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**ELECTROCHEMICAL BEHAVIOUR
AND ELECTROANALYTICAL METHODS
FOR THE DETERMINATION
OF ARSENIC COMPOUNDS**

Herbert GRESCHONIG
Institute of Analytical Chemistry, Karl Franzens University
A-8010 Graz

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The electrochemical behaviour of inorganic and organic arsenic compounds is subject of investigations presented here. Macro scale electrolysis at mercury, carbon and noble metal electrodes in aqueous or non-aqueous solutions allows the synthesis of compounds usually difficult to prepare by traditional chemical methods. A new technique for the electrochemical generation of arsine with subsequent determination by atomic spectroscopy is proposed as an alternative to chemical reduction.

A variety of different toxic inorganic and organic arsenic compounds are found in the environment. Living organisms are capable of transforming arsenic compounds, some alkyl and aryl compounds are transferred to the environment by industrial activities, e.g. warfare agents, pharmaceutical products and herbicides. Electrochemical methods offer simple and accurate procedures for the determination of arsenic compounds, however, often restricted to relatively pure solutions. In most cases reductions are carried out at dropping mercury electrodes and allow the determination of inorganic arsenic at low ppb levels. Electrochemical determinations of organic arsenic compounds in real samples

offer the possibility to differentiate between arsenic(III) and arsenic(IV) compounds. For all types of compounds, the electrode reactions and reduction pathways are extensively investigated.

A new field in the electrochemistry of arsenic compounds has been made available by the introduction of sensors for the determination of gaseous arsines with or without gas chromatographic separation as well as the new possibility of capillary electrophoretic separations of anionic and cationic arsenic compounds.

Introduction

Arsenic compounds are ubiquitous in the environment. Arsenic is the main constituent in more than 200 minerals and is also present in traces in a great variety of other minerals. Weathering of rocks may mobilize arsenic as salts of arsenious and arsenic acid. Inorganic arsenic compounds can be converted to methylated arsenic derivatives by microorganisms, by plants, by animals, and by man. Methylarsonic acid, dimethylarsinic acid, trimethylarsine oxide, arsenobetaine, arsenocholine and arsenosugars represent a variety of substances which are synthesized by biological processes. The ubiquitous occurrence and especially the different toxicity of arsenic compounds promoted the development of analytical techniques for identification and quantitative determination of these substances. Spectrophotometry, atomic spectroscopy, plasma spectroscopy, or gas chromatography are techniques often used for the determination of arsenic. Electrochemistry offers simple and effective techniques for arsenic analysis, especially for differentiation between high and lower oxidation states.

This article gives an overview of the electrochemistry of arsenic as well as preparative and analytical applications. Further details are available in the secondary sources [1,2].

Electrochemical Methods and Electrodes

The most common methods used are the classic d.c. and differential pulse polarography. Square-wave and phase-selective a.c. voltammetry have been rarely used for analytical applications. Cyclic voltammetry and chrono-coulometry are the methods of choice for mechanistic investigations. Occasionally, titrations with amperometric or potentiometric indication have been carried out, but have no practical importance.

Modern and powerful separation techniques, such as capillary electrophoresis or electrochromatography, which depend on the more or less fast migration of ions in an electrical field, represent applications of electrochemical principles apart from usual current-potential measurements. A description and practical applications are given later.

Mercury is the best suitable and mostly used electrode material for the reductive large scale electrolysis as well as voltammetric determination of arsenic compounds. The low solubility of As(0) in mercury makes mercury less than ideal for stripping techniques. Additives, such as selenite or copper(II), eliminate these difficulties. Adsorptive voltammetric stripping methods at mercury drops with supporting electrolytes containing mercapto compounds were employed for the determination of arsenite. Gold, or platinum electrodes are used in anodic oxidation experiments, but are also suitable for stripping voltammetric determination of arsenite.

At glassy carbon or carbon paste electrodes, arsenic compounds are incompletely reduced or not electroactive. In some applications they serve as support for the preparation of mercury or gold thin film electrodes. Coatings with redox-couples of Ru(III)/Ru(II)-cyanide complexes [3] or Ir(III)/Ir(IV) oxides [4] allow catalytic oxidation of lower-valent arsenic compounds. Studies at carbon paste electrodes modified with mercapto compounds were carried out for the determination of arsenite.

Reduction of Pentavalent Arsenic Compounds

Arsenate (AsO_4^{3-}) is electrochemically inactive in aqueous acidic or alkaline solutions. Macro-scale electrolysis in high acidic solutions at platinum or mercury-pool electrodes produces, in a very slow and incomplete reduction, low amounts of arsine (AsH_3) [5].

Electrochemical reduction of pentavalent compounds has been the most active area of the electrochemistry of organic arsenic compounds. This is due to the widespread application of pentavalent compounds for pharmaceutical and agricultural purposes. The compounds of interest may be divided into four groups (R = alkyl and/or aryl groups) [6]:

Quarternary (or arsonium) compounds	: R_4As^+
Arsonic acids	: $\text{RAsO}(\text{OH})_2$
Arsinic acids	: $\text{R}_2\text{AsO}(\text{OH})$
Tertiary arsine oxides	: R_3AsO

The arsonium compounds are strong electrolytes in polar solutions. Electrochemical studies have been carried out in buffered aqueous solutions as well as in aprotic solvents such as dimethylformamide or dimethoxyethane. Mercury, lead or platinum were used as electrode materials during all electrolysis experiments.

From coulometric measurements after complete reduction of known amounts of substrate a two-electron transfer can be determined for the most compounds [7]. Gas chromatographic analysis of the reaction products showed that after cleavage of an As-C bond a tertiary arsine and the corresponding

hydrocarbon compound is formed. The overall reaction can be described by Eq. (1) [8]



A detailed reaction mechanism has not been established, but there is some evidence for the formation of R_4As^\cdot radicals or R_4As^- anions as intermediate products after the first electron transfer. The second reduction step leads to the products given in Eq. (1). The pathway *via* radicals or anions depends on the nature of the substituents as well as on the solvent [9]. The following order of decreasing As-C bond cleavage in unsymmetrically substituted arsonium salts was found:

Allyl > Acetyethyl > Benzyl > Toly > Butyl > Phenyl > Ethyl > Methyl

The possibility of selective As-C bond cleavage was later on used for the synthesis of optically active arsines, e.g. methyl-ethyl-phenyl arsine, which was prepared by electrolysis of methyl-ethyl-phenyl-benzyl arsonium-methylsulfate [10].

The half-wave potentials of arsonium salts, which contain at least one phenyl group, were determined in aqueous solutions by classic direct current polarography. The potentials are dependent on the nature and concentration of substrates. The values, reported in the literature were found to be in the range from -1.1 to -1.4 V vs. NHE. All electrode reactions are irreversible two-electron processes. The current-potential curves exhibit large polarographic maxima due to adsorption processes [6].

All these compounds are not observable in the environment and therefore, no analytical applications were tried. Unfortunately, arsenobetaine and arsenocholine, the two most important arsonium compounds in the environmental arsenic cycle, cannot be detected by any polarographic method. The reduction waves probably coincide with the waves of hydrogen discharge and cannot be used for analytical purposes.

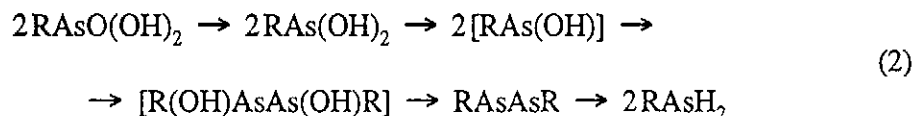
Up to the last decade methylated derivatives of arsonic and arsinic acids were widely used as herbicides. These compounds are also part of the natural arsenic cycle and are therefore present in the environment [11]. Naturally, the electrochemical behavior was studied in some detail. Electrolysis of the acids in acidic aqueous solutions at a mercury pool electrode produces the corresponding arsines as proved by gas chromatography [12]. Cyclic voltammograms of dimethylarsinic acid at a hanging mercury drop in 0.1 M sulfuric acid show a reduction peak at -1.2 V. The determination of dimethylarsinic acid in the range from 0.8 to 10 ppm was carried out by differential pulse polarography in Britton-Robinson buffer at pH 4. Methanarsonic acid gave waves very close to electrolyte discharge. Measurements in acetonitrile containing 0.1 M guanidinium perchlorate showed a peak at -1.7 V well suitable for analytical determinations

[13].

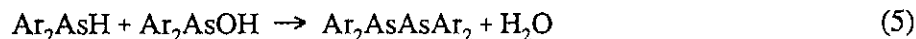
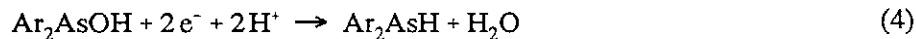
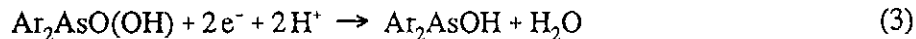
Aryl substituted arsonic acids were used extensively in agricultural applications, predominantly as animal growth promoters and feed stock additives. D.c. and differential pulse polarographic experiments showed that it is feasible to quantify these compounds electrochemically down to concentrations slightly below 1 ppm [14]. The reduction takes place only in acid solutions, with half-wave potentials ranging from -0.7 V to -1.1 V vs NHE. The structure and also the pK value have serious influences on the half-wave potentials. It can be remarked that—like most other organic arsenic containing compounds—the arsonic acids are more or less susceptible to adsorption [15].

The limiting polarographic currents are diffusion-controlled. The number of electrons consumed in the reduction process was estimated to be six and the final product was the corresponding arsine. The first step consists in a two electron reduction to arylarsine oxide, followed by a four-electron transfer to aryl arsine. Phenylarsonic acid reacts with reduction products and a number of polymeric, oxygen-containing compounds are formed. In cyclic voltammograms at a mercury drop a peak due to the reduction appeared in the cathodic scan. In the reverse (anodic) scan the current peak due to the reoxidation of the prior reduction product (arsine) can be found [16].

The electrolysis of 4-hydroxy-3-amino phenylarsonic acid in acidic solution thus goes through the following stages [17]



The electrochemistry of arsinic acids is very similar to that of arsonic acids. The half-wave potentials in acidic solutions depend on the substituents (usually between -0.5 and -1.1 V vs. NHE) and the pH of the solution. Naturally, the reduction pathway is different from the reduction of arsonic acids and was proposed to be as follows [16]



The largest number of studies concerning trisubstituted arsine oxides was carried out with triphenylarsine oxide. This compound is electroactive over a wide pH range. At pH 4, a well-defined wave occurs at -1.1 V. Microcoulometric measurements indicated a two electron reduction to triphenylarsine [18]. Trimethylarsine oxide is a more interesting compound because of its occurrence

in the environment. The substance also is the oxidation product of naturally occurring trimethylarsine. Trimethylarsine is also a trace constituent of earth gas and must be removed with catalysts. In our institute, we established a differential pulse polarographic method for the determination of 0.8 ppb trimethylarsine oxide directly in copper-nickel catalysts after extraction with acetate buffer at pH 4 [19].

Electroanalytical Determination of Arsenate

Inorganic arsenate only shows polarographic signals in very acidic solutions (about 11 M hydrochloric acid). These signals are too complex to be useful for analytical work at arsenic concentrations above 0.004 mol l^{-1} . However, when phenols, such as catechol and pyrogallol, or aliphatic polyhydroxy compounds, such as D-mannitol, are added to 2 M perchloric acid, arsenate becomes electroactive. A sharp maximum at -0.6 V appears in the differential pulse polarogram and allows the determination of approximately $800 \mu\text{g l}^{-1} \text{ As}$ [20]. The exact mechanism of this activation is not known. Condensation of the hydroxyl groups with arsenic acid with formation of spiro compounds may be a probable mechanism.

Another method consists in the reduction of As(V) to elemental arsenic on a freshly prepared gold-coated platinum-fiber electrode at the electrolysis potentials below -1.6 V vs. Ag/AgCl. Reoxidation leads to an analytically applicable arsenic peak between -0.1 and $+0.15 \text{ V}$ [21].

Reduction of Trivalent Arsenic Compounds

Inorganic Arsenic

Arsenious acid (arsenite, AsO_3^{3-}) can easily be reduced electrochemically in aqueous solutions as well as in nonaqueous solvents, such as dimethylformamide or acetonitrile. Normally, the final reaction product is arsine in sufficiently high amounts. However, depending on the reaction conditions (acidity of reaction solution, current density, applied potential) and the concentration of arsenite, the reduction can stop at the level of elemental arsenic. Then the originally colorless solution changes to black or dark red, caused by formation of colloidal dispersed elemental arsenic modifications. These products are not further reducible [2].

However, under selected conditions, elemental arsenic can also be reduced to arsine. For use in the semi-conductor industry, a method for the electrochemical formation of high purity arsine from elemental arsenic in alkaline solution was suggested [22].

The excellent electrochemical activity of arsenious acid was used to develop systems for the electrochemical generation of arsine. This method—as

an alternation to chemical reduction methods with zinc/HCl or sodium borohydride—was first introduced to atomic spectroscopy in the batch arrangement. More recent reports employ more flexible flow injection arrangements. A continuous flow of dilute sulfuric acid is pumped through a tube serving as the cathode. The anodic part is separated from the cathodic channel by a Nafion membrane. The sample is injected into the catholytic stream which is used as carrier. The gaseous products, arsine and hydrogen, formed at the platinum cathode are separated from the waste in a gas-liquid separator. Atomic absorption and atomic emission spectroscopy, recently inductive coupled plasma spectroscopy were employed as detection systems [23-25].

Electroanalytical Determination of Arsenite

The predominant number of analyses of arsenic compounds deals with the determination of arsenite. Arsenate is also normally determined as arsenite after reduction with sulfur dioxide or hydroiodic acid. Conventional dc polarography is rarely used today for the determination of arsenite. Most of the polarographic determinations were carried out with the differential pulse technique. The polarograms of arsenite in acidic solution consist of two waves attributed to the reduction of arsenite to As(0) and of As(0) to arsine. The half-wave potentials vs SCE which are used for analytical purposes are at approximately -0.4 V and -0.8 V. Depending on pH and the nature of the supporting electrolytes, one, two or three waves occur in the polarograms. The electrode process is irreversible as proved by cyclic voltammograms [2].

Arsenite has been determined mainly in sea- and freshwater, in alloys, in soils and in biological materials in the range from 0.8 to 10 ppm As. Stripping techniques allow lower working ranges, approximately between 0.5 and 1 ppm [26]. Extremely low detection limits were reported for measurements in acetonitrile at gold electrodes. However, difficult handling of the runs makes the method impracticable for real analytical work [27].

Organic Arsenic Compounds

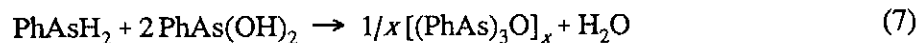
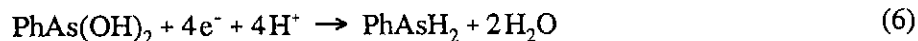
Trivalent organic arsenic compounds have been much less dealt with in electrochemical studies and analytical applications. The measurements have been carried out in nonaqueous solutions (dimethylformamide, tetrahydrofuran, acetonitrile) and aqueous solutions depending on the solubility of the compounds. The substances can be divided into the following groups based on the identity of the substituents (R = alkyl, aryl; X = Cl, Br, I, OH):

Diorganyl arsine	: R_2AsX
Organyl arsine	: $RAsX_2$
Tetraorganyl arsine oxide	: $R_2AsOAsR_2$
Triorganyl arsine	: R_3As

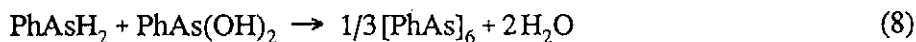
Very few studies of the electrochemical reduction of diorganyl arsines have been undertaken. Dimethylchlorarsine (cacodyl chloride), $(CH_3)_2AsCl$ was earlier shown to be electroactive, and it was demonstrated that the dimeric product, tetramethylarsine (cacodyl), $(CH_3)_2AsAs(CH_3)_2$ was an intermediate on the way to the final product $(CH_3)_2AsH$ (dimethylarsine). In a present study at our institute, we investigate the reduction behaviour of dimethylhydroxyarsine as the hydrolysis product of dimethylchlorarsine in aqueous solution. With traditional hydride generation methods it is not possible to differentiate between diorganylarsenic(III) and diorganylarsenic(V) compounds. The final reduction product always is dimethylarsine. Now differential pulse polarography allows the simultaneous determination of the two compounds at different oxidation states. The peak potentials of dimethyl arsenic acid and dimethylhydroxyarsine in 0.5 M sulfuric acid were found to be -1.35 V and -0.68 V vs SCE.

Diphenylarsine chloride and diphenylarsine cyanide $[(C_6H_5)_2AsX]$; $X = Cl, CN$ were used as warfare agents during the First World War and are known as Clark I and Clark II. After the war, thousands of tons of Clark I and II were buried in the soil or submerged in the sea. Nowadays, diphenylarsinyl fragments are found in soil extracts or appear in the groundwater. In contact with water, the compounds are hydrolyzed to the corresponding hydroxy compounds, which are slowly oxidized to diphenylarsinic acid in the presence of oxygen. Therefore, an electrochemical method was established for the simultaneous determination of diphenylarsinic acid and its trivalent analogues. The current peaks at -0.65 V (for diphenylarsinous acid) and -0.95 V (for diphenylarsinic acid) in differential pulse polarograms allow determinations in the upper ppb level.

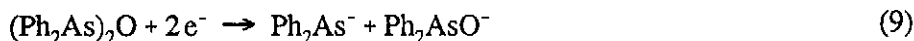
The reduction behaviour of phenylarsine oxide (PhAsO) was studied in aqueous solution [28]. In the solid state phenylarsine oxide exists in a tetrameric form, in aqueous solution the monomeric phenylarsinedihydroxid is formed. Polarographic studies at $pH > 2$ show two cathodic waves at -0.4 V and -0.8 V. Both waves appear to be diffusion controlled, are pH dependent, with the wave heights proportional to the substrate concentration. In more detailed studies it could be shown, that phenyl arsine – the final reduction product – may react with not reduced phenylarsine oxide with formation of polymeric compounds [14]



or

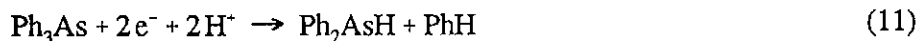
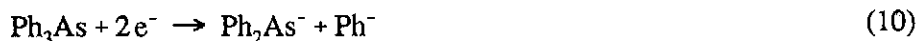


Tetraorganylarsine oxides are the dimer condensation products of diphenylarsine hydroxide. Only $(\text{Ph}_2\text{As})_2\text{O}$ was investigated by cyclic voltammetry in DMF or THF at Pt electrodes. A two electron reduction peak appears at -1.8 V . In the reverse scan, two oxidation peaks appear in the voltammogram due to reoxidation of the products given in Eq. (9) [29]



Trisubstituted arsines are electrochemically inert within a large potential range. In DMF solutions using a mercury electrode, triphenylarsine shows a half-wave potential of -2.55 V vs. NHE. Other substituents cause shifts of half-wave potentials in anodic direction [30].

The two electron reduction in DMF causes a As-C bond cleavage. In the presence of traces of H^+ , the overall reaction leads to diphenylarsine and benzene. In completely dried aprotic solvents the anions are relatively stable, but may react with substrates which exist in the solution.



The dimeric compound of the structure R_2AsAsR_2 contains As in the formal oxidation state of II. Reduction of the tetraphenyl compound in an aprotic solvent such as DMF causes a cleavage of the As-As bond and the formation of relative stable anions of R_2As^- type. These anions react with substrates which are present in the solution [29]. This is a possibility for the preparation of otherwise not easily obtainable arsines, arsenic acids or metal arsinides [10].

Anodic Oxidation of Trivalent Arsenic Compounds

Studies of the electrochemical oxidation of arsenic compounds have been focussed on oxidation of arsenite (AsO_3^{3-}), of arsines with different substituents (R_3As , R = H, alkyl, aryl) and of aryl derivatives of arsine oxides (RAsO).

Several attempts were made to exploit the anodic oxidation of arsenite to arsenate at noble metal electrodes. In dilute sulfuric acid, an anodic peak at approximately $+1.1\text{ V}$ is obtained at a gold electrode. Similar results were

obtained at platinum electrodes. The detection limits are approximately $750 \mu\text{g l}^{-1} \text{As}$ [31-33]. The surface of clean Pt or Au anodes are oxidized in aqueous media with formation of metal hydroxides and oxides, respectively. These layers play an important role in the oxidation process of arsenite. They may act as catalyst and transfer oxygen from aqueous solution the substrate. A similar mechanism was postulated in the oxidation process of phenylarsine oxide in aqueous sulfuric acid [34].

Anodic oxidation of arsenite at gold or platinum electrodes has been carried out in amperometric sensors at flow-injection analysis [2].

A number of investigations have been focussed on the electrochemical oxidation behaviour of arsines. Most of the studies have been carried out in acetonitrile with varying amounts of water. Half-wave potentials of trisubstituted arsines—measured at platinum or gold electrodes—have been found in the range from +1.2 V to +1.8 V vs NHE. Modified carbon paste electrodes were employed for the determination of triphenylarsine. The electrode process consists of an irreversible two-electron transfer. The oxidation product was identified as triphenylarsine oxide. The preparative electrochemical oxidation of R_3As in "wet" acetonitrile represents an alternative route to the synthesis of triorganylarsine oxide derivative. In the presence of perchlorate or tetrafluoroborate the corresponding triphenylarsine oxide compounds are formed [35-37].

The oxidation of arsine (AsH_3) or alkyl-substituted arsines is of practical analytical interest. Attempts were made to develop sensors for the determination of gaseous, oxidable gases. For example, a gas chromatographic detector has been established for the determination of 1 ng arsine [38]. In general, the anodic part of the sensor consists of a platinum electrode in dilute sulfuric acid and is separated from the cathodic part by a gold-coated, gas-permeable membrane. The metallized membrane surface serves as the working electrode. The carrier gas stream containing the gaseous sample compounds flows through the cathodic tube. The oxidation occurs at the gold-coated membrane [39,40].

Titrimetric Determination with Electrochemical End-point Detection

Titrations require solutions of relatively high concentrations (about 0.001 M) and are therefore not suitable for trace determinations. Endpoint determinations with amperometric and potentiometric detections decrease the detection limits. Several methods for the titration of arsenite with iodine or potassium iodate have been proposed. Studies dealing with arsenate-selective electrodes have been published. However, all these methods are rarely used in practical analysis of arsenic [41].

Some arsenic species can also be titrated on ion-pairing principles, and ion-selective electrodes can be used to monitor such titrations [42]. Hexafluoroarsenate can be titrated using quarternary ammonium salts such as cetyltri-

methylammonium, cetylpyridinium halides, etc. [43-45]. For titrations of tetraphenylarsonium ions, both triiodide [46] and periodate [47,48] were used as titrants. It should be mentioned that tetraphenylarsonium chloride has also been recommended as the titrant for direct potentiometric titrations of perchlorate and fluoroborate and as a reagent for back-titrations of numerous complex anions (see Ref. [42] and references therein).

Capillary Electrophoresis

Both ends of a fused silica capillary tube (1 m long, 0.75 μm inner diameter) are dipped in two vessels each equipped with electrodes and filled with electrolyte. Approximately 8–10 nl sample solution is introduced into one end of the capillary. When a high voltage (between 10 and 30 kV) is applied, the ions migrate through the capillary to the corresponding electrode. The detection system is mounted at the end of the capillary. The separation of ions depends on the ion mobilities and the flux of the electroosmotic flow.

In the last five years, a number of authors have published methods for the separation of inorganic and selected organic arsenic anionic compounds. The advantages of the method are the high separation efficiency (about 10^5 theoretical plates), small consumption of electrolyte solutions, and simple construction principles. Disadvantages are interferences from temperature and relatively high working ranges.

The separation of 15 ppm solutions of inorganic arsenic compounds, dimethylarsinic acid, methylarsonic acid and selenium compounds was reported in the literature. The detection limits with the use of UV and conductivity detectors, respectively, were calculated to be at approximately 0.09 ppm [49-51].

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