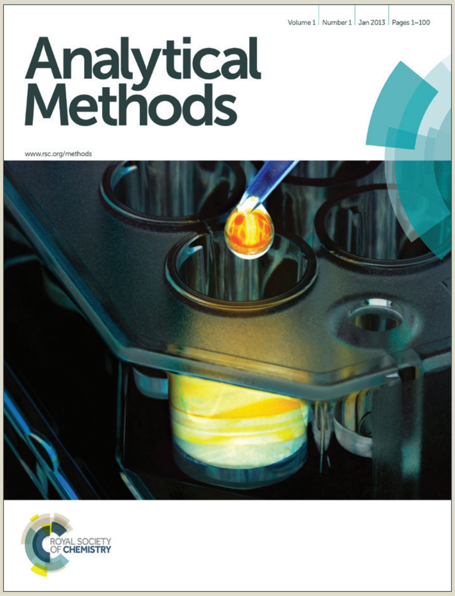
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Recent advances in electrochemical detection of arsenic in drinking and ground waters

John H.T. Luong[a*], Edmond Lam[b] and Keith B. Male[b]

[a]*Innovative Chromatography Group, Irish Separation Science Cluster (ISSC), Department of Chemistry and Analytical, Biological Chemistry Research Facility (ABCRF), University College Cork, Cork, Ireland.*

[b]*National Research Council Canada, Montreal, Quebec, Canada H4P 2R2*

* Corresponding author: j.luong@ucc.ie

Abstract

Anodic stripping voltammetry (ASV) using noble electrodes is based on the reduction of As^{3+} to As^0, followed by its stripping or oxidation to As^{3+} or As^{5+} species, the two predominant forms of arsenic in water. The rapid and convenient ASV method can detect As (III) at the low ppb level, but it is susceptible to interferences from various endogenous metals or organic compounds in waters. Electrode surface modification with metallic nanoparticles (NPs), carbonaceous nanomaterials (carbon nanotubes and graphene) and even enzymes (arsenite oxidase) can improve detection sensitivity and selectivity, while circumventing such interferences. All electrochemical methods aim for a detection limit below the World Health Organization guideline value of 10 ppb (133.3 nM). Despite numerous publications in this field during the last ten years with respect to novel electrode materials and electrolytes, reproducibility of electrochemical detection is still problematic and the analysis of arsenic in real ground-water samples is far from certainty and triviality. Considerable efforts are still needed to develop electrode materials and analytical procedures for reliable detection of arsenic with sub-ppb levels in the presence of endogenous toxic metals and organics in water matrices.

Introduction

The presence of inorganic arsenic in drinking water has received considerable attention over the past 50 years due to its high toxicity and wide spreading. Arsenic enters drinkable water from natural earth deposits (e.g., realgar, As_4S_4; orpiment, As_2S_3; arsenopyrite, FeAsS; and lollingite, $FeAs_2$) or from industrial and agricultural pollution. In Bangladesh, India, China, Taiwan, and Canada (Nova Scotia), arsenic is introduced into drinking water from the earth crust (~2 mg kg^{-1} arsenic). In particular, the presence of unusually high As(III) concentrations in Bangladeshi ground water could be due to the reductive dissolution of hydrous ferric oxide by iron-reducing bacteria. In the southwestern regions of the USA (such as Nevada), arsenic concentration can be as high as 500 ppb in well water. Other regions of the USA (New England, Michigan, Minnesota, Wisconsin and the Dakotas) also have significant arsenic concentrations in ground water. Typical concentrations of arsenic in open ocean seawater are 2 ppb compared to <10 ppb in rivers and lakes. Arsenic levels in ground water average about 1-2 ppb, but can be as high as ppm in areas with volcanic rock and sulfide mineral deposits.[1] Anthropogenic sources of arsenic contamination come from certain types of mining, smelting, pesticide runoffs, and manufacturing activities (wood preservatives, glass manufacture, electronics, veterinary chemicals, etc.). Arsenic contamination of drinking and ground waters affects more than 140 million people in 70 different countries on all six inhabited continents. A map from the British Geological Survey showing documented problems with arsenic in groundwater and the environment is illustrated in Fig. 1.

Fig. 1. A world map showing documented areas affected by arsenic. (Adapted from Ref. 2 with permission. Copyright© 2014 National Environment Research Council).

Consumption of drinking water with high arsenic concentrations is the most harmful human threat in many parts of the world. Arsenic is highly poisonous, about four times more poisonous than mercury and poisoning can occur with inhalation of arsenic gas (AsH_3). In acute poisoning, As(III) binds and inactivates sulfhydryl-containing enzymes and affects other biological activities whereas As(V) elicits toxicity by mimicking phosphate and interfering with ATP production in mitochondria (Fig. 2).[3] Therefore, sensitive and selective analysis of arsenic and metallic elements in ground and drinkable waters is of importance to identify the contaminated source, the efficiency of water treatment, as well as to inform public health regulatory agencies with pertinent important information.

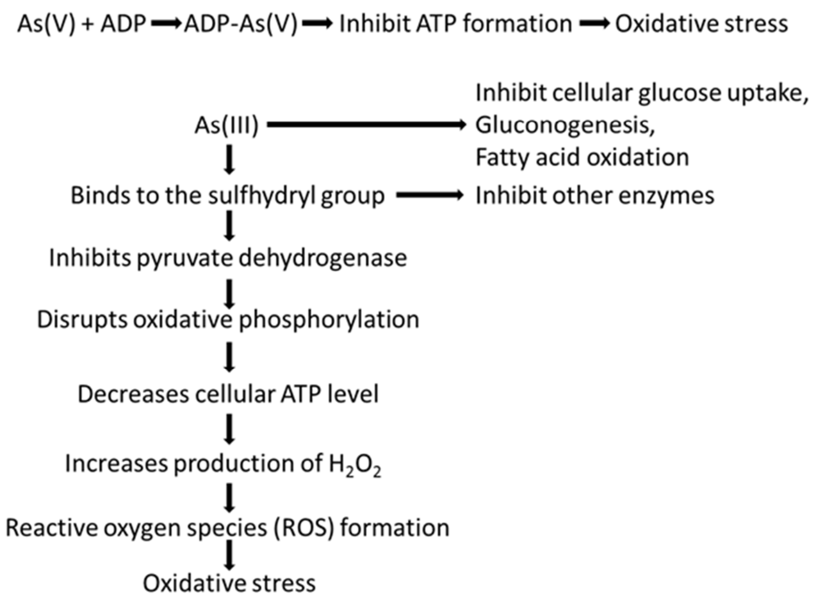


Fig. 2. The biological poisoning effects of As(III) and As(V)

As a carcinogen, arsenic can cause bladder, kidney, liver, lung, and skin cancer. It also compromises the body's immune function and is linked to birth defects and serious reproductive problems. Arsenic damages lung cells and causes inflammation of heart cells. Chronic exposure to arsenic at 19 ppb shows signs of reduced lung function in human beings, and at >120 ppb, the lungs' ability to take in oxygen is comparable to that of long-term smokers. Being tasteless and odorless, the presence of arsenic in drinking water and foodstuffs cannot be easily detected. At very low concentrations, its effect is not immediately visible. Uptake of drinking water with high arsenic concentrations over a short period of time can cause diarrhea, nausea, muscle pain, and hyperkeratosis on the palm or feet. The maximum arsenic concentration in drinking water is 10 ppb as specified by the World Health Organization (WHO)[4] and the US Environmental Protection Agency (USEPA).[5] The U.S. Food and Drug Administration (USFDA) also sets 23 ppb as the "level of concern" for inorganic arsenic in apple and pear juices based on non-carcinogenic effects.[6] This is also the maximum allowable level for imports and domestic products for human consumption in the USA and other countries.

Lab-based instrumentation such as atomic absorption spectrometry (AAS); atomic fluorescence spectrometry (AFS); atomic emission spectrometry; electrothermal AAS, and inductively coupled plasma-mass spectrometry (ICP-MS) have been used for the accurate detection of arsenic. However, such techniques do not measure individual arsenic species (speciation) and must be used together with an upstream separation scheme. For instance, atoms absorb light at some characteristic wavelength, depending upon their atomic structure and the energy required for the promotion of their electrons from one quantum level to another. The amount of light absorbed can be correlated to the element concentration within the linear calibration range. A wavelength of 193.7 nm is recommended for arsenic with a reliable calibration range of 1-5 ppb to 200 ppb. Graphite furnace AAS is one of the USEPA methods for measuring arsenic in drinking water.[7] ICP-MS can serve as element-specific detectors when coupled to chromatographic separation techniques such as HPLC and GC. Some detailed information of lab-based analytical methods for arsenic is available elsewhere.[8] However, low cost electrochemical methods with ease of miniaturization, minimal sample pretreatment and portability might provide more convenient means for the arsenic detection process with rapid analysis times. Therefore, considerable efforts have been made to develop portable electrochemical sensors for monitoring arsenic and other metallic elements in the environment. In this context, electrochemical stripping voltammetry has been widely used because of its high selectivity and sensitivity for arsenic with minimum sample pretreatment.

This review updates recent advances in new electrode materials for electrocatalytic and electrochemical sensing of arsenic. Incorporation of nanomaterials into electrochemical sensors will be addressed with respect to the analytical performance in terms of sensitivity, selectivity, multiplexed detection capability and portability. The potentials and drawbacks of different analytical schemes for the detection of arsenic in contaminated ground water will be addressed and discussed in detail.

General aspects of arsenic chemistry and electrochemical detection

As a metalloid, arsenic exists in the four oxidation states 5^+, 3^+, 0 and 3^-, i.e., As(V), As(III), As(0) and As(-3). Arsenic is also found in a number of organic compounds such as monomethylarsonic acid and dimethylarsonic acid in surface waters by microbial/biological activities. In ground water, inorganic arsenite (As(III)) and arsenate (As(V)) are the two dominant forms of arsenic contamination. In many wells, up to 80% of the total arsenic is in the more toxic As(III) form. As(V), the stable form in oxygenated environments is less mobile and 10 times less toxic than As(III). Depending on pH, there are four different forms of As(III) and As(V): H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} vs. H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. Arsenic is mainly present in aqueous solutions as $HAsO_4^{2-}$ and $H_2AsO_4^-$, and most likely partially as H_3AsO_4 (aq), AsO_4^{3-} or $H_2AsO_3^-$. Arsenic trioxide (As_2O_3), with the 3^+ oxidation state is soluble in dilute acids and alkalis, and practically insoluble in organic solvents. Its solubility in water is 20 g L^{-1} at 25 °C. Arsenic pentoxide (As_2O_5) with oxidation state of 5^+ is relatively unstable and highly soluble in water: 658 g L^{-1} at 20 °C. As(III) is uncharged at neutral pH while As(V) is negatively charged. The groundwater pH is often between 6 to 8, thus As(III) is more mobile than As(V) because the movement of As(V) is retarded by its electrostatic attraction to positively charged particles, e.g., iron hydroxides.[9] Consequently, many current arsenic removal technologies, in particular, ion exchange resin can effectively remove arsenic (V), but not arsenic (III). As_2O_5 can be prepared by heating As_2O_3 under oxygen in a reversible reaction. Strong oxidizing agents such as ozone, hydrogen peroxide, and nitric acid convert As_2O_3 to As_2O_5. The oxidation is not effective with simple aeration and requires several days or weeks. Vice versa, As(V) can be reduced to As(III) by organic compounds and dissolved sulfide. As(III) can be measured directly by various electrochemical techniques, whereas the total arsenic can be measured after chemical or electrochemical reduction of As(V) to As(III).

ASV is a popular and powerful technique for trace metal analysis. The process involves electrochemical deposition of trace metals on a suitable electrode for a few minutes at pertinent reduction potentials, and then the oxidation of the metal back into solution by a reverse potential scan (linear, differential, pulse or square). A major problem with ASV is hydrogen evolution at the negative potential required for As(III) deposition using an Au or Pt electrode. Therefore, the detection of arsenic by ASV must be performed in highly acidic media. Mineral acids such as HCl, H_2SO_4, and HNO_3 are often used, with HCl as the most common due to enhanced As(0) formation by Cl^- serving as an ionic bridge between the detecting electrode and As(III) species. Regardless of the acid used, the shift in ASV peak potential is a function of acid concentration as given by the following half-reaction and potential equation (Equations 1 and 2):

$$As + 3H_2O \rightarrow H_3AsO_3 + 3\,H^+ + 3e^- \qquad (1)$$

$$E = E^0 + \frac{0.0591}{3}\log([H_3As\,O_3][H^+]^3 \qquad (2)$$

The suppression of hydrogen gas bubbles is accomplished using ultramicro- and nano-array electrodes, high efficiency rotating disc side-mounted electrodes, or vibrating electrodes. ASV in a flow cell or flow injection analysis (FIA) may sweep hydrogen bubbles away.

Different electrode materials have been used for the detection of arsenic. The most popular is bulk Au followed by a thin Au film deposited on glassy carbon (GC) or graphite, Hg (as hanging drop mercury electrode), Pt, Cu, and boron-doped diamond (BDD). Recently, metal NPs with excellent conductivity, high surface area and catalytic activity have been used widely in electroanalysis of diversified analytes. In particular, Au NPs can decrease the overpotentials of electroanalytical reactions and maintain the reversibility of redox reactions. Various schemes have been exploited for electrochemical deposition of metallic NPs on electrode surfaces.

Anodic stripping voltammetry (ASV)

Solid and thin film electrodes

Electrode materials such as Au, Pt, Hg, BDD, and modified GC have been used in combination with a variety of acids such as HCl, H_2SO_4, $HClO_4$, HNO_3, etc., as the supporting electrolyte for arsenic determination since the electrochemical reduction of arsenic must be performed in an acidic milieu.[10] High pH media are not viable because dissolved Fe(II) in solution will co-precipitate arsenic and other metals.

A typical cyclic voltammogram (CV) of As(III) obtained by a silver disk electrode shows a well-defined As(III) reduction wave at -0.3 V and a corresponding oxidation wave at +0.24 V (As(0) to As(III)). Based on such behavior, it is easy to obtain the lowest detectable As(III) concentration by applying a negative reduction voltage (-0.4 to -0.8 V vs. Ag/AgCl) with sufficient deposition times (300 to 2000 s) to electroplate As(0) on the Ag working electrode.[11] During the stripping step, the potential of the working electrode is reversed to a positive potential (>0.3 V) to oxidize As(0) to As(III), i.e., to strip off As(0) from the electrode's active surface. The anodic stripping step can be linear, pulse, staircase, or square wave. The best limit of detection (LOD) is 0.09 ppb when the accumulation time is set for 2000 s at –0.6 V. This LOD is significantly lower than those of a Pt electrode (7.5 ppm),[12] a hanging mercury drop electrode (0.6 ppb),[13] and a Pt electrode in FIA (5 ppb).[14] For the Pt electrode in FIA, the detection is based on the reduction of As(III) by $NaBH_4$.[14] Derived arsine diffuses through a porous polytetrafluoroethylene membrane into the acceptor flow stream and is amperometrically determined on a Pt working electrode. As(V) is determined after its pre-reduction with KI to As(III).

To date, different electrode materials are tested and applicable for determining unknown samples at concentrations below the required limit of 10 ppb by WHO for drinking or tap water. Despite some controversial information about Ag as an electrode material, the Ag electrode has been reported to detect both high and low As(III) concentrations in a mixture with As(V).[11] For a sample with As(V) or a mixture of As(V) and As(III), the sample must be treated with a mixture of KI and ascorbic acid to enable the reduction of As(V) to As(III).[13] The Pt electrode is less sensitive for the detection of arsenic compared to the Au electrode. An LOD of 0.5 ppb for As(III) is obtained by a Pt electrode using the differential pulse ASV (DPASV) technique in 1 M perchloric acid with 10 min pre-deposition, compared to 0.02 ppb on an Au electrode.[15] Nevertheless, Au might be the best electrode substrate as exemplified by several reports about arsenic detection on Au electrodes (Table 1).

Table 1. Detection of arsenic by Au electrodes

Electrode materials	Method	Deposition time (s)	Limit of detection (ppb)	Linear range (ppb)	Supporting electrolyte	Potential interferences
Au wire (0.25 mm diameter x 1 cm length)[15]	DPASV	600	0.02	up to 1000	1 M $HClO_4$	Cu and Hg (interfere)
Au ultramicroelectrode (25 µm diameter)[16]	CCSV	240 (flow)	0.15	0.15-5.0	5 M HCl	Cu, Hg (no interference)
Au disk (0.6-1.0 mm diameter x 25 mm length)[17]	DPASV	300	0.15	0.2-250	1 M H_2SO_4 + 0.1 M HCl	Cu and Pb may interfere
Au disk (1 mm diameter)[18]	Sonication + SWASV	60	0.75	up to 300	1 M HNO_3	Cu (no interference)
Au film modified on glassy electrode[19]	ASV	200	1.12	up to 50	1 M H_2SO_4	(not discussed)
Rotating Au disk (6 mm diameter at 3000 rpm)[20]	DPASV	240	0.20	up to 20	1 M H_2SO_4 + 0.05 M HCl	(not discussed)
Rotating Au disk (6.4 mm diameter at 5000 rpm)[21]	DPASV	240	0.19	1-1000	2 M HCl	(not discussed)
Au ultramicroelectrode array (564 x 12 µm diameter)[22,23]	SWASV	80	0.05	up to 500	2 M HCl	Cu, Hg (interfere) Zn, Fe (no interference)

DPASV: differential pulse anodic stripping voltammetry; CCSV: constant current stripping voltammetry; SWASV: square wave anodic stripping voltammetry; LSV: linear stripping voltammetry

The prevention of hydrogen bubbles as a potential interferent is demonstrated on an Au disk rotating electrode at a rotation speed of 1000 rpm.[24] It should be noted that trace amounts of Cu(II) in the electrolyte could enhance the detection of As(III). With DPASV in very acidic HCl samples, the total arsenic concentration of ground water samples obtained is comparable with the AAS technique (15% variation for samples in the range of 10–50 g L^{-1}) with a LOD of 2 ppb. In this instance, trace amounts of Cu(II) in the electrolyte enhances the detection of As(III). In a reverse role, arsenic is used in ASV for the determination of Cu in water samples using an L-cysteine modified Au electrode.[25] The electrode is fabricated by immersing an Au electrode in an ethanolic solution of 5 mM L-cysteine for 60 min. Cu(0) is accumulated at -0.3 V (vs. SCE) for 60 s in 0.1 M phosphate buffer pH 5.0 at different arsenic concentrations. The same sensitivity and LOD for Cu are obtained in the presence of arsenic concentration between 2 to 20 μM. Later examples will show how the presence of Cu could interfere with determination of arsenic by ASV.

For Ag electrodes, the arsenic stripping peak appears as a shoulder on the oxidation waves of the Ag electrode for arsenic determination via ASV.[11] However, when the electrolyte is HNO_3 instead of HCl, the oxidation of Ag that masks the arsenic stripping signal is shifted to allow for a clear and detectable As(III) stripping signal.[26] With HNO_3, a lower deposition potential is possible without hydrogen evolution and offers an LOD of 6.3×10^{-7} M (47.3 ppb) for As(III). Use of ultrasound further reduces the LOD down to 1.4×10^{-8} M (1.1 ppb) for As(III). Interestingly, the effect of ultrasound on the LOD and the accumulation time for the detection of arsenic are also improved with the Au electrode.[18] Under quiescent conditions, an LOD of 1.8×10^{-7} M (13.5 ppb) is achievable using a 120 s accumulation time. Under optimized ultrasound, the accumulation period is reduced to 60 s with a corresponding LOD of 1×10^{-8} M. (0.8 ppb) i.e., detection sensitivity is increased by 18-fold.

Commercial pencil lead (Pb) can serve as a working electrode for the development of a simple and inexpensive method for As(III) detection by ASV.[27] A potential of -0.8 V (vs. Ag/AgCl) is applied to Pb in an aqueous solution of 5 mg L^{-1} Cu(II) and 1 M HNO_3 for 10 min under nitrogen, followed by sweeping potential from -0.8 to 0.8 V at 0.05 V s^{-1}. An anodic wave due to the oxidation of Cu(0) with a peak potential at 0.13 V is obtained. In the presence of As(III) with 5 mg L^{-1} Cu(II) in solution, the anodic peak potential shifts to more positive potentials with an increase in the electric charge of the anodic wave. With further optimization and validation, this method might serve as a rapid method for screening As(III) in environmental water samples.

A polytaurine nano-Au film has been fabricated on a GC electrode and indium tin oxide (ITO) using cyclic voltammetry (CV).[28] The nano-Au film modified GCE displays linearity of 6 to 28 μM and an LOD of 0.46 μM (34.5 ppb) for lab samples. The linearity and LOD are comparable for the detection of arsenic in spring water samples. *n*-Butanethiol (n-BT) is self-assembled to form a monolayer on polycrystalline Au (poly-Au). The partial reductive desorption of n-BT of this surface allows the selective blockage of the Au(100) and Au(110) surface domains by n-BT while the Au(111) domain remains untouched.[29] SWASV using the Au(111)-like poly-Au electrode shows linearity for As(III) up to 15 μM, with an LOD of 0.28 ppb and is not sensitive to Cu(II). This approach could be promising for the electrochemical detection of trace level of As(III) in real samples without any interference from Cu(II).

The ASV determination of arsenic with a low LOD is feasible, but may suffer from interference by various metals that are present in large concentrations in ground water. Common metals in ground water include Cu, Zn, Fe, Pb, Ag, Se, Bi, Sb and Hg. Cu(II) often co-exists with arsenic at comparable levels in water systems.[30] As mentioned previously, an L-cysteine modified Au electrode has the same sensitivities and limits of detection for Cu in the presence of arsenic ranging from 2 μM to 20 μM. Cu can easily be co-deposited with the arsenic at the same reduction potential to form Cu_3As_2 and bulk Cu metal on an Au surface.[25] Therefore, there will be an overlapping interference peak from the stripping of Cu(0) from the arsenic peak, as the Cu peak has only a slightly more positive potential than the arsenic stripping peak. Another concern is the contamination of As(III) and other metals in commercially available HCl and HNO_3. HCl (<10 ppt arsenite, environmental grade plus), and H_2SO_4 (<100 ppt arsenite, environmental grade) must be used in such analyses. Nevertheless, with Ag as the detecting electrode, the neutral and basic media of inorganic salts enhance the electrode sensitivity more than the acidic media. Thus, it is possible to work in alkaline medium (Na_2SO_4 as supporting electrolyte) for the detection of As(III) with a LOD of 0.1 ppb by a Ag wire electrode.[11] This approach should be investigated further and the result must be corroborated with reference analytical techniques.

Nanoparticle modified electrodes

Metallic NPs, particularly Au or Pt can be easily electrodeposited on any electrode surface to enhance active surface area. As an example, Au NPs can be formed on the surface of a GC electrode in a cross flow thin layer electrochemical cell using an Au solution (0.1 mM $HAuCl_4$ in 0.5 M H_2SO_4) with an applied potential of 0.18 V (vs. Ag/AgCl) for 15 s. After deposition, a noticeably shiny green film is observed on the electrode surface, suggesting a uniform layer (30 ± 13 nm) of Au NPs. A flow analysis system equipped with the Au NP-modified GC electrode is capable of detecting As(III) with linearity up to 15 ppb and an LOD of 0.25 ppb.[31] In comparing HNO_3, HCl and H_2SO_4, the reproducibility is far superior in HNO_3. Similarly, Au NPs are electrodeposited onto a GC electrode via a potential step from +1.055 to -0.045 V vs. SCE for 15 s from a solution of 0.1 mM $HAuCl_4$ in 0.5 M H_2SO_4. The modified electrode provides an LOD of 0.0096 ppb for As(III) with LSV.[32]

Besides electrodeposition, a seed-mediated growth method is an alternative for modification of a GC electrode with Au NPs.[33] The polished GC electrode is simply immersed in the $HAuCl_4$ seeding solution consisting of trisodium citrate and $NaBH_4$ for 30 min. After rinsing and nitrogen drying, the resulting electrode is immersed in a second $HAuCl_4$ growth solution containing CTAB and ascorbic acid for 2, 10 and 30 min to reach different degrees of coverage. Au NPs with a spherical shape and an average size of 40 nm diameter are formed on the electrode surface after 30 min of incubation in the growth solution. The CV of the Au NP-modified GC electrode in 1 mM $Pb(NO_3)_2$ and 0.1 M NaOH shows a sharp stripping peak at -0.58 V (vs. SCE) in the Au(111) domain and a broader stripping peak at -0.38 V (vs. SCE) in the Au(110) facet. No relevant contribution of Au(100) domains is observed in the CV. Au NPs/GC electrodes can also be prepared by simply casting citrate stabilized Au NPs onto a well-polished GC electrode.[34] The Au NPs/GC electrode in 1 M HCl using SWASV exhibits good performance for As(III) analysis with an impressive LOD of 0.025 ppb and a linear range of 0.05 to 1 ppb.

Abrasively modified basal and edge-plane graphite, carbon-paste, and carbon-epoxy electrodes have been used to create Au-carbon composite electrodes for detection of As(III). Micron sized Au particle arrays on carbon-paste electrodes provide an LOD of $(5 \pm 2) \times 10^{-9}$ M (0.4 ppb), with a sensitivity of 10 ± 0.1 A·M.[35] An Au NP-modified BDD thin-film electrode (a nominal particle size of 23 ± 5 nm) to detect total inorganic arsenic was fabricated using DPASV.[36] As(III) is pre-concentrated with the modified diamond surface during the deposition step and detected oxidatively during the stripping step. As(V) is detected by a pre-reduction step with Na_2SO_3, followed by the normal DPASV determination of As(III). Sharp and symmetric stripping peaks are observed for the Au-coated diamond electrode with LODs of 0.005 ppb for As(III) and 0.08 ppb for As(V) in standard solutions. Excellent electrode response stability is observed even in the presence of up to 5 ppm of added humic acid. The Au NP-modified BDD electrode exhibits better performance for total inorganic arsenic analysis compared to Au NP-modified GC or Au foil electrodes.

Au nanoelectrode ensembles and Au nanoseeds (GNEEs and GNSs), prepared on a thiol-functionalized sol gel-derived silicated matrix on an Au electrode, enables the selective determination of As(III) over Cu(II).[37] With the SWASV technique, a deposition potential of −0.35 V (vs. Ag/AgCl) for 100 s results in the best sensitivity. However, the modified electrode suffers a 7% decrease in the signal response (peak height) after 6 days. The reduction of Cu(II) interference is improved by using GNEE on basal-plane graphite-modified electrodes instead of GNEE on the GC or macro Au electrodes. The stripping peaks obtained by the NP electrodes are narrower and more symmetrical compared to the Au macro electrode. A GC electrode modified with internal-electrolysis deposited Au NPs is useful for selective detection of As(III) by ASLSV.[38] The Au NP/GC electrode is prepared based on the redox replacement reaction between a supporting electrolyte-free aqueous $HAuCl_4$ and a Cu sheet in saturated KCl separated by a salt bridge. The ASLSV peak current for the As(0)-As(III) oxidation is proportional to As(III) concentration from 0.02 to 3 μM with an LOD of 0.9 nM (0.1 ppb). In comparison, the As(III)-As(V) oxidation is linear with As(III) concentration from 0.02 to 1 μM with an LOD of 4 nM (0.3 ppb).

The behavior of ASV detection of As(III) at Au NP-modified GC electrodes prepared by electrodeposition in the presence of various additives deserves a brief description because the dimension and morphology of Au NPs are strongly affected by the presence of such additives. Hossain *et al*. performed the electrodeposition of Au NPs onto the GC electrode using the chronocoulometric technique in 0.5 M H_2SO_4 containing $Na[AuCl_4]$ in the presence of KI, KBr, Na_2S and cysteine additives.[39] Of interest is the performance of the nano-Au/GC electrodes, prepared using different concentrations of $Na[AuCl_4]$ (0.05-0.5 mM) and KI additive (0.01-1.0 mM) at various deposition times (10-30 s). For the detection of As(III) by LSV, the resulting electrode has an LOD of 0.024 μM (1.8 ppb). Poly(L-lactide) stabilized Au NPs (PLA-Au NP) with an average particle size of 10 nm can be used to modify a disposable screen-printed carbon electrode (SPE) for the detection of As(III) by DPASV.[40] The PLA-Au NP/SPE exhibits an LOD of 0.09 ppb with linearity up to 4 ppm for the detection of As(III) in an HCl medium. Most importantly, the PLA-Au NP/SPE is not subject to any interference from Cu, Cd, Fe, Mn, Ni, or Zn.

BDD macro- and microelectrodes are modified by electrodeposition of Pt NPs using a multi-potential step electrodeposition technique and used for the oxidative determination of As(III).[41] LSV performed with the modified BDD microelectrode outperforms its macrocounterpart with linearity up to 100 ppb and an LOD of 0.5 ppb. The electrochemical system is applicable for processing tap and river water samples. Cu and Cl ions, the two most severely interfering species at levels commonly found in ground water, do not interfere with the assay. Over 150 repetitive runs could be performed, and electrochemical etching of Pt allows the reuse of the BDD microelectrode. Ag NP/chitosan-modified GC electrodes have been prepared for the detection of As(III) by DPASV.[42] Based on unique three-dimensional networks and strong adsorption ability, the nanostructured electrode displays a wide linear range (10-100 ppb) and an LOD of 1.20 ppb. The electrode suffers from As(V) interference, but could be used to determine total arsenic after chemical reduction of As(V) to As(III).

Considering the high adsorptivity of Fe_3O_4 microspheres toward As(III), a Fe_3O_4-RTIL (room temperature ionic liquid) composite-modified screen-printed carbon electrode shows better electrochemical performance than most noble metals.[43] The composite modified sensor offers direct detection of As(III) within the desirable range (10 ppb) in drinking water with an estimated LOD of 8×10^{-4} ppb. Magnetic Fe_3O_4 and Au NPs have also been used to modify GC electrodes.[44] The magnetic NPs are dropped first onto the GC electrode followed by electrodeposition of Au NPs. Using SWASV, the sensitivity of As(III) is significantly improved on the Au NPs/Fe_3O_4/GC electrode in comparison with the Au NPs/GC electrode. The composite-modified GC electrode exhibits an LOD of 0.073 ppb, excellent reproducibility and high stability.

Amperometric detection: oxidation and reduction

ASV using Ag, Au or Pt electrodes is problematic due to significant interference from Cu and other metals as described earlier. An alternative approach is based on the As(III) oxidation peak for the analytical detection, i.e. As(III) → As(V) using Pt NP-modified GC electrodes.[45] Pt NPs (average diameter of 105 nm) can be deposited on GC electrodes by potential cycling in 0.1 M aqueous KCl containing 1 mM K_2PtCl_6 for 25 cycles. The potential is poised at +0.5 V (vs. SCE) for 0.01 s and at -0.7 V (vs. SCE) for 10 s for each cycle. Although the approach only offers an LOD of 2.1 ± 0.05 ppb, it is still appreciably below the WHO's guideline value (10 ppb). The oxidation of As(III) to As(V) initiated by adsorbed species on the PtOH surface at high oxidation potentials (above +0.8 V vs. Ag/AgCl) is more vulnerable to electroactive interefence from other species in water samples. In this approach, upstream ion exclusion HPLC is needed to measure As(III) in water samples with an LOD of 15 ppb.[46] An iridium-implanted BDD (Ir-BDD) electrode is also capable of detecting As(III) in a flow injection system.[47] The electrode is applied at +0.6 V (vs. Ag/AgCl) in 0.1 M H_3PO_4 or 0.1 M PBS for the oxidation of As(III) to As(V). The electrode exhibits excellent stability for the electrode material, at least three months in regular usage with a LOD of 1.5 ppb. Another interesting approach is electrocatalytic oxidation of As(III) to As(V) on a cobalt oxide NP-modified GC electrode at 0.75 V (vs. SCE).[48] Cobalt oxide NPs are deposited on the GC substrate by CV scan (−1.1 to +1.1 V) of 1.0 mM $CoCl_2$ solution in PBS at pH 7 with the following electrocatalysis:

$$Co_3O_4 + H_2O + OH^- \rightarrow 3CoOOH + e^- \quad (3)$$

$$6CoOOH + H_3AsO_3 + 2OH^- \rightarrow 2Co_3O_4 + HAsO_4^{2-} + 5H_2O \qquad (4)$$

The modified electrode shows excellent catalytic activity toward arsenic oxidation over a wide pH range, 5-11. At +0.75 V (vs. Ag/AgCl) in phosphate buffer (pH 7), the electrode exhibits an LOD of 11 nM (0.8 ppb), linearity up to 4 orders of magnitude and a response time of <2 s. The interference of various reducing compounds on the signal response of As(III) is negligible. The use of cobalt oxide NPs is promising towards the development of a new class of electrode materials for arsenic detection.

Multilayers of poly(diallyldimethylammonium chloride) and citrate-capped Au NPs anchored on a sodium 3-mercapto-1-propanesulfonate-modified Au electrode by electrostatic layer-by-layer assembly are an excellent architecture for the direct oxidation of As(III).[49] The five bilayers with redox activity are applicable for arsenic sensing via the direct electrocatalytic oxidation of As(III) with an LOD of 4.36 ppb. IrO_2 nanotubes, with estimated uniform diameters of 110 ± 10 nm and a length of 1-3 μm, are synthesized by electrodeposition in a polycarbonate template.[50] The GC-IrO_2 nanotube-modified electrode also displays electrocatalytic activity toward Cr^{3+} and As^{3+} oxidation. The LOD of As(III) detection was 0.1 μM (7.7 ppb).

In addition to the As(III)/As(V) pair, of interest is a novel method of stirring-only-driven accumulation and electrochemical determination of As(III), with both of the oxidation and reduction peaks associated with As(0)/As(III) using an Au nano-film electrode in neutral solution.[51] With stirring, a large amount of As(III) is deposited on the modified electrode, resulting in a significant signal response. The accumulated As(III) on the electrode shows a well-defined redox couple in 0.1 M phosphate buffer solution (pH 7). As(III) could be detected in the range from 0.20 to 375 ppb with an LOD of 0.04 ppb. In particular, with the use of the reduction peak of As(III), the modified electrode exhibits excellent performance for As(III) determination even in the presence of Cu(II). The regeneration of the electrodes is facile with good reproducibility.

An indirect approach for the detection of As(III) is based on a wall-jet electrogenerated iodine approach using a disposable screen-printed ring disk carbon electrode.[52] In this detection scheme, iodide (I^-) is first oxidized to iodine (I_2) at the disk electrode; I_2 is effectively reduced back to I^- in the presence of As (III). The inhibited reduction current of I_2 to I^- can thus be monitored and used for As(III) analysis. Under the optimized conditions, the detection scheme shows linearity up to 10 μM with an LOD of 70 nM (5.3 ppb). Its applicability was also demonstrated to detect As(III) in ground water obtained from a Blackfoot disease endemic village in Taiwan. Su *et al.* [53] examined the electrochemical deposition and chemisorption studies of an iodide film on a GC electrode and a polycrystalline Au electrode (poly GE). The electrochemically deposited iodide film on the GC electrode shows good stability and active at pH 1.5 and 4 whereas the chemisorbed iodide film on the poly GE is active and stable at pH 9 and 13. The iodide-modified GC electrode exhibits good electrocatalysis for the oxidation of As(III) with an LOD of 0.2 nM (0.015 ppb).

Arsenate and arsenite are strongly toxic to life, however, a number of prokaryotes use these compounds as electron acceptors or donors, respectively, for bioenergetic purposes via respiratory arsenate reductase and arsenite oxidase. Therefore, such enzymes can be isolated and purified for the development of a biosensor for arsenic. To date, only one electrochemical biosensor has been reported for As(III), perhaps due to commercial unavailability of arsenite oxidase, the enzyme with capability of oxidizing As(III) to As(V). Nevertheless, arsenic oxidase was isolated and purified toward the development of an arsenic biosensor.[54] The enzyme is deposited on a CNT-modified GC electrode. CNT facilitates direct electron transfer from the enzyme to the electrode without a mediator to achieve an LOD of 1 ppb at an applied potential of 0.3 V (vs. Ag/AgCl) with a response time of 10 s. Due to the selectivity of the enzyme for arsenic, this approach is not subject to Cu interference and applicable for analysis of As(III) in tap water, river water and mineral water. However, both storage and operational stabilities of this enzyme must be fully addressed and large scale preparation of this enzyme has not been demonstrated.

Nanocomposites and nanostructures

Carbon nanotubes (CNTs) exhibit a popular support structure due to their high surface area, high conductivity and ease of functionalization to immobilize other chemical species such as metallic NPs and organic molecules to improve detection sensitivity and selectivity. Multiwall CNTs (MWCNTs) with thiol groups are attached to an Au electrode and used for the determination of As(III) and Bi(III) in natural and high-salinity waters. The MWCNTs can be oxidized with HNO_3, followed by reaction with $SOCl_2$ and mercaptoethanol to yield the thiol groups. MWCNTs are less expensive and have a larger number of structural defects compared to single-wall CNTs (SWCNTs), suitable for derivatization. A mechanism for As(III) pre-concentration at the electrode is proposed with linearity of 0.3-50 μg L^{-1} and an LOD of 0.3 ppb.[55] Conversely, an ethylenediamine-monolayer modified GC electrode grafted by non-covalent and covalent sulfhydryl groups jointly modified SWCNTs has been developed for arsenic(III) detection with an LOD of 0.01 ppb.[56] The greater sensitivity is attributed to a higher specific surface area of SWCNTs and lower contact resistance compared to MWCNTs.

An electrode consisting of carbon paste-modified with CNTs was used to determine arsenic concentration in sugar cane brandy samples. The detection is performed through LSV and DPASV with cathodic stripping in the presence of Cu^{2+}. As(III) reacts with Cu^{2+} to generate an intermetallic compound Cu_xAs_y which is deposited on the electrode surface and stripped cathodically to produce a detection signal. The LOD is 10.4 ppb and 3.4 ppb, respectively with mineral oil[57] or silicone[58] as a binder.

Au NPs (~100 nm) were fabricated within microchannels by electrochemical deposition on SWCNT/PDMS surfaces and used as electrocatalytic materials for both glucose detection and suitable sensing surfaces for As(III) detection up to 30 ppb and sensitivity of 4.49 ± 1.01 μA cm^{-2} ppb^{-1} within an accumulation time of 60 s (Fig. 3).[59] The continuous streaming solution in microfluidic devices allows for enhanced mass transport to the electrodes and elimination of fouling effects, resulting in increased currents and high sensitivities. Electroless or redox reaction based deposition of Au NPs on CNTs can be achieved by in situ chemical reduction of $HAuCl_4$ by $NaBH_4$. The Au NP-CNT modified GC electrode exhibits a large surface area compared to Au NPs deposited on a normal size GC electrode. The LOD of this electrode in 0.1 M HCl using SWASV is 0.1 ppb. Similarly, Au NPs are deposited on GC microspheres and wired together with MWCNTs for fabricating As(III) electrodes with extremely minimal Au required (99% less than required for an Au macrodisk). Nevertheless, this electrode still achieves an LOD of 2.5 ppb.

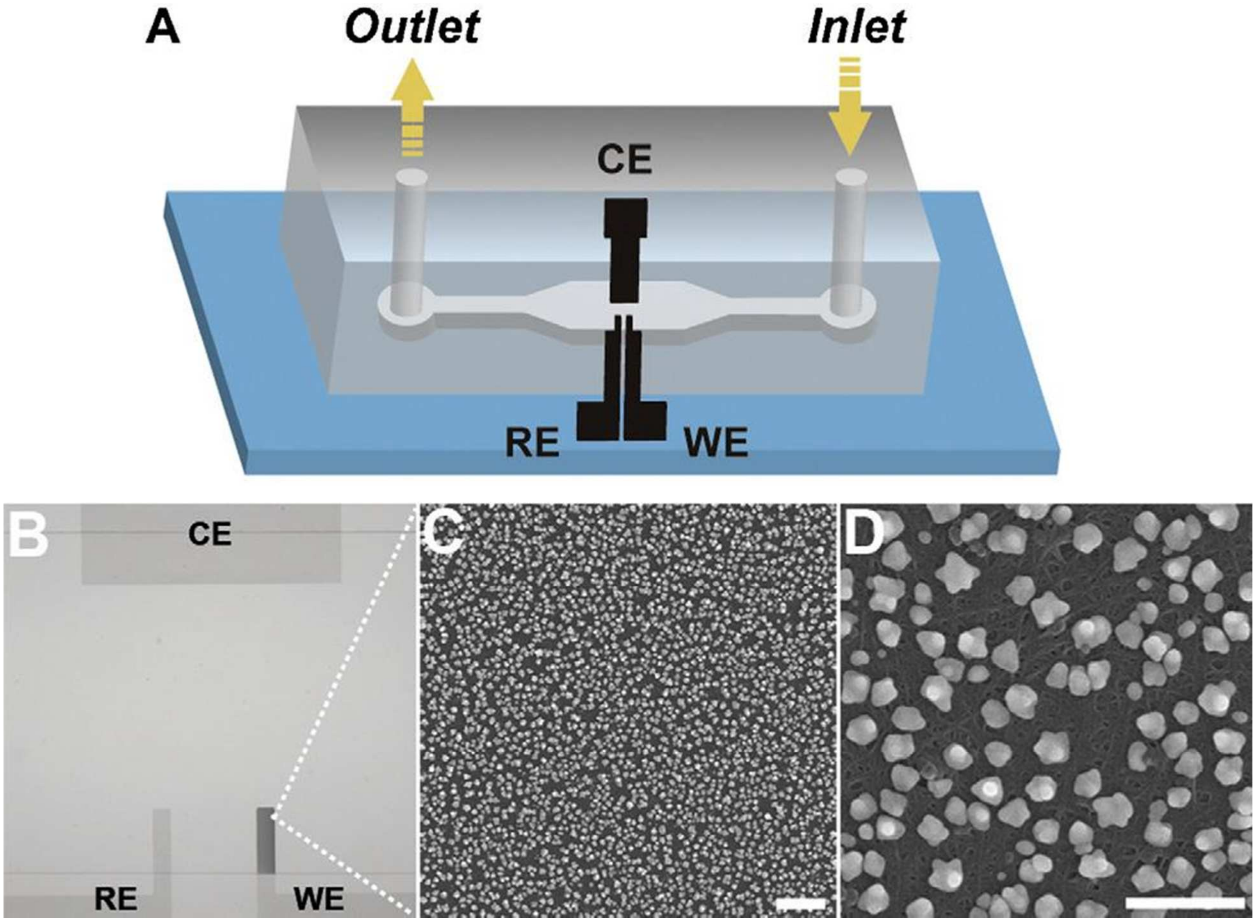


Fig. 3. (A) Schematic of a SWCNT-based microfluidic device (WE, working electrode; RE, reference electrode; CE, counter electrode). (B) Optical microscope image of a device after electrochemical deposition of Au particles in 0.05 M H_2SO_4 containing 1 mM $HAuCl_4$ at −0.8 V (vs. SWCNT pseudo-reference electrode) for 10 s. The flow rate in the device is 0.5 μL min^{-1}. (C), (D) SEM images of the dark region on the WE. The scale bars in (C) and (D) represent 1 μm and 500 nm, respectively. (Adapted from Ref. 59 with permission. Copyright© 2013 Elsevier).

The electrochemical detection of As(III) by ASV has been investigated on a Pt-Fe(III) NPs-modified MWCNT on GC electrode (nanoPt-Fe(III)/MWCNT/GC) in 0.1 M H_2SO_4.[60] The nanoPt-Fe(III)/MWCNT/GC electrode is simply prepared via continuous potential cycling in the range from -0.8 to 0.7 V (vs. Ag/AgCl), in 0.1 M KCl solution containing 0.9 mM K_2PtCl_6 and

0.6 mM $FeCl_3$. For the detection of As(III), the nanoPt-Fe(III)/MWCNT/GC electrode shows an LOD of 10 nM (0.75 ppb) and suffers no interference from Cu ion. In another example, Pt NPs with a nominal diameter of 15 ± 3 nm on CNTs can be rapidly synthesized by microwave radiation and applied for the oxidative determination of As(III). The LOD of the Pt NPs/CNT/GC electrode is 0.12 ppb, i.e., about 1–2 orders of magnitude lower than that of Pt nano/GCE or Pt foil electrode. The improved performance can be attributed to the increased surface area of Pt NPs, while the CNT provides a support for the NPs to remain immobilized for repeated use.[61]

A different approach is the development of a DNA biosensor for As(III) based on SWCNT-modified GC for analysis of As(III) at neutral pH.[62] The As(III) is simply deposited in open circuit by immersing the electrode in the solution for 180 s, removed, rinsed, and followed by LSV. The reduction of As(III) to As(0) enables an LOD of 0.05 ppb. Another work involving DNA focuses on the interaction of As(III) with calf thymus double-stranded DNA (dsDNA), calf thymus single-stranded DNA (ssDNA) and also 17-mer short oligonucleotides.[63] The study involves the use of a carbon paste electrode and DPV and potentiometric stripping analysis techniques using a pencil graphite electrode as two electrochemical biosensors. Weak interactions between As(III) and guanine are inferred, implying the potential usefulness of this approach for indirect determination of As(III). Another biosensor based on a DNA-CNT film is immobilized at the surface of a screen-printed carbon electrode. The damage to DNA caused by As(III) compounds can be evaluated by means of an electrochemical DNA marker, $[Co(phen)_3]^{3+}$ in the presence of glutathione, as the portion of original dsDNA survives the cleavage medium.[64]

Graphene is another emerging carbon-nanomaterial with a monoatomic layer thickness with novel properties. Graphene along with lead oxide can detect As(III) at 10 nM (0.75 ppb) and might open up the possibility for simultaneous detection of toxic metals using graphene-modified electrodes.[65] An electroreduced graphene oxide (ERGO)-Au NPs composite film was electrodeposited on a GC electrode and used to determine trace As(III) in 0.20 M aqueous HCl by ASV for real water samples.[66] The linearity of detection with As(III) ranges from 0.01 to 5 μM, with a sensitivity of 12.2 μA/μM and an LOD of 2.7 nM (0.20 ppb). The low LOD could be attributed to the abundant oxygen-containing active groups on ERGO which are beneficial for the ASV determination of As(III).[67] Ag NPs-graphene oxide have also been used for the detection of As(III).[68] Ag NPs are synthesized using beta-cyclodextrin as a stabilizing agent and ascorbic acid as a reducing agent on graphene oxide and deposited on a GC electrode. Under ASV, As(III) detection is linear from 13.33 to 375.19 nM with an LOD of 0.24 nM (0.02 ppb).

A GC electrode has been modified with a thin conducting polyaniline (PANI) layer followed by Au deposition with and without 0.1 mM KI additive.[69] This procedure results in a high dispersion of Au NPs in the PANI matrix. The reported LOD is 0.04 ppb As(III) in 0.1 M HCl with SWASV as the electroanalytical technique. Three different hybrid films, ruthenium oxide (RO), RO/hexachloroiridate and RO/hexachloroiridate/(Pt), have been attempted as electrode materials for the detection of arsenic.[70] Of particular interest is the deposition of RO/hexachloroiridate/(Pt) on GC, Au and ITO electrodes by repetitive CV scans in 0.1 M KNO_3 (pH 2). The presence of Pt enhances active sites for the electrochemical oxidation of As(V). A linearly decreasing current value obtained by a rotating disc electrode reflects the reduction of As(V) to As(III). The LOD for As(III) is 4.5 ppb for RO/hexachloroiridate/(Pt) on the GC electrode. An Au/TiO_2 modified GC electrode with a three-dimensional porous structure has been evaluated for selective determination of As(III) by SWASV (Fig. 4).[71] The composite electrode exhibits a high active surface area and excellent electron transfer properties. Under optimal conditions, the SWASV peak current for As(III) concentration is obtained in the range of 10^{-7} to 8×10^{-6} M with an LOD of 0.04 μM (3 ppb). Simultaneously, good repeatability and stability prevents the effects of interfering species, which is suitable for As(III) determination in "real world" samples.

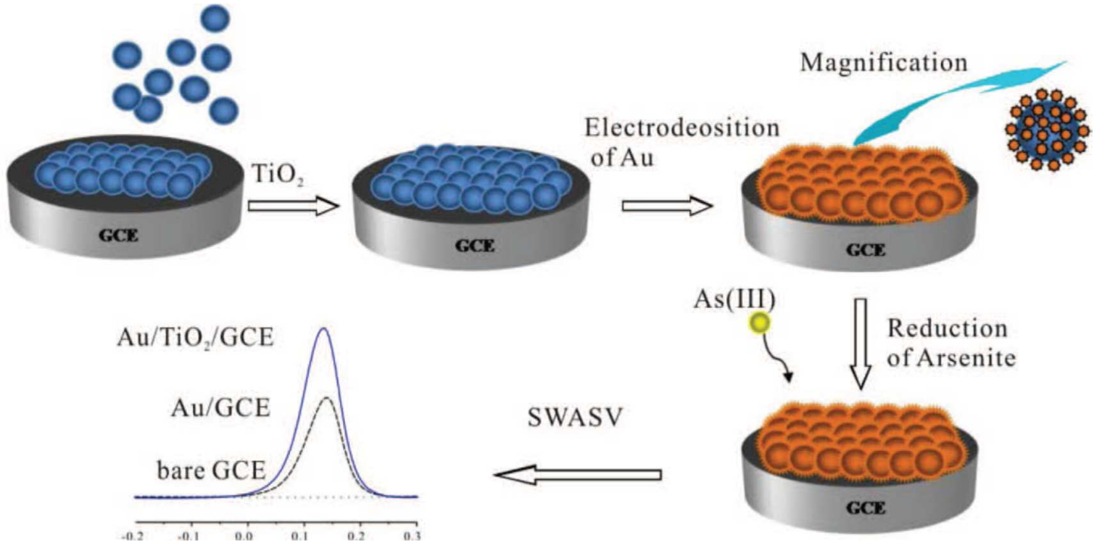


Fig. 4. Detection of As(III) via synergy effect enhanced electrochemical signal of gold nanoparticle dropped TiO_2 microsphere hybrids. (Adapted from Ref. 71 with permission. Copyright© 2013 Royal Society of Chemistry).

Novel gold-decorated Te hybrids with a tripod-shaped planar microstructure are prepared through a two-step hydrothermal process: the synthesis of Te single crystals and the subsequent self-sacrificial reaction of the Te template with $HAuCl_4$.[72] The Au/Te sensor has an LOD of 0.0026 ppb for As(III) and exhibits excellent selectivity for both As(III) and Cu(II) ions in complex mixtures containing other metallic element ions. The enhanced electrocatalytic property may be attributed to the synergetic interaction between the noble metal and semiconductor and the presence of a large number of active sites on the hybrid surface.

A novel method for the oxidative determination of trace As(III) is feasible using highly ordered Pt-nanotube array electrodes (PtNTAEs).[73] The PtNTAEs with a highly organized structure are fabricated by electrodeposition of Pt in a 3-aminopropyltrimethoxysilane-modified porous anodic alumina template (PAA). The PtNTAEs exhibit better performance for As(III) detection compared to the Pt NPs-coated GC electrode or the Pt foil electrode. The PtNTAEs provide higher reproducibility and an LOD of 0.1 ppb, typically 1-2 orders of magnitude lower than that of the Pt NPs/GC electrode or the Pt foil electrode.

A simple and efficient electrochemical assay based on self-assembled monolayers has been described for sensitive determination of As(III) in water samples (Fig. 5).[74] The synergy of glutathione, dithiothreitol and *N*-acetyl-L-cysteine mixed SAMs enhances the detection specificity and sensitivity of As(III) in water samples, resulting from the immobilization of a large number of As(III) moieties on the Au electrode surface via As-O and As-S linkages. After the accumulation of As(III) in 1 M HCl at a deposition potential of -0.35 V (vs. Ag/AgCl) and a deposition time of 150 s, LSV is performed to achieve an LOD of 0.5 ppb with linearity ranging from 3-100 ppb.

Cathodic stripping voltammetry (CSV)

Mercury as the working electrode is a classical technique for analysis of anions and metallic elements. However, the use of mercury is forbidden in many countries owing to its high toxicity and waste disposal problems. Nevertheless, there are still some reports on the potential detection of arsenic by CSV using hanging drop mercury electrodes (HDME) and static mercury drop electrodes (SMDE) since such electrodes only involve the consumption of minimal amount of mercury. Analysis involving mercury electrodes for arsenic analysis is complicated, vulnerable to organic interferences and requires careful sample preparation. However, methods involving mercury do not require electrode conditioning and cleaning for repeated and routine analysis. Table 2 summarizes some work related to mercury for the detection and speciation of arsenic in water and soil samples.

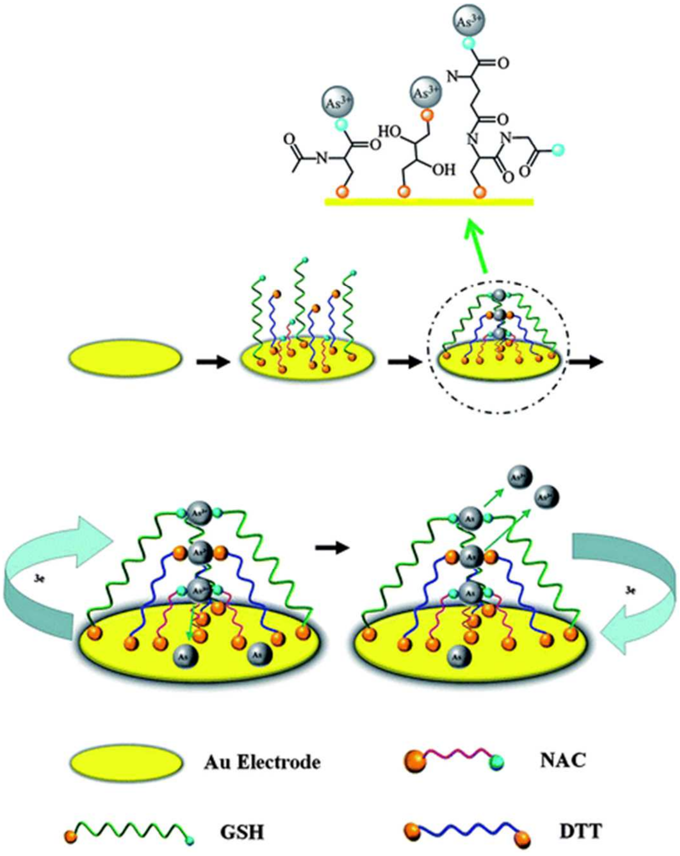


Fig. 5. Amplified electrochemical detection of As(III)via mixed SAMs on the gold electrode. (Adapted from ref. 74 with permission. Copyright© 2011 Royal Society of Chemistry).

Table 2. Cathodic stripping voltammetry using mercury as the sensing electrode

Method	**Key results**
The speciation of arsenic in the field using DPCSV on a HDME based on the deposition of intermetallic species $Cu_xSe_yAs_z$ followed by reductive stripping.[75]	Deposition : $2As^{3+} + 3MHg + 6e^- \rightarrow M_3As_2 + 3Hg$ Stripping : $M_3As_2 + 12H^+ + 12e^- + 3Hg \rightarrow 2AsH_3 + 3H_2 + 3MHg$ (where M = Cu or Se)
LSV with HBr instead of HCl as the supporting electrolyte to reduce the deposition time for the detecion of arsenic in mineral water, geothermal water, and seawater.[76]	LOD of 0.75 ppb for As(III) and 1.5 ppb for As(V).
Simultaneous analysis of Cu(II), Pb(II), Cd(II), Zn(II), As(III), Se(IV), Mn(II), Fe(III) from different food matrices: SWASV for the first four, SWCSV for As(III) and Se(IV).[77] Simple SWV for Mn(II) and Fe(III) at mg L^{-1} level.	Electrolyte: 0.5 M HCl and ammonia–ammonium chloride buffer, pH 8.8. For As(III), the LOD is 0.014 ppb with peak area vs. 0.168 ppb with peak height.
As(III) can be determined in the presence of dissolved organic matter such as fulvic acid. Real and synthetic samples spiked with fulvic acid are analyzed using the adsorptive SWCSV technique.[78]	The Cu–fulvic acid and As–fulvic acid complexes have higher affinity of adsorption than Cu(II) and As(III) on the Hg electrode.
A hanging copper amalgam drop electrode for determination of As(III) using DPCSV.[79] The copper amalgam is prepared separately by partially dissolving Cu wire in a pool of Hg to avoid adding Cu(II) in solution.	Interferences are observed in presence of Se(IV), Te(IV), and synthetic surfactants. Reference materials and natural water samples are tested for total arsenic. LOD for As(III) as low as 0.33 nM (0.02 ppb) with a deposition time of 240 s.
A CSV procedure with HDME for the determination of As(III) and As(V) in soil extracts. The As(V) of inorganic arsenic is determined after the reduction of As(V) with KI and ascorbic acid.[80]	For the extraction of arsenic from soil, The HCl/HNO_3 extraction combination provides the highest efficiency, but also oxidizes As(III) to As(V). H_3PO_4 and methanol/water do not oxidize the As(III) to As(V), so they could be used to differentiate between the two arsenic species.
An adsorptive CSV technique for the measurement of As(III) at a HDME in the presence of sodium diethyl dithiocarbamate (SDDC).[81]	SDDC forms a stable complex with As(III) on the Hg-electrode surface through adsorptive deposition. The As(III) in the adsorbed complex can be reduced to As(0) in a cathodic stripping scan.
Deposition times as short as 50 s using SDDC as a complexing agent for As(III).[82] The higher deposition time is required at lower Cu(II) concentration (1 mM or less) for the needed Cu_3As_2 intermetallic compound formation. The same technique is applied for the speciation of As(III) and As(V) in water and saline samples after a chemical reduction of As(V) with a mixture of $Na_2S_2O_5/Na_2S_2O_3$.[83]	LOD = 0.004 ppb. This sensitivity enhancement is due to the presence of Cu(II). The methodology is applied for the determination of As(III) and As(V) in mineral water samples at 0.1 g L^{-1} or less.

Concluding remarks and Outlooks

Despite numerous publications in this field with respect to novel electrode materials, electrolytes, and nanocatalysts, reproducibility of surface preparation is still problematic and the analysis of arsenic in real world samples is far from certainty. Most publications focus on the finding of new sensing interfaces such as NPs, CNTs and graphene for analyzing As(III) in simple water samples and spiked water samples. In many cases, such reported analytical techniques were not even tested for reference arsenic samples of various water matrixes, which are available from the National Institute of Standards and Technology (USA). The claim for the LOD deserves a brief comment here since in general, the LOD reported in the literature is based on the calculated value from the signal to noise ratio. In many cases, an LOD of sub-ppb or even ppt (part-per-trillion) has been claimed, although ten to hundred times these limits were never tested in such studies. As mentioned earlier, mineral acids with ppt contamination of several metallic elements including arsenic are very expensive and must be used in such analysis. Therefore, any claim on LOD of ppt levels for arsenic needs to be verified and reconfirmed by testing the signal response at these extremely low arsenic levels.

Among different electrochemical methods, stripping voltammetry is still an active research using Au electrodes or Au NPs on GC in HCl for analysis of As(III) in contaminated water samples. The method is particularly convenient to measure the most toxic As(III) at low ppb level in the presence of high concentration of As(V). A drawback of this method is its susceptibility to interferences from various metals or organic compounds, especially in real sample water. In addition, it cannot be coupled with an upstream separation scheme for speciation analysis. Therefore, ASV using a gold or copper disk electrode needs to be compared and validated for analysis of As(III) using reference samples and “real-world” samples. It is also necessary to establish a vigorous protocol for cleaning and characterization of the electrode surface. As a surface-based process, the primary source of irreproducible results is due to the change in electrode surface from one electrode to another electrode. This might be more problematic with NP-modified electrodes, CNT- and graphene based materials for routine measurements and the development of commercial instruments. Therefore, macro electrodes of a few millimeters in diameter are still widely used because they are easy to handle and fabricate and offer excellent reproducibility. Purity of sulfuric and hydrochloric acids is another concern since commercial acids contain considerable amounts of metal ions including arsenic. The results obtained by ASV must be corroborated with those of reference analytical methods including neutron activation analysis.[84]

The component of environmental groundwater is complex and different from location to location. It includes various metal ions and organic compounds which have been proven to affect the arsenic response signal. As a few examples, for trace determination of As(III) using an *in situ* plated-Bi film on edge-plane graphite as the electrode, there is no As(III) response unless both Bi(III) and Se(IV) are present in solution.[85] The stripping current of As(III) is also affected by the presence of humic acids (HA), a ubiquitous species in aquatic systems, due to electrode surface blockage by HA adsorption.[86] Groundwater in Inner Mongolia, China may contain up to 22 ppm of HA and the interference caused by this acid on the signal response of As(III) has been described in various publications.[87-90] Therefore, the measurement must be validated by lab-based AAS, atomic emission and other hyphenated techniques.

Over 20 countries[91] show arsenic levels in ground water above the WHO threshold value of 10 ppb and Bangladesh is at the top of the list with the average arsenic level in several districts higher than 50 ppb.[92] It is of utmost importance to have materials and methods for the removal and detection of arsenic and other toxic metals in different water matrices. The development of electrochemical biosensors is very limited owing to the unavailability of exotic arsenite oxidase or reductase. Of course, this approach has also been challenged by the development of a simple test kit based on *Bacillus subtilis* that is capable of producing indigo in the presence of arsenic or a molybdenum blue colorimetric method with detction limits as low as 1 ppb.[93,94] If applicable, either of these visual approaches (color change) is much better than an electrochemical system for the detection of arsenic contamination. A different approach is the development of a biosensor strain containing a fusion construct of the native promoter of acrA with egfP, which produces dose-dependent fluorescence at the threshold concentrations set by the WHO.[95] Another whole cell biosensor is a system based on the arsenate-responsive promoter of the *Escherichia coli* arsenic detoxification system, using urease to increase pH in the absence of arsenate, and β-galactosidase (LacZ) to decrease pH in the presence of arsenate.[96] The pH gives a clear response to an arsenate concentration of 5 ppb. However, like other whole cell based biosensors, both operational and storage stability of microbial cells is limited and may not be suitable for field testing. Metallic elements and organics in different water matrices are anticipated to inhibit microbial activity and affect the analytical performance of such whole cell based biosensors. Despite such challenges, there is an attempt to develop a commercial and portable biosensor to measure arsenic As(III) concentrations in water using *Escherichia coli* bioreporter cells. *Escherichia coli* expresses green fluorescent protein in a linearly dependent manner as a function of the arsenic concentration.[97]

The review is concluded with a brief remark for the availability of a fully automated, online arsenic analyzer for monitoring drinking water arsenic levels (ArsenicGuard™).[98] The equipment with ASV exhibits a measurement range of 1-100 ppb with an overall measurement time of <30 min. However, the normal detection limit for this equipment is confirmed as 4 ppb. Based on Au-film technology on carbon, this electrochemical system (about $8,000) can perform ASV, CSV, CV and chrono-amperometric measurements. The system and supporting chemistry can detect several metallic elements (arsenic and Hg) to 1 ppb. The "ArsenicGuard" system is a fully automated online operation and offers some users' friendly features to ensure accuracy to 1 ppb with measurement times of less than 30 min. The system has four online samples ports and provides a strong correlation with ICP-MS (±10 % typical). The detection is based on the Nano-Band™ electrode; consisting of 100 sub-electrodes each with a surface area that is less than 2 μm^2. The technology is certainly a step-forward towards on-demand testing for arsenic in real-life water samples. However, it is still a challenge to use this analytical system that requires some technical ability and it is not suitable for a non-technical operator. It is also necessary to establish a vigorous protocol for cleaning and characterization of the electrode surface. Doubtlessly, the cost to introduce such technology to areas in desperate need of arsenic analysis, such as Bangladesh, India, China, will likely be prohibitively too high. The analysis of As(III) is straightforward, but for the determination of As(V), this species must be reduced at elevated temperature with lengthy reaction time to As(III). Consequently, electrochemical detection has not become a routine analytical technique despite its cost advantage and portability for field analysis.

Bangladesh continually faces the world's most serious arsenic crisis with an estimate that 20-60 million people (total population of 125 million) might be exposed to arsenic in drinking water over the Bangladesh standard of 50 ppb.[99] An arsenic field test kit[100] (Arsenic CheckTM Field Test Kit 481196, Industrial Test Systems Inc) is available to provide a simple and reliable method for aqueous inorganic arsenic with a detection range of 0 to 800 ppb. The test is based on the conversion of inorganic arsenic compounds to arsine gas (AsH_3) by zinc dust and tartaric acid with a reaction time varying from 10 to 30 min.[101] The gas then passes through or over a piece of paper impregnated with mercuric bromide to form mixed arsenic/mercury bromides (AsH_2HgBr). The color change (white to yellow to brown) is compared with a calibrated color scale. Sulfur, selenium, and tellurium compounds are potential interfering species. However, the estimation is based on color visualization with an LOD of 2 ppb do not corroborate well with laboratory methods. The kit is sold at $120 and good for 100 tests, i.e., over $1 per test. This could be a big technical and economical challenge since there are over 11 million wells that require continuous testing to verify that the water is safe to drink in Bangladesh.[102] Nepal is another developing country afflicted with arsenic contamination.[103]

Considering the very low annual income per capita of some affected countries in Asia, the monitoring and treatment of arsenic in drinking water requires a concerted effort from the World Bank and various international agencies. Perhaps, collaborative efforts from various research groups are needed to address the above mentioned technical challenges. International comparability of analytical results must be demonstrated by the analysis of “real-world” samples. Although solving arsenic contamination is of utmost importance, significant efforts are also needed to detect and remove other toxic metal ions including zinc, cadmium and chromium from drinking water, an important factor in survival of human-beings. The arsenic contamination has caused significant damage has been to Bangladesh's workforce and economy.

References

---

(1) A. Gomez-Caminero, P. Howe, M. Hughes, E. Kenyon, D.R. Lewis, M. Moore, J. Ng, A. Aitio and G. Becking, *Environmental Health Criteria 224: Arsenic and Arsenic Compounds*. World Health Organization, Geneva, 2001.

(2) Arsenic contamination in ground water, https://www.bgs.ac.uk/arsenic, (Accessed March 22, 2014).

(3) C. J. Saranko, N.C. Halmes and S.M. Roberts, *The Toxicity of Arsenite and Arsenate*, Center for Environmental and Human Toxicology, University of Florida, Gainesville, FL, 1998.

(4) World Health Organization, *Guidelines for drinking-water quality, 3rd edition incorporating 1st and 2nd addenda. Vol. 1. Recommendations*. World Health Organization, Geneva, 2008.

(5) National primary drinking water regulations; arsenic and clarifications to compliance and new source contaminants monitoring, http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations.cfm, (Accessed March 22, 2014).

(6) Supporting document for action level for arsenic in apple juice, http://www.fda.gov/Food/GuidanceRegulation/GuidanceDocumentsRegulatoryInformation/ChemicalContaminantsMetalsNaturalToxinsPesticides/ucm360023.htm, (Accessed March 22, 2014).

(7) U.S. Environmental Protection Agency. *Analytical Methods Support Document for Arsenic in Drinking Water*. Washington, 1999.

(8) J. H. T. Luong, E. Majid and K. B. Male, *Open Anal. Chem. J.*, 2007, **1**, 7-14.

(9) P. Domenico and F. Schwartz, *Physical and Chemical Hydrogeology*, John Wiley & Sons, Inc. New York, 2nd edn., 1998.

(10) G. Hignett, J. D. Wadhawan, N. S. Lawrence, D. Q. Hung, C. Prado, F. Marken and R. G. Compton, *Electroanalysis*, 2004, **16**, 897-903.

(11) M. C. Aguirre, B. L. Rivas, L. Basáez and C. Peña-Farfal, *J. Braz. Chem. Soc.*, 2011, **22**, 2362-2370.

(12) T. D. Cabelka, D. S. Austin and D. C. Johnson, *J. Electrochem. Soc.*, 1984, **131**, 1595-1602.

(13) C. M. Barra and M. M. C. Santos, *Electroanalysis*, 2001, **13**, 1098-1104.

---

(14) A. Lolic, S. Nikolic and J. Mutic, *Anal. Sci*. 2008, **24**, 877-880.

(15) G. Forsberg, J. W. O'Laughlin and R. G. Megargle, *Anal. Chem*., 1975, **47**, 1586-1591.

(16) C. Hua, D. Jagner and L. Renman, *Anal. Chim. Acta,* 1987, **201**, 263-268.

(17) M. Kopanica and L. Novotny, *Anal. Chim. Acta*. 1998, **368**, 211-218.

(18) A. O. Simm, C. E. Banks and R. G. Compton, *Electroanalysis*, 2005, **17**, 335-342.

(19) T. W. Hamilton and J. Ellis, *Anal. Chim. Acta,* 1980, **119**, 225-233.

(20) F. G. Bodewing, P. Valenta, H. W. Nurnberg and Z. Fresenius, *Anal. Chem*., 1982, **311**, 187-191.

(21) Y.-C., Sun, J. Mierzwa and M.-H. Yang, *Talanta*, 1997, **44**, 1379-1387.

(22) R. Feeney and S. P. Kounaves, *Anal. Chem*., 2000, **72**, 2222-2228.

(23) R. Feeney and S. P. Kounaves, *Talanta*, 2002, **58**, 23-31.

(24) R. Prakash, R. C. Srivastava and P.K. Seth, *Electroanalysis*, 2002, **15**, 1410-1414.

(25) X. Dai and R. G. Compton, *Electroanalysis*, 2005, **170**, 1835-1840.

(26) A. O. Simm, C. E. Banks and R.G. Compton, *Electroanalysis*, 2005, **17**, 1727-1733.

(27) K. Arai and K. Shimada, *Bunseki Kagaku*, 2012, **61**, 411-418.

(28) M. Rajkumar, S.-C. Chiou, S.-M. Chen and S. Thiagarajan, *Int. J. Electrochem. Sci.,* 2011 **6**, 3789-3800.

(29) M. R. Rahman, T. Okajima and T. Ohsaka, *Anal. Chem*., 2010, **82**, 9169-9176.

(30) H.M. Anawar, J. Akai, K. M. G. Mostofa, S. Safiullah and S. M. Tareq, *Environ. Int*., 2002, **27**, 597-604.

(31) E. Majid, S. Hrapovic, Y. Liu, K. B. Male and J. H. T. Luong, *Anal. Chem*. 2006, **78**, 762-769.

(32) X. Dai, O. Nekrassova, M. E. Hyde and R. G. Compton, *Anal. Chem*., 2004, **76**, 5924-5929.

(33) Y. Wang, E. Laborda, C. Salter, A. Crossley and R. G. Compton, *Analyst*, 2012, **137**, 4693-4697.

(34) Y. Lan, H. Luo, X. Ren, Y. Wang and L. Wang, *Anal. Lett*., 2012, **45**, 1184-1196.

(35) A. O. Simm, C. E. Banks, S. J. Wilkins, N. G. Karousos, J. Davis and R. G. Compton, *Anal. Bioanal. Chem*., 2005, **381**, 979-985.

(36) Y. Song and G. M. Swain, *Anal. Chem*., 2007, **79**, 2412-2420.

(37) B. K. Jena and C.R. Raj, *Anal. Chem*., 2008, **80**, 4836-4844.

(38) T. Gu, L. Bu, Z. Huang, Y. Liu, Z. Tang, Y. Liu, S. Huang, Q. Xie, S. Yao, X. Tu, X. Luo, and S. Luo, *Electrochem. Commun*., 2013, **33**, 43-46.

(39) M. Hossain, M. Islam, S. Ferdousi, T. Okajima and T. Ohsaka, *Electroanalysis*, 2008, **20**, 2435-2441.

(40) Y.-S. Song, G. Muthuraman, Y.-Z. Chen, C.-C. Lin and J.-M. Zen, *Electroanalysis*, 2006, **18**, 1763-1770.

(41) S. Hrapovic, Y. Liu and J. H. T. Luong, *Anal. Chem*. 2007, **79**, 500-507.

(42) S. Prakash, T. Chakrabarty, A. K. Singh and V. K. Shahi, *Electrochim. Acta*, 2012, **72**, 157-164.

(43) C. Gao, X.-Y. Yu, S.-Q. Xiong, J.-H. Liu and X.-J. Huang, *Anal. Chem*., 2013, **85**, 2673-2680.

(44) H. Cui, W. Yang, X. Li, H. Zhao and Z. Yuan, *Anal. Methods*, 2012, **4**, 4176-4181.

(45) X. Dai and R. G. Compton, *Analyst*, 2006, **131**, 516–521.

(46) R.S. Stojanvic and A.M. Bond, *Anal. Chem*., 1990, **62**, 2692-2697.

(47) T.A. Ivandini, R. Sato, Y. Makide, A. Fujishima and Y. Einaga. *Anal. Chem*. 2006, **78**, 6291-6298.

(48) A. Salimi, H. Mamkhezri, R. Hallaj and S. Soltanian, *Sens. Actuator. B-Chem*, 2008, 129, 246-254.

(49) M. M. Ottakam Thotiyl, H. Basit, J. A. Sánchez, C. Goyer, L. Coche-Guerente, P. Dumy, S. Sampath, P. Labbé and J.-C. Moutet, *J. Colloid Interface Sci*., 2012, **383**, 130-139.

(50) E. Mafakheri, A. Salimi, R. Hallaj, A. Ramazani and M. A. Kashi, *Electroanalysis*, 2011, **23**, 2429-2437.

(51) Y. Du, W. Zhao, J.-J. Xu and H.-Y. Chen, *Talanta*, 2009, **79**, 243-248.

(52) J.-W. Sue, H.-H. Ku, H.-H. Chung and J.-M. Zen, *Electrochem. Commun*., 2008, **10**, 987-990.

---

(53) B.-W. Su, S. Thiagarajan and S.-M. Chen, *J. Electrochem. Soc.*, 2008, **155**, F157-F164.

(54) K.B. Male, S. Hrapovic, J. M. Santini and J. H.T. Luong, *Anal. Chem*., 2007, **79**, 7831-7837.

(55) A. Profumo, M. Fagnoni, D. Merli, E. Quartarone, S. Protti, D. Dondi and A. Albini, *Anal. Chem.*, 206, **78**, 4194-4199.

(56) Y. Liu and W. Wei, *J. Electroanal. Chem*. 2008, **624**, 299-304

(57) M. C. Teixeira, E. F. T. Lisboa, A. A. Saczk, L. L. Okumura, M. das G. Cardoso, M. F. Oliveira and Z. M. Magriotis, *ECS Transactions*, 2012, **43**, 225-229.

(58) M. C. Teixeira, E. de F.L. Tavares, A. A. Saczk, L. L. Okumura, M. das Graças Cardoso, Z. M. Magriotis and M. F. de Oliveira, *Food Chemistry,* 2014, **154**, 38–43.

(59) K.N. Han, C. A. Li, M.-P. N. Bui, X.-H. Pham, B. S. Kim, Y. H. Choa, E. K. Lee and G. H. Seong, *Sens. Actuators B-Chem.*, 2013, **177**, 472-477.

(60) S.-H. Shin and H.-G. Hong, *Bull. Korean Chem. Soc*., 2010, **31**, 3077-3083.

(61) H. Xu, L. Zeng, S. Xing, Y Xian and L. Jin, *Electrochem. Commun*. 2008, **10**, 551-554.

(62) Y. Liu and W. Wei. *Electrochem. Commun*., 2008, **10**, 872-875.

(63) M. Ozsoz, A. Erdem, P. Kara, K. Kerman and D. Ozkan, *Electroanalysis*, 2003, **15**, 613-619.

(64) A. Ferancová, M. Adamovski, P. Gründler, J. Zima, J. Barek, J. Mattusch, R. Wennrich and J. Labuda, *Bioelectrochemistry*, 2007, **71**, 33-37.

(65) G. K. Ramesha and S. Sampath, *Sens. Actuator. B-Chem*., 2011, **160**, 306-311.

(66) Y. Liu, Z. Huang, Q. Xie, L. Sun, T. Gu, Z. Li, L. Bu, S. Yao, X. Tu, Z. Luo and S. Luo, *Sens. Actuators B-Chem*., 2013, **188**, 894-901.

(67) J. R. Kalluri, T. Arbneshi, S. Afrin Khan, A. Neely, P. Candice, B. Varisli, M. Washington, S. McAfee, B. Robinson, S. Banerjee, A. K. Singh, D. Senapati and P. C. Ray*, Angew. Chem. Int. Ed.* 2009, **48**, 9668-9671.

(68) R. A. Dar, N. G. Khare, D. P. Cole, S. P. Karna and A. W. Srivastava, *RSC Adv*. 2014, **4**, 14432-14440.

(69) A. Chowdhury, S. Ferdousi, M. Islam, T. Okajima and T. Ohsaka, *J. Appl. Polym. Sci*., 2007, **104**, 1306-1311.

(70) U. Yogeswaran, S.-M. Chen and S.-H. Li, *Electroanalysis*, 2008, **20**, 2324-2332.

(71) J. Wu, M. Yang, J. Xiao, X. Fu, J. Jin, L. Li, W. Chang and C. Xiez, *J. Electrochem. Soc.*, 2013, **160**, B225-B230.

(72) D. Wang, Y. Zhao, H. Jin, J. Zhuang, W. Zhang, S. Wang and J. Wang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5733-5740.

(73) H. Xu, L. Zeng, S. Xing, G. Shi, J. Chen, Y. Xian and L. Jin, *Electrochem. Commun.*, 2008, **10**, 1893-1896.

(74) L. Chen, N. Zhou, J. Li, Z. Chen, C. Liao and J. Chen, *Analyst*, 2011, **136**, 4526-4532.

(75) Y. He, Y. Zheng, M. Ramnaraine and D. C. Locke, *Anal. Chim. Acta,* 2004, **511**, 55-61.

(76) A. Profumo, D. Merli and M. Pesavento, *Anal. Chim. Acta*, 2005, **539**, 245-250.

(77) C. Locatelli and G. Torsi, *J. Electroanal. Chem*., 2001, **509**, 80-89.

(78) T. Tongesayi and R. B. Smart, *Electroanalysis*, 2007, **20**, 434-437.

(79) R. Piech, B. Bas, E. Niewiara and W.W. Kubiak, *Talanta*, 2007, **72**, 762-767.

(80) J. Kowalska, K. Chalko and E. Stryjewska, *Electroanalysis*, 2002, **14**, 1508-1511.

(81) L. M. de Carvalho, P. C. do Nascimento, D. Bohrer, E. J. Pilau, R. Stefanello and M. Lauer, *Electroanalysis*, 2006, **18**, 1081-1089.

(82) R. Piech and W.W. Kubiak, *J. Electroanal. Chem*. 2007, **599**, 59-64.

(83) L. M. Carvalho, P. C. do Nascimento, D. Bohrer, E. J. Pilau, R. Stefanello and M. Lauer, *Electroanalysis*, 2007, **20**, 776-781.

(84) M. T. Islam, S. A. Islam and S. A. Latif, *Bull. Environ. Contam. Toxicol*., 2007, **79**, 327-330.

(85) L. Jiajie and Y. Nagaosa, *Anal. Chim. Acta*, 2007, **593**, 1-6.

(86) Z.-G. Liu, X. Chen, Y. Jia and J.-H. Huang, *J. Hazard. Mater*., 2014, **267**, 153-160.

(87) P. Salaun, B. Planer-Friedrich and C. M. G. van den Berg, *Anal. Chim. Acta*, 2007, **585**, 312-322.

(88) K. Gibbon-Walsh, P. Salaun and C. M. G. van den Berg, *Anal. Chim. Acta*, 2012, **710**, 50-57.

(89) P. Salaun, K. B. Gibbon-Walsh, G. M. S. Alves, H. M. V. M. Soares and C. M. G. van den Berg, *Anal. Chim. Acta*, 2012, **746**, 53-62.

(90) K. Gibbon-Walsh, P. Salaun and C. M. G. van den Berg. *Anal. Chim. Acta*, 2010, **662**, 1-8.

---

(91) World Health Organization, Fact Sheet No. 210, May 2001.

(92) U. K. Chowdhury, B. K. Biswas, T. R. Chowdhury, G. Samanta, B. K. Mandal, G. C. Basu, K. Paul, C. R. Chanda, D. Lodh, K. C. Saha, S. K. Mukherjee, S. Roy, S. Kabir, Q. Quamruzzaman and D. Chakraborti, *Environ. Health Perspect*. 2000, 108, 393-397.

(93) Detecting arsenic using bacteria, http://www.bgs.ac.uk/arsenic/Bio-bricks and biosensors, (Accessed March 22, 2014).

(94) S. Tsang, F. Phu, M. M. Baum and G. A. Poskrebyshev, *Talanta*, 2007, **71**, 1560-1568.

(95) S.-I. Choe, F. N. Gravelat, Q. Al Abdallah, M. J. Lee, B. F. Gibbs and D. C. Sheppard, *Appl. Environ. Microbiol.*, 2012, **78**, 3855-3863.

(96) J. Aleksic, F. Bizzari, Y. Cai, B. Davidson, K. de Mora, S. Ivakhno, S. L. Seshasayee, J. Nicholson, J. Wilson, A. Elfick, C. French, L. Kozma-Bognar, H. Ma and A. Millar, *IET Synth. Biol.*, 2007, **1**, 87–90.

(97) F. Truffer, N. Buffi, D. Merulla, S. Beggah, H. van Lintel, P. Renaud, J. R. van der Meer and M. Geiser, *Rev. Sci. Instrum.*, 2014, **85**, 015120.

(98) ArsenicGuard™ Online Arsenic Analyzer, http://www.tracedetect.com/arsenicguard.html, (Accessed March 22, 2014).

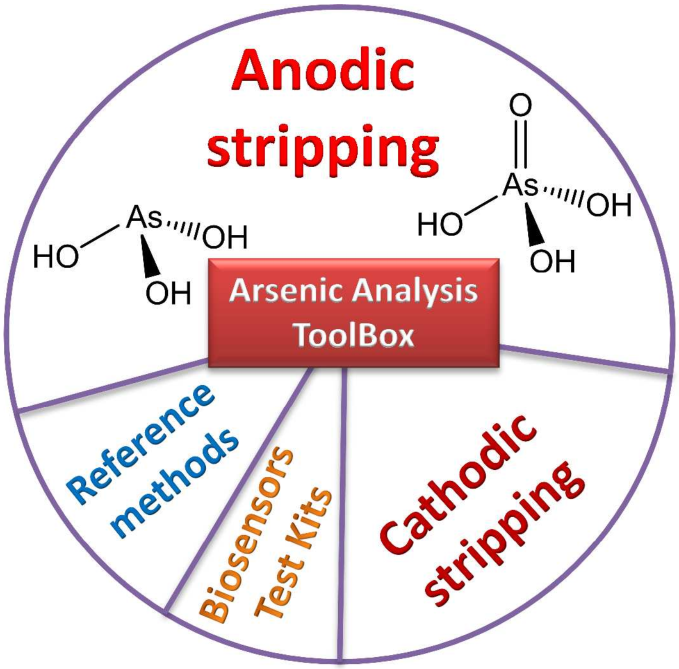
(99) J.M. McArthur, *Water Res. Res*. 2001, **37**, 109-117.

(100) A. Abbgy, T. Kelly, C. Lawrie and Karen Riggs, *Environmental Technology Verification Report: ETV Advanced Monitoring Systems Center: Quick™ Arsenic Test Kit*, Battelle, Columbus, 2002.

(101) A. Hussam, *Env. Sci. Tech.,* 1999, **33**, 3686-3688.

(102) Chronic Arsenic Poisoning: History, Study and Remediation, http://users.physics.harvard.edu/~wilson/arsenic/measurement/arsenic_project_measurement.html, (Accessed March 22, 2014).

(103) J. K. Thakur, R. K. Thakur, A. Ramanathan, M. Kumar and S. K. Singh, *Water*, 2011, **3**, 1-20.


Anodic stripping
O
As
HO
OH
OH
As
HO
OH
OH
Arsenic Analysis ToolBox
Reference methods
Biosensors Test Kits
Cathodic stripping

TOC Figure