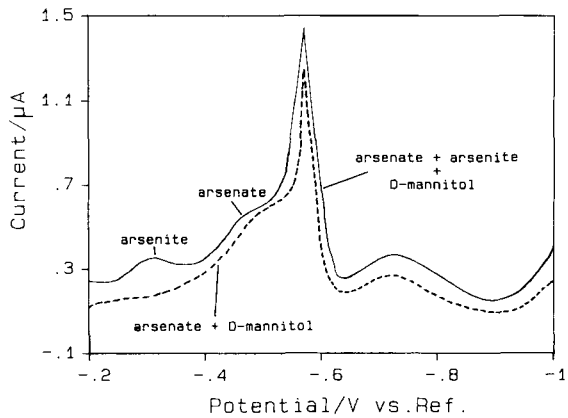

Fig. 3 Differential-pulse polarograms of arsenate (----) and an arsenate–arsenite mixture (———) in aqueous solutions containing D-mannitol and perchloric acid.

The ideal reductant should quantitatively reduce arsenate to arsenite and the products of the redox reaction should not interfere with the determination of arsenite. Several reducing agents, such as potassium iodide, copper(I) chloride, hydroxylamine, hydrazinium sulfate, sodium sulfite and sulfur dioxide, were investigated. Best results were achieved with sodium sulfite or sulfur dioxide in acidic solutions. Tables 3 and 4 list the reductants investigated and the conditions used for the determination of arsenite.

When the samples, such as fresh-water and seawater samples, contain only arsenite and arsenate, the arsenate can be reduced to arsenite or the arsenite can be oxidized to arsenate. The

determination of total arsenic can be performed by the polarographic reduction of arsenite or arsenate using any electrochemical technique responsive to these inorganic arsenic compounds.

A simultaneous differential-pulse polarographic determination of arsenate and arsenite in the presence of D-mannitol is possible at arsenite concentrations between 20 to 200 $\mu g\,m^{-3}$ and arsenate concentrations greater than the arsenite concentration. Otherwise the arsenite reduction peak at -0.34 V and the arsenate reduction peak at -0.55 V are influenced by each other.[59]

Total arsenic has been determined in seawater by constant-current stripping voltammetry. In a fully automated flow system, arsenate was reduced with an acidified (HCl) solution of potassium iodide. Arsenite was quantified by standard addition.[8]

ELIMINATION OF INTERFERENCES IN THE ELECTROCHEMICAL DETERMINATION OF ARSENIC

During cathodic scans serious problems may occur when heavy-metal ions, such as lead(II), tin(II), thallium(III), bismuth(III), and antimony(III), or selenite are present, because signals from the reduction of these ions may overlap with the arsenite peak. Anodic scans are interfered with by the presence of elemental mercury or copper.

To minimize or prevent these interferences, attempts were made to remove arsenic from the sample solutions prior to the determination of arsenite. Arsenic may be extracted as arsenic tribromide into toluene[104, 109] or as arsenic trichloride into benzene.[103] The arsenic halides may be re-extracted into water[108, 117] or determined directly in the organic phase by an electrochemical method.[103]

Reductillation, a term coined for the reduction of arsenate with HCl/CuCl and simultaneous distillation of arsenic trichloride, was used by several workers for the electrochemical determination of arsenic via arsenite.[49, 1112–114]

Arsenite can be reduced with zinc/HCl[110] or potassium tetrahydroborate[118] to arsine, which can be flushed into solutions of gold(III) or of silver nitrate. After oxidation of the arsine, the arsenite formed was determined electrochemically. Ions interfering with the determination of arsenic may be removed by ion exchange using Amberlite IRA-400[71, 105] or Chelex 100 [lead(II), thallium(I)].[81] Alternatively, the ions may be extracted by dithizone into carbon tetrachloride.[28]

Two sequential electrochemical measurements may be used to compensate for interferences by ions such as lead, thallium, and tin. After recording the signal from the sample, arsenite is oxidized to arsenate with cerium(IV). Excess cerium(IV) may be reduced with ascorbic acid or with mercury.[42, 107] Because arsenate is not electroactive, the oxidized sample provides the background signal that should be subtracted.

Naturally occurring organic compounds such as humic, fulvic, and amino acids appear to interfere with the determination of arsenite and total arsenic in surface waters. The organic compounds can be destroyed by ultraviolet irradiation of the acidified samples.[30]

Table 3 Determination of total arsenic by differntial-pulse polarography after reduction of arsenic(V) to arsenic(III)

Sample containing arsenic	Potential (V)	Supporting electrolyte [M = mol dm^{-3}]	Working range (μg As dm^{-3})	Reducing agent	References
Artificial mixtures	-0.38^a	Benzene/ethanol/LiBr	7–25	HI/H_2SO_4	103
Glass	—	HCl/HBr	100–300	$N_2H_4.H_2SO_4$	104
Ash, dust	—	2 M-$HClO_4$	20[c]	—	105
Natural water	-0.38^b	1 M-$HClO_4$	7[c]	$NaHSO_3$	106, 107
Artificial mixtures	-0.40^b	1 M-HCl/gelatine	5[c]	$NaHSO_3$	16
Ores	-0.38^a	1.25 M-HCl/0.05 M-KNO_3	100[c]	$HBr/N_2H_4.H_2SO_4$	108
Lead	-0.38^b	1.5 M-HCl/0.012 M-NaBar	—	$HBr/N_2H_4.H_2SO_4$	109
Various materials	-0.42	—	—	$KI/SnCl_2$	110
Soils	-0.41	1 M-HCl	—	$N_2H_4.H_2SO_4$	111

[a] Measured vs Ag/AgCl. [b] Measured vs saturated calomel electrode (SCE). [c] Detection limit.

Table 4 Determination of total arsenic by cathodic (CSV) or anodic (ASV) stripping techniques at $\mu g\ dm^{-3}$ levels

Method	Supporting electrolyte [M = mol dm^{-3}]	Potential (V)	Reducing agent	Sample containing arsenic	References
DPASV	1 M-HCl	0.3 (−0.7)[a]	Na_2SO_3/HCl	Artificial mixture	40
DPASV	Ascorbic acid/H_2SO_4	0.05 (−0.3)[a]	Gaseous SO_2	Seawater	42
ASV	0.8 M-H_2SO_4	—	Na_2SO_3/KI	Talcum	43
DPASV	7 M-HCl	0.19 (−0.15)[a]	Cu_2Cl_2/HCl	Biological materials	49, 112, 113 114, 115
DPCSV	0.7 M-H_2SO_4/ 6×10^{-4} M-Se(IV)	−0.72 (−0.5)[a]	NaBr/$N_2H_4.H_2SO_4$	Orchard leaves	28
DPCSV	Lumatom/0.1 M-HCl/Se(IV)	−0.78 (−0.4)[a]	$NH_2OH.HCl$/HCl	Oyster tissue	29
DPCSV	0.75 M-HCl/Cu(II)	−0.6 (−0.35)[a]	HCl/HBr	Natural water	30
DPCSV	0.75 M-HCl/Cu(II)	−0.75 (−0.6)[a]	KBr/HCl/$N_2H_4.H_2SO_4$	Chinese herbs	32
DPCSV	Mineral acid/Se(IV)	— (−0.43)[a]	Gaseous SO_2	Natural water	116
ASV	1 M-HCl	— (−0.3)[a]	$N_2H_4.H_2SO_4$	Steel	117
ASV	6 M-HCl	— (0.1)[a]	—	Reagent-grade HCl	44
ASV	Dilute HCl	—	KBH_4	Artificial mixture with antimony and bismuth	118
ASV	HCl/HNO_3	0.13 (−0.3)[a]	$N_2H_4.H_2SO_4$	Water	119

[a] Pre-electrolysis potential

ELECTROCHEMICAL BEHAVIOR OF ORGANIC ARSENIC COMPOUNDS

Aryl and alkyl derivatives of arsenic are used in agriculture as pesticides and herbicides. Methylated arsenic compounds are part of the natural arsenic cycle. The differentiation of inorganic and organic arsenic compounds and the identification of organic arsenic compounds is of great environmental and toxicological importance. The polarographic behavior of several organic arsenic compounds has been investigated.[120] The shape of the polarograms and the half-wave potentials are highly dependent on the pH value and the composition of the supporting electrolyte. Adsorption processes at the electrode surfaces, especially at higher concentrations, make it difficult to measure peak currents reliably. The electrode reactions are irreversible. The frequently present pre-waves may sometimes be suppressed by addition of Triton-X-100 or gelatine.

Differential-pulse polarograms of arylarsonic acids are characterized by a single, well-defined reduction wave at −0.8 V in HCl–KCl mixtures at pH 1.1. This wave is caused by the initial two-electron reduction of the arylarsonic acid to aryldihydroxyarsine followed by a four-electron transfer yielding arylarsine. Arsine, the end-product of the reduction, may react with aryldihydroxyarsine, the initial reduction product, to form arsenobenzene. A linear calibration curve was obtained from the detection limit of about 0.4 mg dm^{-3} to 80 mg dm^{-3} for phenylarsonic acid and to 25 mg dm^{-3} for other arylarsonic acids.[121, 122]

Diarylarsinic acids react similarly. Diphenylhydroxyarsine is formed at −0.7 V in acidic solutions and is immediately reduced to diphenylarsine. The condensation between the two reaction products is repeated to yield tetra-aryldiarsines.[123, 124]

The reduction of phenylarsine oxide in acidic solution (e.g. pH 4) produces two cathodic peaks at −0.4 V and −0.8 V. For each wave a two-electron transfer was postulated. In alkaline solution (pH 8–11) only one peak, at −0.8 V, was observed. The minimal observable concentration

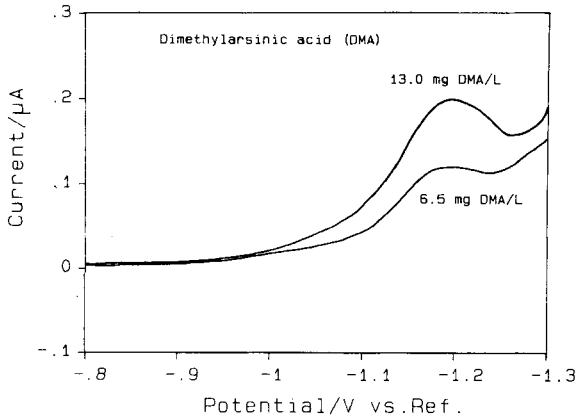

Fig. 4 Differential-pulse polarograms of DMA in Britton–Robinson buffer at pH 4.

by differential-pulse polarography was found to be 3 mg dm^{-3} arsenic.[125,126]

Solutions of triphenylarsine oxide were examined at pH values between 1 and 12 over a concentration range of 10^{-4} to 10^{-5} mol dm^{-3}. In 0.1 mol dm^{-3} HCl, two reproducible waves, appear at -0.96 and -1.1 V. The first wave is not observable in solutions above pH 9. Triphenylarsine oxide in the concentration range 3–30 mg dm^{-3} is best determined at pH 4.[126,127] The differential-pulse polarographic behavior of an arsenazo dye, not identified in the abstract, was also studied. Three cathodic peaks appeared in solutions at pH < 3. The first (-0.17 V) and the second peak (-0.28 V) may be ascribed to the reduction of the azo group, the third (-0.6 V) to the overall six-electron reduction of the arsonic acid group. The signal at -0.6 V is analytically useful.

The composition of mixtures of organic arsenic compounds (phenylarsine oxide and triphenylarsine oxide) and arsenite may be ascertained at a suitable pH.[126] Alkylarsonic acids and dialkylarsinic acids were studied in some detail. Cyclic voltammograms of methylarsonic acid and dimethylarsinic acid in 0.1 mol dm^{-3} sulfuric acid showed that the reduction of these acids produces the corresponding arsines at -1.2 V. The arsines are adsorbed on the mercury surface. During the anodic scan the sorbed arsines are desorbed at a potential between -0.05 and -0.2 V.[128] Calibration curves were linear in the range 1–45 mg dm^{-3} for methylarsonic acid and 0.3–16 mg dm^{-3} for dimethylarsinic acid (DMA). Figure 4 presents differential pulse polarograms of dimethylarsinic acid at two different concentrations in Britton–Robinson buffer at pH 4. Polarographic reduction data for a series of alkylarsonic and dialkylarsinic acids were reported. The peak potential of alkylarsonic acids in HCl–KCl mixtures at pH 1.78 increases anodically from -1.33 V (methylarsonic acid) to -0.84 V (octylarsonic acid) with increasing number of methylene groups in the alkyl chain. A decrease of the detection limits was observed between methylarsonic acid (88 mg dm^{-3}), ethylarsonic acid (5 mg dm^{-3}) and the other acids (1.0–0.2 mg dm^{-3}). The half-wave potentials of dialkylarsinic acids are pH-dependent. Detection limits between 250 and 50 μg dm^{-3} arsenic were observed.[129] Aromatic arsonic and arsinic acids show the expected pH dependence of their half-wave potentials. In HCl–KCl mixtures (pH 1.5), peaks were observed at potentials between -0.67 and -0.88 V. Detection limits in the range 0.1 to 0.5 mg dm^{-3} were reported.[124]

Guanidine fluoroborate was found to be suitable as a supporting electrolyte in non-aqueous media for the detection of 13–100 mg dm^{-3} methylarsonic acid at -2.25 V.[130] The mechanism of the anodic oxidation of trialkyl- and triarylarsines was studied.[131]

TITRIMETRIC DETERMINATION OF ARSENITE AND ARSENATE WITH ELECTROCHEMICAL INDICATION OF THE END-POINT

In general, titrations require solutions of relatively high concentrations (about 0.001 mol dm^{-3}) and are therefore not suitable for trace determinations. However, when the endpoint is determined by electrochemical methods, solutions down to at least 10^{-5} mol dm^{-3} of arsenite or arsenate can be titrated.

Arsenite and arsenate were titrated with silver nitrate using a silver ion-selective electrode as sensor.[132,133] Furthermore, potentiometric titrations of arsenite were carried out iodometrically with potentiometric end-point detection[134] with an 18-crown-6-potassium ferricyanide complex in aqueous acetonitrile,[135] with dichromate,[136] persulfate[137] or cerium(IV)[138] as oxidimetric titrants. In an indirect potentiometric method the chemically generated arsine is transferred into a cell containing an iodine solution. The concentration of iodide, formed in a reaction between arsine and ionide, was measured by an iodide-selective electrode.[134,138,139]

An amperometric end-point detection improves the detection limit in the titration of arsenite. Under optimal conditions arsenite can be determined in solutions containing 1.5–1000 mg As dm^{-3}.[140] Suitable titrants for arsenite are iodine,[141,142] morpholine-4-carbodithioate,[143] potassium iodate[144] and potassium permanganate.[145]

When the indicator electrodes were pulse-polarized (a method called 'switching potentiostatic amperometry'), arsenite could be determined titrimetrically in the low $\mu g\ dm^{-3}$ range.[146]

Oscillopolarographic titrations of arsenite with potassium bromate[147] and arsenate with solutions of lead(II)[148] were suggested. A study of the waveforms in ac polarographic titrations of arsenite in HCl has been performed.[149]

Coulometrically generated bromine[150] or iodine[101,151,152] has been employed to determine traces of arsenite using amperometric or potentiometric end-point detection. A potentiometric solid-state sensor for measuring gaseous arsenic oxides and/or arsine at high temperatures has been constructed.[153]

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