Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 64 (2004) 269–277
Talanta
www.elsevier.com/locate/talanta

Review

Analytical methods for inorganic arsenic in water: a review

Dang Q. Hung, Olga Nekrassova, Richard G. Compton*

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK

Received 7 November 2003; received in revised form 22 January 2004; accepted 23 January 2004

Abstract

Inorganic arsenic, a term which encompasses both As (III) and As (V) species, constitutes the highest toxicological risk associated with arsenic in water in contrast to the organic arsenic species. Different determination methods of inorganic arsenic have been developed over 40 years providing timely and efficient risk assessments of inorganic arsenic contamination world wide. The current report gives an overview of more than 100 papers, regarding existing methods for analysis of As (III) and As (V) in water, including various spectroscopic, ICP and electrochemical techniques. Recent field portable analytical applications are also reviewed.

Keywords: Inorganic arsenic; Detection strategies; Groundwater

---

1. Introduction

Living organisms are exposed to the toxic arsenic (As) species primarily from food and water. Exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects [1].

Arsenic occurs in the natural environment in four oxidation states: As (V), As (III), As (0) and As (−III). The mobility and toxicity of arsenic are determined by its oxidation state [2], thus the behaviour of arsenic species will change depending on the biotic and abiotic conditions in water. In groundwater, arsenic is predominantly present as As (III) and As (V), with a minor amount of methyl and dimethyl arsenic compounds being detected (Scheme 1). In this review, we therefore, focus on the determination methods for inorganic arsenic species (total As, As (III) and As (V)).

The contamination of groundwater with arsenic has already been reported in 20 countries, out of which four major instances are from Asia [3–11]. These include Bangladesh, India, Inner Mongolia and Taiwan. Fifty districts of Bangladesh and nine in West Bengal (India) have arsenic levels in drinking water above the World Health Organization's arsenic guideline value of $10\,\mu g\,L^{-1}$ [12]. The area and population of these districts with contaminated drinking water are $118\,848\,km^2$ and 104.9 million in Bangladesh and $38\,865\,km^2$ and 42.7 million in West Bengal [11]. Severe contamination has also been reported in Vietnam, where several million habitants are at considerable risk of chronic arsenic poisoning, with contamination levels reach up to $3050\,\mu g\,L^{-1}$ in rural groundwater samples [13].

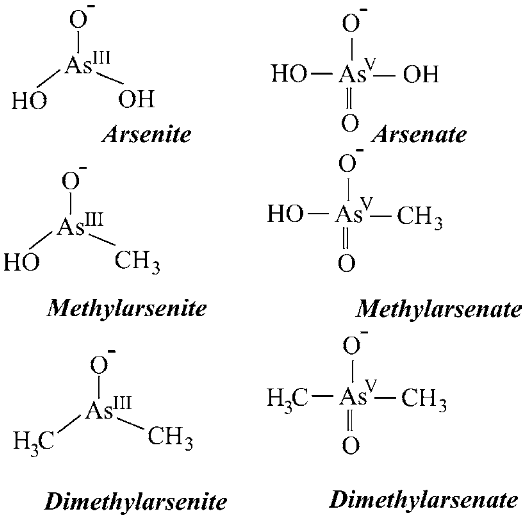
The importance of arsenic detection is a well recognised fact that is emphasised by the extensive studies carried out in this area, as illustrated in a recent issue of Talanta (Vol. 58 (1), 2002) entirely dedicated to various aspects of arsenic exposure in nature. At present, a plethora of detection methods have been developed, reported and reviewed elsewhere [14–16]. Most of them obtain limits of detection below the WHO arsenic guideline value of $10\,\mu g\,L^{-1}$. However, a vast number of existing methods are suitable for laboratory conditions only. In these cases analysis is time consuming and not suitable for routine monitoring of large numbers of samples. Therefore in light of these problems, a rapid portable

---

Abbreviations: AAS, atomic absorption spectrometry; AFS, atomic fluorescence spectrometry; AES, atomic emission spectrometry; DDP, differential pulse polarography; ETAAS, electrothermal atomic absorption spectrometry; ETV, electrothermal vaporization; FI, flow injection; GFAAS, Graphite furnace atomic absorption spectrometry; HG, hydride generation; HMDE, hanging mercury drop electrode; HPLC, high pressure liquid chromatography; ICP, inductively coupled plasma; MS, mass spectrometry; OES, optical emission spectrometry; UMEA, ultramicroelectrode array

* Corresponding author. Tel.: +44-01865-275413;
fax: +44-01865-275410.
E-mail address: richard.compton@chemistry.ox.ac.uk (R.G. Compton).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.01.027



Scheme 1. Arsenic species found in water.

sensor needs to be developed. The use of electrochemical methodologies has recently come to the forefront of research as a possible means of fulfilling these requirements. These electrochemical methods along with other commercially available analytical kits will be covered in the final sections of this review.

2. Chemical pre-reduction of arsenic (V)

It has long been realised that the determination of the total arsenic concentration is insufficient for environmental considerations [14]. The total inorganic arsenic content detection is normally based on the concentration of As (III) after converting all arsenic species to the trivalent arsenic form. This is especially applied in electrochemical techniques (see below), as pentavalent arsenic is electroinactive [17].

The most popular prereductant of As (V) to As (III) is potassium iodide, which can be used with ascorbic acid, in order to prevent the oxidation of iodide to triiodide by air [18]. However, potassium iodide can reduce arsenic only in a strong acidic media [19]. The combined use of potassium iodide with tin chloride [20] or sodium sulphite [21] has also been reported in the literature. Other reagents used for reduction of As (V) are mercaptoacetic acid [22] and L-cysteine, which was found also to reduce interferences and increase the sensitivity [18]. Some techniques require a specific reagent, thus sodium thiosulphate along with titanium (III) chloride has been used in solvent extraction technique [23,24], gaseous sulphur dioxide, sodium sulphite in stripping voltammetry [25,26] and the use of hydrazine in flow injection analysis [27] has been reported.

In cases there the speciation of arsenic compounds is required, the combination of a pre-separation method and direct detection instruments is applied and will be reviewed further.

In order to add clarity to the text and give an overview on limit of detection all the analytical data related to the various techniques published during last decade is summarised in Table 1.

$$As(OH)_3 + 3BH_4^- + 3H^+ \longrightarrow AsH_3 + 3BH_3 + 3H_2O$$
$$BH_3 + 3H_2O \longrightarrow H_3BO_3 + 3H_2$$

Scheme 2. Hydride generation reaction.

3. Spectrometric techniques

3.1. Hydride generation atomic absorption spectrometry and hydride generation atomic fluorescence spectrometry (HG-AAS and HG-AFS)

Hydride generation is, perhaps, the most popular sample derivatization method used for inorganic arsenic detection, since Holak [28] first reported it in 1969. Initially it was developed as a method for AAS, whereby sodium or potassium tetrahydroborate (III) is used for arsine production (Scheme 2). The reduction reagents $NaBH_4$ and KBH_4 have proved to be exceptionally reliable reagents for the conversion of the sample to volatile forms [29]. The hydride generation procedure can be also used for differential determination of As (III) and As (V), based on the fact that As (III) reacts with tetrahydroborate at a higher pH than As (V). Thus tetrahydroborate is acting as a reductant for As (V) as well as a hydride source. The inclusion of on-line HG generally increases the sensitivity of detection and reduces the possible interferences from the sample matrix. AHG based sample introduction is particularly beneficial to AFS detection where the interferences had previously been the major problem due to scattering and sample matrix [15].

Transition metals might interfere with the determination of arsenic when hydride generation is used [30]. The predominant mechanism is probably due to the reaction of the interfering transition metal ions with $NaBH_4$ reductant, with the formed precipitate is able to capture and catalytically decompose evolved hydrides [31]. Generally L-cysteine has proved to be very useful for preventing iron interferences, which are commonly present at high concentration in many types of samples [32]. Moreover, it was found that the cysteine-tetrahydroborate intermediate has a higher reducing power than tetrahydroborate alone [18]. Furthermore, the inclusion of the flow injection (FI) technique allowed the elimination of transition metal interferences [19,33,34]. It has been reported that by using the FI system instead of the batch system, the concentration of the reductant is usually lower and formation of the interfering precipitates, e.g. borides, is decreased [19,34]. Another reason is so called kinetic discrimination. The reduction of the hydride-forming elements is fast and the reaction is completed before the reduction of the transition metal ion to the interfering species.

HG can be used for pre-column or post-column derivatisation. The pre-column derivatisation is based on the formation of volatile arsines, which are cryogenically trapped,

Table 1
Analytical parameters obtained by various detection techniques for arsenic in water samples over the last 10 years

Species	Pre concentration/separation	Derivatisation	Detection	LoD ($\mu g\,L^{-1}$)	References
Atomic spectrometry					
As (III)		HG	AAS	0.6	[150]
As (V)				0.5	
As (III)	FI-SE	HG	AAS	0.05	[151]
As (V)				2	
As (III)	FI	HG	AAS	0.037	[30]
As (III)	FI-KR: PDC	HG	AFS	0.023	[161]
As (III)		HG	AFS	0.67	[152]
As (III)	IC	HG	AFS	4	[153]
As (III)	SPE		GFAAS	0.11	[154]
As (V)				0.15	
As (III)	PDC		GFAAS	0.02	[155]
As (III)	AE-resin: PDC		GFAAS	6.6	[41]
As (III)	SPE		GFAAS	0.04	[48]
ICP techniques					
As (III)		HG	ICP-AES	0.7	[149]
As (III)	FI-KR		ICP-MS	0.021	[156]
As(V)				0.029	
As (V)	SPE		ICP-MS	0.008	[157]
As (III)		HG	ICP-MS	0.003	[158]
As (III)	HG-GF		ICP-MS	0.002	[159]
As (III)	HPLC		ICP-MS	0.02	[79]
As (III)	HPLC		ICP-MS	0.06	[160]
Nuclear techniques					
As (III)	PDC		NAA	0.001	[108]
As (V)					
As (III)	CE		NAA	0.02	[162]
Electrochemistry					
As (III)			CSV	0.52	[163]
As (III)			CA	0.15	[164]
As (III)			CCSA	3	[165]
As (V)				0.5	
As (III)			ASV	0.19	[25]
As (III)			SWCSV	0.0045	[118]
As (III)			ASV	0.32	[135]

LoD, limit of detection; HG, hydride generation; AAS, atomic absorption spectrometry; FI, flow injection; SE, solid extraction; KR, knotted reactor; PDC, pyrrolidinedithiocarbamate complex; AFS, atomic fluorescence spectrometry; IC, ion chromatography; SPE, solid phase extraction; GFAAS, graphite furnace atomic absorption spectrometry; AE, anion exchange; ICP, inductively coupled plasma; AES, atomic emission spectrometry; MS, mass spectrometry; GF, graphite furnace; HPLC, high pressure liquid chromatography; NAA, neutron activation analysis; CE, cation exchange; CSV, cathodic stripping voltammetry; CA, chronoamperometry; CCSA, constant current stripping analysis; ASV, anodic stripping voltammetry; and SWCSV square wave cathodic stripping voltammetry.

sequentially desorbed and carried to the detector [35]. In the post-column detection HG is used after the separation of the arsenic species on a HPLC system [36,37], but only low volumes of sample can be injected with a consequent decrease in sensitivity. An advantage of the later approach is the possibility of the analysis of non-volatile compounds when a photooxidation or microwave [38] step is included prior to HG.

Hydride generation (HG) combined with atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) and also coupled with different separation techniques such as liquid–liquid extraction [39,40], resin based low pressure ion exchange chromatography [41,42], cold trapping [32,43–45], selective derivatisation [22] and HPLC [29,46,47] have brought a high level of sensitivity to speciation of arsenic compared to the colorimetric detection techniques often used for environmental samples.

3.2. Graphite furnace atomic absorption spectrometry (GFAAS)

Graphite furnace absorption spectrometry or electrothermal atomic absorption spectrometry (ETAAS) is one of the spectrometric methods, which can run without HG. The technique is based on the absorption of free atoms produced from the sample deposited in a small graphite tube, which can be heated by the application of high temperatures. However, most of reported methods for arsenic detection based on GFAAS require pre-concentration in order to increase sensitivity.

Hata et al. [48] proposed a soluble membrane filter technique for the solid-phase extraction of trace elements, including arsenic, in water before determination using electrothermal atomic absorption spectrometry (ETAAS). In this technique, the analyte is converted into hydrophobic species, which are retained on a membrane filter. Further material collected with the membrane filter is dissolved in sulphuric acid or organic solvent. Finally the sample is pre-concentrated and analysed with ETAAS. This simple and rapid method provides similar limit of detection to FI-HG-AAS limit of detection and been successfully applied in river water sample analysis.

Another popular approach is based on the formation and extraction of the As (III)—ammonium pyrrilidinedithiocarbomate complex, with further dispersion in nitric acid containing Ni (II) species and injection of the obtained suspension to a graphite furnace. Possible interferences of Cu (II), Pb (II) and Sn (II) could be removed by extraction as the respective ammonium pyrrilidinedithiocarbomate complexes at the higher pH, where no As (III) is extracted. The loss of arsenic during the charging cycle of the graphite atomiser is prevented by matrix modification with salts of nickel and palladium. Currently GFAAS is one of the most reliable techniques [41].

4. Inductively coupled plasma (ICP) techniques

4.1. ICP-AFS and ICP-Mass Spectrometry (MS)

The technology for the ICP method was first employed in the early 1960's [49]. The ICP technique uses the plasma to ionise components, whereby the sample is acidified and sprayed into the plasma. The high temperature of the plasma atomises and ionises all forms of arsenic so that the response does not vary with species as in the more traditional AAS methods which require thorough digestion prior analysis. Often, ICP is used in conjunction with other analytical techniques, such as MS [50] and AES [51–53], as inclusion of ICP eliminates any sample preparation time, which would be required in the absence of ICP.

ICP–AES is a less used technique and normally applied for a comparison and more accurate analysis of a multi-element sample. In contrast, the ICP-MS technique is one of the most widely applied analytical protocols for arsenic detection. Numerous reports on the determination of arsenic in water have appeared since 1993 [54–78]. The main advantages of ICP-MS over ICP-AES are isotope analysis capability of high precession and lower detection limits. The possible drawback of ICP-MS equipped with a direct nebuliser is the possible interference from high levels of chloride due to the formation of argon chloride(^{40}Ar^{35}Cl) in the plasma, which has the same mass as arsenic (^{75}As) [79–83]. In order to overcome this, sample introduction should be carried via electrothermal vaporisation (ETV), which additionally has the potential advantages of small sample sizes, increased sensitivity and low absolute detection limits. Recently, it has become clear that chemical modifiers are as important in ETV-ICP-MS as they are in conventional GFAAS [84,85]. In most cases, the modifier acts as a physical carrier of the vaporised analyte, where addition of a chemical modifier enhances the analytical signal. Fairman et al. [66] have optimised a mixed modifier of palladium and nickel nitrates for quantitative multi-element analysis. The mixture of these two salts provided the best peak shapes and linearity.

However, the determination of low concentrations of arsenic in real samples suffers from low sensitivity due to the poor ionisation efficiency in ICP. In order to overcome this, several ICP-MS applications combined with hydride generation and a cold vapour mercury sample introduction technique have been applied for arsenic determination [56,61,62]. Chen et al. [62] have employed a simple continuous-flow HG system without the conventional gas-liquid phase separator as a sample introduction device for flow injection ICP-MS analysis and found that trace amounts of As (III) could be detected simultaneously with Bi, Sb and Hg.

Feng et al. [68] have developed a method for direct determination of arsenic species in environmental water, by using hydride generation high resolution ICP-MS. High resolution ICP-MS can effectively separate two very near peaks such as ^{75}As and ^{38}Ar^{37}Cl or ^{40}Ar^{35}Cl. Using both pneumatic and ultrasonic nebulization ICP-MS, Richter et al. [71] obtain significantly lower detection limits than obtained with HG-AAS.

Further effective applications of ICP-MS in the speciation of arsenic by coupling with HPLC will be reviewed in Section 4.2.

4.2. High pressure liquid chromatography (HPLC) and ICP-MS

A coupled system including HPLC and ICP-MS gives a suitable method for the determination of non-volatile species of elements such as arsenic. Although, ICP-MS has multi-element capability, this coupled technique has hitherto mainly been used for speciation analysis of single elements [86–90]. However, the simultaneous speciation analysis of different elements has recently received an attention [91–94]. Direct coupling between HPLC and AAS [95] was shown to give poor detection limits (mg L^{-1}), which could be improved by using combination of HPLC-ICP-MS [87,96].

The choice of HPLC column was shown to improve the selectivity of the assay. Therefore, Thomas and Sniatecki [97] used directly coupled ion-pair reversed-phase (RP) HPLC-ICP-MS for the identification of various arsenic species, including As (III) and As (V) in spring waters. At the same time it was found that by using an ion exchange HPLC column rather than a reverse phase column, enhanced separation and selectivity of arsenic species could be achieved [98–101]. In case of ion-exchange based system, the analyte ions interact directly with the stationary phase of the chromatographic column and are therefore less prone to interferences from co-chromatographed matrix constituent other than the analyte-ion/counter–ion pair in the

RP chromatographic system [102]. For the determination of arsenic species mentioned above at lower concentrations, Saverwyns et al. [86] reported a hyphenated technique incorporating an anion-exchange column and ICP-MS, using an in-house developed thermospray nebuliser as an interface. The sensitivity was shown to be improved by 10-fold by application of the thermospray nebuliser in comparison with the standard pneumatic nebulizer.

Moldovan et al. [103] have successfully separated arsenite, arsenate, monomethylarsonate, dimethylarsinate, arsenobetaine and arsenocholine in one chromatographic run in a mixed mode column. Furthermore, the use of an aqueous mobile phase with low buffer salt concentration minimises the problems associated with the coupling of HPLC and ICP-MS.

A comparison between using HPLC-HG-AFS and HPLC-HG-ICP-MS performance has been made by Gomez-Ariza et al. [104] for the speciation of arsenite, arsenate and other arsenic compounds in fresh water. It was found that the limit of detection were similar for both techniques, however AFS presented the benefits of much lower running costs, shorter warm up times prior to analysis (15–90 min) and easy handling.

Suitable detection limits for environmental samples, below the mg L^{-1} levels, are obtained using both HPLC-HG-AFS [47] and HPLC-HG-ICP-MS [105,106].

5. Neutron activation analysis (NAA)

In NAA target nuclides in the sample undergo activation with formation of radioactive nuclides, which in most cases decay through the emission of beta particle and gamma rays with a unique half-life. Produced gamma rays are detected by NAA high-resolution gamma-ray spectrometer. NAA is one of the most sensitive analytical techniques and often used as a reference method for new procedures. However, it has not found wide application for detection of arsenic in water, possibly due to a high content of salt in sea water, which causes spectral interferences [107]. This problem might be overcome by using $Pb(NO)_3$ and $TiCl_3$ as the carrier and reducing agent [108].

6. Electrochemical methods

6.1. Polarographic techniques

Polarography (or linear sweep voltammetry at the hanging mercury drop electrode (HMDE)) is the oldest electrochemical method for the determination of trace inorganic metals [109–111], which, however, suffers from low limits of detection due to high capacitive currents. Differential pulse polarography (DPP) offers the same benefits of selectivity as well as lower capacitive currents and as a result improved limits of detection. DPP was popular for routine analysis of trace metals due to its high sensitivity for a wide range of elements, including arsenic, which do not form mercury amalgams readily and because of the availability of inexpensive commercial instruments [112].

However, only few works related to the determination of arsenic in water using differential pulse polarography [113–115] have been published recently, mainly because of the limited sensitivity.

6.2. Cathodic stripping voltammetry (CSV)

Generally, stripping analysis is better suited than direct polarography for trace determinations in ‘real’ samples because the substance of interest is pre-concentrated on the working electrode, although the detection limits under ideal conditions may sometimes be comparable [116]. Cathodic stripping analysis of arsenic at the HMDE is based on arsenic pre-concentration in highly acidic media with further scanning in the cathodic direction to obtain peak due to the formation of arsine [116]. In order to increase sensitivity, intermetallic complexes of arsenic are stripped from HMDE, whereby As (III) reacts with copper [117,118] or selenium [116] to form the relevant complex, which can be stripped cathodically (Scheme 3). Additionally arsenic complexes with ammonium pyrrolidine dithiocarbamate have been utilised in bioanalysis [119].

$$\textbf{\textit{Deposition:}}\ 2As^{3+} + 3MHg + 6e^{-} \longrightarrow M_3As_2 + 3Hg$$

$$\textbf{\textit{Stripping:}}\ M_3As_2 + 12H^{+} + 12e^{-} + 3Hg \longrightarrow AsH_3 + H_2 + 3MHg$$

$$M = Cu \text{ or } Se$$

Scheme 3. Processes occur during cathodic stripping voltammetry.

Copper is expected to interfere with this method, since it would also deposit at the potential applied. Copper (II) at a concentration 10 times that arsenic was found to reduce the arsenic peak height by about half [116].

The use of mercury film electrodes has rarely been considered for both CSV and cathodic stripping potentiometric (CSP) determination of arsenic. Based on the CSV and CSP methods developed for the determination of selenium [120] and lead [121], Adeloju et al. [122] determined As (III) by CSP on a glassy carbon mercury film electrode in the presence of copper (II) ions. By using a mercury film electrode with the application of a constant cathodic stripping current, interference problems can be overcome, unlike methods for arsenic which utilise gold film electrodes and suffer from copper interferences [123,124]. Detection limit obtained at mercury films electrodes was comparable to the levels accomplished by CSV on a HMDE [117] and to that reported for anodic stripping potentiometric analysis on a gold film electrode [125].

Most cathodic stripping techniques are carried out by using a HMDE, as this electrode does not suffer from the disadvantages of the solid electrodes, such as the response being

$$\textbf{\textit{Deposition:}}\ \mathrm{As}^{3+} + 3e^{-} \longrightarrow \mathrm{As}^{0}$$
$$\textbf{\textit{Stripping:}}\ \mathrm{As}^{0} \longrightarrow \mathrm{As}^{3+} + 3e^{-}$$

Scheme 4. Processes occur during anodic stripping voltammetry.

dependent on past history or the formation of oxide films. However, anodic stripping of arsenic using a HMDE is not analytically useful due to interference from the oxidation of mercury [112].

6.3. Anodic stripping voltammetry (ASV)

Kaplin et al. [126,127] established the anodic stripping voltammetry technique for trace arsenic analysis, which is based on the deposition of metal arsenic on the electrode surface with subsequent anodic stripping (Scheme 4). Later, Forsberg et al. [128] investigated in detail the determination of arsenic by ASV and differential pulse anodic stripping voltammetry (DPASV) at various electrode materials (HMDE, Pt and Au). It was found that the arsenic oxidation peak appeared as a shoulder on the mercury oxidation wave on a HMDE and was little of analytical utility. Platinum was a suitable electrode material and was employed in the initial studies. Gold was found to be superior to platinum as a working electrode material due to a higher hydrogen overvoltage. This solved the problem of simultaneous evolution of hydrogen while depositing arsenic. Experiments done by Forsberg et al. [128] showed that ASV proved to be an exceedingly sensitive technique as for the determination arsenic, while the use of DPASV greatly shortened deposition times.

Parallel to solid gold electrodes [128–130], macro-sized gold film electrodes have also been used [25,131–133]. Since it had been stated that ASV of As (III) with gold suffers from lack of reproducibility, several attempts were performed in order to overcome that problem. Thus, for optimum reproducibility, the electrode was re-plated and washed with the sample before each measurement [134]. Re-activation of the electrode surface before each measurement was also found to ensure good reproducibility [135].

Another cause of poor reproducibility are hydrogen bubbles forming during the deposition time. Bodewig et al. [130] used a gold rotating disk electrode, which removed the hydrogen bubbles mechanically allowing good reproducibility of results. The rotating disk electrode approach was further investigated in other works [25,136] with variation in design of the electrodes. Sun et al. [25] reported a new method of gold film deposition on a rotating glassy carbon electrode. Additionally, other factors likely to affect the stability of an electrode including, acidity, deposition time, rotation rate, scan rate, the electrode reaction and also the reduction step of As (V) to As (III), were investigated [25].

An application of a flow-though cell with a stationary gold disc electrode for the ASV determination of arsenic allowed to obtain detection limits at parts per billion (ppb) and sub-parts per billion levels [137]. Longer deposition periods were found to improve the limit of detection. The flow cell approach was also used in an inexpensive portable stripping voltammetric instrument with a simple procedure for on-field analysis of As (III) and As (V) [138]. The instrument ran with low power consumption and had a simple flow cell, which operated with the aid of gravity. A gold film deposited on a platinum wire served as the working electrode.

6.4. Microlithographic fabricated arrays

Recently, the electroanalytical use of microfabricated arrays has increased. Several advantages including a well defined and reproducible geometry, employment of various materials for a working electrode and finally low cost of chips have enchased research in on-filed analysis area. Tomčík et al. [139] developed an analytical technique based upon the evaluation of the influence of As (III) on the iodine collector versus generator current plot, whereby the collector potential is set at the limiting current value of iodine cathodic reduction and serves as its amperometric detector. A thin-film microsystem based on the planar interdigitated array (IDA) of Pt electrodes was used. The titration curves (collector versus generator current plots) measured with a slowly scanning generator current showed very good reproducibility, albeit with poor detection limits.

Feeney et al. [140] achieved rapid on-site analysis of arsenic in groundwater with a small battery-powered unit used in conjunction with a microfabricated gold ultramicroelectrode array (Au-UMEA). These arrays offer several benefits, such as uniform ultramicroelectrode geometry, sensitivity, cost efficiency, and applicability for use in field portable or in-situ instrumentation [16]. The use of UMEAs offer analytical advantages including low noise level, amplification of the signal while keeping UME behaviour, background current rejection, and potential incorporation into field portable instrumentation. The application of microfabricated arrays have been demonstrated for field measurements [141–144]. Unlike colorimetric field kits presently in use, voltammetric techniques can yield precise quantitative data when careful analytical methods are used [16]. However, the majority of commercially available sensors are still based on colorimetric techniques. These are reviewed in the following section.

7. Commercially available sensors

The majority of field sensors are based on the hydride generation described earlier, whereby gas either can be detected photometrically or electrochemically.

Currently, most of the kits utilise zinc powder as a reducing agent for As (V) and As (III) to arsine (Scheme 5) [145]. The generated gas passes through or over the reagent paper and the colour change is either compared visually with calibrated colour scale or transferred into a digital readout. The

$$As_4O_6 + 12Zn + 24H^+ \longrightarrow 4AsH_3 + 12Zn^{2+} + 6H_2O$$

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

Scheme 5. Hydride generation reaction as used in commercial analytical kits.

analysis time is limited by hydride generation reaction and varies from 10 to 30 min based on reagents used [145]. The arsine gas reacts with mercuric bromide, deposited on indicator paper to form mixed arsenic/mercury bromides (e.g. AsH_2HgBr) [146], which cause a change in colour of the indicator paper from white to yellow to brown. In order to overcome possible interferences from hydrogen sulphide, which leaves grey spots on the paper, the commercial oxidising agent Oxone® (DuPont) is added prior to arsine generation. Alternatively, the generated arsines are passed through a piece of paper impregnated with lead acetate before they reach the mercuric bromide reagent [147].

There are several arsenic sensors currently on the market with a similar chemical reaction design. The differences between tests lie mostly in the number of chemicals steps (e.g. additional pre-reduction) and sensor design. Thus it was shown that results are optimal if the arsine gas passes though the reagent paper rather than over it [147]. Finally some tests are equipped with a calibrated colour scale, which enables an estimate of the concentration of arsenic to be made, rather than with digital readout device [147].

The best reported limit of detection with these kits is $2\,mg\,L^{-1}$(ppb) [145], however recently it was reported that there is a weak correlation between the field kits and laboratory methods, especially if methods are based on a visual estimation of colour [148]. Thus there is a clear need for more sensitive and precise portable sensors on the market.

8. Conclusion

The most popular analytical methods for the determination of inorganic arsenic have been described in this review. It was shown that there is a plethora of analytical techniques available for the determination of arsenic species in water samples. Also various combinations of techniques have been described, which cover a wide range of needs. Namely, ICP-MS and GFAAS applications provide accurate and reproducible results in the laboratory environment, in contrast to the commercially available colorimetric assays which offer rapid but not necessarily correct results in on-site conditions. Thus a need for a rapid and accurate sensor is clear. Electrochemical techniques to date have proven to be able to give reliable results in laboratory conditions and as such have potential for a further development into a mobile, low cost analytical devise capable of fulfilling the requirements of a rapid and accurate sensor.

Acknowledgements

DQH gratefully acknowledges the Royal Society Southeast Asia for Fellowship support. ON thanks the Analytical Division of the RSC for PhD studentship.

References

[1] B.K. Mandal, K.T. Suzuki, Talanta 58 (2002) 201.
[2] X. Meng, C. Jing, G.P. Korfiatis, ACS Symp. Ser. 835 (2003) 70.
[3] P.C. Ray, J. Forensic Med. Toxicol. 16 (1999) 30.
[4] D. Chakraborti, B.K. Mandal, R.K. Dhar, B. Biswas, G. Samanta, K.C. Saha, Ind. J. Environ. Protec. 19 (1999) 565.
[5] D. Chakraborti, M.M. Rahman, K. Raul, U.K. Chowdhyry, M.K. Sengupta, D. Lodh, C.R. Chanda, K.C. Saha, S.C. Mukherjee, Talanta 58 (2002) 3.
[6] A. Charterjee, D. Das, B.K. Mandal, T.R. Chowdhury, G. Samanta, D. Chakraborti, Analyst 120 (1995) 643.
[7] D. Das, A. Chatterjee, B.K. Mandal, G. Smanta, D. Chakraborti, Analyst 120 (1995) 917.
[8] R.K. Dhar, Curr. Sci. 73 (1997) 48.
[9] B.K. Mandal, T.R. Chowdhury, G. Samanta, G.K. Basu, P.P. Chowdhury, C.R. Chanda, D. Lodh, N.K. Kuran, R.K. Dhar, D.K. Tamili, Curr. Sci. 70 (1996) 976.
[10] D.N.G. Mazumder, Curr. Sci. 72 (1997) 114.
[11] M.M. Rahman, U.K. Chowdhury, S.C. Mukherjee, B.K. Mandal, K. Paul, D. Lodh, B.K. Biswas, C.R. Chanda, G.K. Basu, K.S. Saha, S. Roy, R. Das, S.K. Palit, Q. Quamruzzaman, D. Chakraborti, J. Toxicol. Clin. Toxicol. 39 (2001) 683.
[12] 1993, http://www.who.int/inf-fs/en/fact210.html.
[13] M. Berg, H.C. Tran, T.C. Nguyen, M.V. Pham, R. Schertenleib, W. Giger, Environ. Sci. Technol. 35 (2001) 2621.
[14] Z. Gong, X. Lu, M. Ma, C. Watt, X.C. Lee, Talanta 58 (2002) 77.
[15] S. Karthiheyan, S. Hirata, Anal. Lett. 36 (2003) 2355.
[16] R. Feeney, S. Kounaves, Talanta 58 (2002) 23.
[17] H. Greschonig, K.J. Irgolic, Appl. Organometal. Chem. 6 (1992) 565.
[18] H. Chen, I.D. Brindle, X. Le, Anal. Chem. 64 (1992) 667.
[19] B. Welz, M. Sucmanova, Analyst 118 (1993) 1425.
[20] S.P. Quinaia, M.C.E. Rollemberg, J. Braz. Chem. Soc. 8 (1997) 349.
[21] K. Terada, K. Matsumoto, T. Inaba, Anal. Chim. Acta 158 (1984) 207.
[22] R. Anderson, M. Thompson, E. Culbard, Analyst 111 (1986) 1143.
[23] K.S. Subramanian, J.C. Meranger, Anal. Chim. Acta 24 (1981) 131.
[24] C. Chung, E. Iwamoto, M. Yamamoto, Y. Yamamoto, Spectrochim. Acta B 39 (1984) 459.
[25] Y.-C. Sun, J. Mierzwa, M.-H. Yang, Talanta 44 (1997) 1379.
[26] T.W. Hamilton, J. Ellis, T.M. Florence, Anal. Chim. Acta 119 (1980) 225.
[27] J.A. Lown, D.C. Johnson, Anal. Chim. Acta 116 (1980) 41.
[28] W. Holak, Anal. Chem. 41 (1969) 1712.
[29] A.G. Howard, J. Anal. At. Spectrom. 12 (1997) 267.
[30] T. Naykki, P. Perämäki, J. Kujala, A. Mikkonen, Anal. Chim. Acta 439 (2001) 229.
[31] B. Welz, M. Schubert-Jacobs, J. Anal. At. Spectrom. 1 (1986) 23.
[32] A.G. Howard, C. Salou, Anal. Chim. Acta 333 (1996) 89.
[33] M. Yamamoto, M. Yasuda, Y. Yamamoto, Anal. Chem. 57 (1985) 1382.
[34] B. Welz, M. Sucmanova, Analyst 118 (1993) 1417.
[35] J.L. Gomez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, Analyst 125 (2000) 401.
[36] R. Rubio, A. Padró, J. Albertí, G. Rauret, Microchim. Acta 109 (1992) 39.

[37] R. Rubio, A. Padró, J. Albertí, G. Rauret, Anal. Chim. Acta 283 (1993) 160.
[38] X.C. Le, W.R. Cullen, K.J. Reimer, Talanta 41 (1994) 495.
[39] S.A. Amankwah, J.L. Fasching, Talanta 32 (1985) 111.
[40] T. Kamada, Talanta 23 (1981) 935.
[41] K. Anezaki, I. Nakatsuka, K. Ohzenki, Anal. Sci. 15 (1999) 829.
[42] G.E. Pacey, J.A. Ford, Talanta 28 (1981) 935.
[43] M.O. Andreae, Anal. Chem. 49 (1977) 820.
[44] R.S. Braman, D.L. Johnson, C.C. Foreback, J.M. Ammons, J.L. Bricker, Anal. Chem. 49 (1977) 621.
[45] A.G. Howard, M.H. Arbab-Zavar, Analyst 106 (1981) 213.
[46] X.C. Le, M. Ma, N.A. Wong, Anal. Chem. 68 (1996) 4501.
[47] J.L. Gomez-Ariza, D. Sánchez-Rodas, R. Beltran, W. Corns, P. Stockwel, Appl. Organometal. Chem. 12 (1998) 439.
[48] N. Hata, H. Yamada, I. Kasahara, S. Taguchi, Analyst 124 (1999) 23.
[49] G.W. Dickinson, Applications of the Induction Coupled Plasma to Analytical Spectroscopy, Ames Lab, Ames, IA, USA, p. 118.
[50] K.J. Stetzenbach, M. Amano, D.K. Kreamer, V.F. Hodge, Ground Water 32 (1994) 976.
[51] W. Schrader, GIT Fachzeischrift fuer das Laboratorium 26 (1982), 324–326/328–330/332–334.
[52] B. Sansoni, W. Brunner, G. Wolff, H. Ruppert, R. Dittrich, Fresenius Z. Anal. Chem. 331 (1988) 154.
[53] J. Nolte, U.A. Meyer, LaborPraxis 24 (2000) 30.
[54] A.T. Townsend, J. O'Sullivan, A.M. Featherstone, E.C.V. Butler, D.J. Mackey, J. Environ. Monit. 3 (2001) 113.
[55] J. Goossens, L. Moens, R. Dams, J. Anal. At. Spectrom. 8 (1993) 921.
[56] A. Stroh, U. Voellkopf, J. Anal. At. Spectrom. 8 (1993) 35.
[57] B. Holmbom, Aqua Fennica 24 (1994) 93.
[58] C.-J. Hwang, S.-J. Jiang, Anal. Chim. Acta 289 (1994) 93.
[59] R. Bombelka, B. Pohl, LaborPraxis 19 (1995) 80.
[60] M.J. Duane, S. Facchetti, Sci. Total Environ. 172 (1995) 133.
[61] M.-F. Huang, S.-J. Jiang, C.-J. Hwang, J. Anal. At. Spectrom. 10 (1995) 31.
[62] C.-S. Chen, S.-J. Jiang, Spectrochim. Acta: B 51 (1996) 1813.
[63] X. Zhang, R. Cornelis, J. De Kimpe, L. Mees, Anal. Chim. Acta 319 (1996) 177.
[64] J. Bowman, B. Fairman, T. Catterick, J. Anal. At. Spectrom. 12 (1997) 313.
[65] A.G. Cox, C.W. McLeod, M. Nishikawa, D. Wiederin, Plasma Source Mass Spectrom. 202 (1997) 145.
[66] B. Fairman, T. Catterick, J. Anal. At. Spectrom. 12 (1997) 863.
[67] M. Pantsar-Kallio, P.G.G. Manninen, J. Chromatogr. A 779 (1997) 139.
[68] Y.-L. Feng, H.-Y. Chen, L.-C. Tian, H. Narasaki, Anal. Chim. Acta 375 (1998) 167.
[69] D.B. Peart, Analyst 123 (1998) 167.
[70] G. Pinte, M.A.R. Veado, A.H. Oliveira, M. Khalis, S. Ayrault, G. Revel Hydrobiologia 373/374 (1998) 61.
[71] R.C. Richter, K. Swami, S. Chace, L. Husain, Fresenius J. Anal. Chem. 361 (1998) 168.
[72] J.W. Lam, R.E. Sturgeon, At. Spectrosc. 20 (1999) 79.
[73] A. Misund, B. Frengstad, U. Siewers, C. Reimann, Sci. Total Environ. 243/244 (1999) 21.
[74] T. Taniguchi, H. Tao, M. Tominaga, A. Miyazaki, J. Anal. At. Spectrom. 14 (1999) 651.
[75] A. Chatterjee, Y. Shibata, J. Yoshinaga, M. Morita, Anal. Chem. 72 (2000) 4402.
[76] C. Vandecasteele, K. Van der Broeck, V. Dutre, Waste Manage. 20 (2000) 211.
[77] A.F. Roig-Navarro, Y. Martinez-Bravo, F.J. López, F. Hernández, J. Chromatogr. A 912 (2001) 319.
[78] T. Nakazato, H. Tao, T. Taniguchi, K. Isshiki, Talanta 58 (2002) 121.
[79] B.S. Sheppard, W.L. Shen, J.A. Caruso, D.T. Heitkemper, F.L. Fricke, J. Anal. At. Spectrom. 5 (1990) 431.
[80] S. Branch, L. Ebdon, M. Ford, M. Foulkes, P. ONeill, J. Anal. At. Spectrom. 6 (1991) 151.
[81] S.J. Hill, M.J. Ford, L. Ebdon, J. Anal. At. Spectrom. 7 (1992) 719.
[82] M.M. Kershisnik, R. Kalamegham, K.O. Ash, D.E. Nixon, E.R. Ashwood, Clin. Chem. 38 (1992) 2197.
[83] X. Wei, C.A. Brockhoff-Schwegel, J.T. Creed, J. Anal. At. Spectrom. 16 (2001) 12.
[84] I. Havezov, A. Datcheva, J. Rendl, Michrochim. Acta 119 (1995) 147.
[85] D.M. Hughes, C.L. Chakrabarti, M.M. Lamoureux, J.C. Hutton, D.M. Goltz, R.E. Sturgeon, D.C. Grégoire, A.Kh. Gilmutdinov, Spectrochim. Acta B 51 (1996) 973.
[86] S. Saverwyns, X. Zhang, F. Vanhaecke, R. Cornelis, L. Moens, R. Dams, J. Anal. At. Spectrom. 12 (1997) 1047.
[87] E.H. Larsen, G. Pritzl, S.H. Hansen, J. Anal. At. Spectrom 8 (1993) 1075.
[88] N. Jakubowski, C. Thomas, D. Stuewer, I. Dettlaff, J. Schram, J. Anal. At. Spectrom. 11 (1996) 1023.
[89] J. Lintschinger, O. Schramel, A. Kettrup, Fresenius J. Anal. Chem. 361 (1998) 96.
[90] N. Ulrich, Anal. Chim. Acta 359 (1998) 245.
[91] T. Guerin, M. Astruc, A. Batel, M. Borsier, Talanta 44 (1997) 2201.
[92] A. Prange, D. Schaumloffel, J. Anal. At. Spectrom. 14 (1999) 1329.
[93] T. Lindemann, A. Prange, W. Dannecker, B. Neidhart, Fresenius J. Anal. Chem. 364 (1999) 462.
[94] T. Lindemann, A. Prange, W. Dannecker, B. Neidhart, Fresenius J. Anal. Chem. 368 (2000) 214.
[95] H.S. Hansen, E.H. Larsen, G. Pritzl, C. Cornett, J. Anal. At. Spectrom. 7 (1992) 629.
[96] L.S. Zhang, S.M. Combs, J. Anal. At. Spectrom. 11 (1996) 1043.
[97] P. Thomas, K. Sniatecki, J. Anal. At. Spectrom. 10 (1995) 615.
[98] D. Beauchemin, K.W.M. Siu, J.W. McLaren, S.S. Berman, J. Anal. At. Spectrom. 13 (1989) 285.
[99] J.T. van Elteren, Z. Slejkovec, J. Chromatogr. A 789 (1997) 339.
[100] K. Falk, H. Emons, J. Anal. At. Spectrom. 15 (2000) 643.
[101] B. He, G.-B. Jiang, X.-B. Xu, Fresenius J. Anal. Chem. 368 (2000) 803.
[102] E.H. Larsen, Spectrochim. Acta B 53 (1998) 253.
[103] M. Moldovan, M. Gomez, M.A. Palacios, C. Camara, Microchem. J. 59 (1998) 89.
[104] J.L. Gomez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, Talanta 51 (2000) 257.
[105] W.C. Story, J.A. Caruso, D.T. Heitkemper, L. Perkins, J. Chromatogr. Sci. 30 (1992) 427.
[106] M.L. Magnuson, J.T. Creed, C.A. Brockhoff, J. Anal. At. Spectrom. 11 (1996) 893.
[107] J.M. Rottschafer, R.J. Boczkowski, H.B. Mark Jr, Talanta 19 (1972) 163.
[108] Y.C. Sun, J.Y. Yang, Anal. Chim. Acta 395 (1999) 293.
[109] M. Brezina, P. Zuman, Polarography in Medicine, Biochemistry and Pharmacy, Interscience, NY, 1958, p. 883.
[110] P. Zuman, I.M. Kotloff (Eds.), Progress in Polarography, Interscience, New York, 1962, pp. 1–2.
[111] P. Zuman, L. Meites, I M. Kotloff (Eds.), Progress in Polarograpghy, Interscience, New York, 1972, p. 3.
[112] D.J. Myers, J. Osteryoung, Anal. Chem. 45 (1973) 267.
[113] P. Sharma, S. Sanganeria, C. Rawat, Chem. Environ. Res. 2 (1993) 95.
[114] P. Sharma, Anal. Sci. 11 (1995) 261.
[115] E.O. Reyes-Salas, M.A. Dosal-Gomez, M.H. Barcelo-Quintal, J.A. Manzanilla-Cano, Anal. Lett. 35 (2002) 123.
[116] W. Holak, Anal. Chem. 52 (1980) 2189.
[117] R.S. Sadana, Anal. Chem. 55 (1983) 304.
[118] H. Li, R.B. Smart, Anal. Chim. Acta 325 (1996) 25.
[119] H. Fan, W. Shi, Q. Cai, A. Li, Fenxi Huaxue 21 (1993) 59.

[120] C.M.G. van den Berg, S.H. Khan, Anal. Chim. Acta 231 (1990) 221.

[121] D. Janger, L. Renman, Y. Wang, Electroanalysis 5 (1993) 283.

[122] S.B. Adeloju, T.M. Young, D. Jagner, G.E. Batley, Anal. Chim. Acta 381 (1999) 207.

[123] L. Rasmussen, Anal. Chim. Acta 125 (1981) 117.

[124] D. Jagner, M. Josefson, S. Westerlund, Anal. Chim. Acta 129 (1981) 153.

[125] S.B. Adeloju, T.M. Young, Anal. Lett. 20 (1997) 147.

[126] L.F. Trushina, A.A. Kaplin, Z. Anal. Khim. 25 (1970) 1616.

[127] A.A. Kaplin, N.A. Veits, A.G. Stromberg, Z. Anal. Khim. 28 (1973) 2192.

[128] G. Forsberg, J.W. O’Laughlin, R.G. Megargle, S.R. Koirtyihann, Anal. Chem. 47 (1975) 1586.

[129] C. Hua, D. Jagner, L. Renman, Anal. Chim. Acta 201 (1987) 263.

[130] F.G. Bodewig, P. Valenta, H.W. Nurnberg, Fresenius Z. Anal. Chem. 311 (1982) 187.

[131] P.H. Davis, G.R. Dulude, R.M. Griffin, W.R. Matson, E.W. Zink, Anal. Chem. 50 (1978) 137.

[132] E.A. Viltchinskaia, L.L. Zeigman, D.M. Garcia, P.F. Santos, Electroanalysis 9 (1997) 633.

[133] T.W. Hamilton, J. Ellis, T.M. Florence, Anal. Chim. Acta 119 (1980) 225.

[134] U. Greulach, G. Henze, Anal. Chim. Acta 306 (1995) 217.

[135] T. Navratil, M. Kopanica, J. Krista, Chemia Analityczna 48 (2003) 265.

[136] R. Prakash, R.C. Srivastava, P.K. Seth, Electroanalysis 15 (2003) 1410.

[137] J. Wang, M. Ariel, J. Electroanal. Chem. Interfac. Electrochem. 154 (1983) 261.

[138] H. Huang, P.K. Dasgupta, Anal. Chim. Acta 380 (1999) 27.

[139] P. Tomèík, S. Jursa, S. Mesaros, D. Bustin, J. Electroanal. Chem. 423 (1997) 115.

[140] R. Feeney, S.P. Kounaves, Anal. Chem. 72 (2000) 2222.

[141] J. Herdan, R. Feeney, S.P. Kounaves, A.F. Flannery, C.W. Storment, G.T.A. Kovacs, R.B. Darling, Environ. Sci. Technol. 32 (1998) 131.

[142] M.A. Nolan, S.P. Kounaves, Anal. Chem. 71 (1999) 3567.

[143] C. Belmont, C. Belmont, M.-L. Tercier, J. Buffle, G.C. Fiaccabrino, M. Koudelka-Hep, Anal. Chim. Acta 329 (1996) 203.

[144] M.L. Tercier–Waeber, J. Pei, J. Buffle, G.C. Fiaccabrino, M. Koudelka-Hep, G. Riccardi, F. Confalonieri, A. Sina, F. Graziottin, Electroanalysis 12 (2000) 27.

[145] I. Jaunakais, Int. Environ. Technol 12 (2002) 2.

[146] Application Note 124, HACH Company, USA.

[147] N.F. Durham, W. Kosmus, Asian Environ. Technol. 7 (2003) 2.

[148] M.M. Rahman, D. Mukherjee, M.K. Sengupta, U.K. Chowdhury, D. Lodh, C.R. Chanda, S.Roy.Md. Selim, Q. Quamruzzman, A.H. Milton, S.M. Shahidullah, M.D.T. Rahman, D. Chakraborti, Environ. Sci. Technol. 36 (2002) 5385.

[149] D.M. Hueber, J.D. Winefordner, Anal. Chim. Acta 316 (1995) 129.

[150] S.P. Quinaia, M.E. Rollemberg, J. Braz. Chem. Soc. 12 (2001) 37.

[151] S. Karthikeyan, T.P. Rao, C.S.P. Iyer, Talanta 49 (1999) 523.

[152] N.V. Semenova, F.M. Bauza de Mirabo, R. Forteza, V. Cerda, Anal. Chim. Acta 412 (2000) 169.

[153] N. Xu, C. Su, J. Hong, R. Wilkin, Abstracts of Papers, Two Hundred and Twenty Sixth ACS National Meeting, New York, USA, 2003.

[154] C.-J. Hsieh, C.-H. Yen, M.-S. Kuo, Anal. Sci. 15 (1999) 669.

[155] Q. Zhang, H. Minami, S. Inoue, I. Atsuya, Fresenius J. Anal. Chem. 370 (2001) 860.

[156] X.-P. Yan, R. Kerrich, M.J. Hendry, Anal. Chem. 70 (1998) 4736.

[157] C. Yu, Q. Cai, Z.-X. Guo, Z. Yang, S.B. Khoo, Spectrochim. Acta B 58 (2003) 1335.

[158] M.-F. Huang, S.-J. Jiang, C.-J. Hwang, J. Anal. At. Spectrom. 10 (1995) 31.

[159] I. Marawi, J. Wang, J.A. Caruso, Anal. Chim. Acta 291 (1994) 127.

[160] A. Shraim, N.C. Sekaran, C.D. Anuradha, S. Hirano, Appl. Organomet. Chem. 16 (2002) 202.

[161] X.-P. Yan, X.-B. Yin, X.-W. He, Y. Jiang, Anal. Chem. 74 (2002) 2162.

[162] R.-Y. Yang, J. Ye, Y.-B. Zhang, K. Wang, L. Wee, He Huaxue Yu Fangshe Huaxue 22 (2000) 112.

[163] G. Henze, W. Wagner, S. Sander, Fresenius J. Anal. Chem. 358 (1997) 741.

[164] A. Salimi, M.E. Hyde, C.E. Banks, R.G. Compton, Analyst 129 (2004) 9.

[165] I. Švancara, K. Vytøas, A. Bobrowski, K. Kalcher, Talanta 58 (2002) 45.