

Speciation and Analysis of Arsenic(III) and Arsenic(V) by Electrochemical Hydride Generation Spectrophotometric Method

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A simple method was developed for speciation and spectrophotometric determination of inorganic As(III) and As(V) using an electrochemical hydride generation technique. For speciation of As(III) and As(V), a graphite rod was used as cathode to reduce As(III) to AsH₃, the rod was then replaced with a tin-lead alloy wire for reducing As(V) to AsH₃. The spectrophotometric determination was based on the reaction of AsH₃ with silver diethyldithiocarbamate to give an absorbing complex at 510 nm. Under the optimized conditions, the calibration curves were linear over the ranges of 0.1 – 5 µg ml⁻¹ for As(III) and 0.5 – 4.0 µg ml⁻¹ for As(V). The concentration detection limits of 0.02 and 0.06 µg ml⁻¹ were achieved for As(III) and As(V), respectively. The relative standard deviations for five replicate speciation and determination of 3.0 µg ml⁻¹ As(III) and As(V) were 0.8 and 7.2%, respectively. The accuracy and recovery of the method were evaluated by analyzing tap water spiked with As(III) and As(V).

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Introduction

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

Arsenic occurs in the natural environment in several chemical forms.² The mobility and toxicity of arsenic are determined by its oxidation states;³ thus, As(III) is reported to be 25 – 60 fold more toxic than As(V).⁴ It is therefore necessary to determine different species of arsenic in a real sample in order to know the toxicological and environmental impact of the arsenic present. Highly efficient separation techniques such as high performance liquid electrochemical techniques^{5,6} are often used for speciation of arsenic species.

These procedures are time consuming and require high instrumental investments and specially trained operators. Different methods⁷⁻⁹ have been published for inorganic arsenic speciation by chemical hydride generation (CHG) (coupled with AAS) using different reducing agents for pre-reduction of As(V). However, the CHG techniques based on using NaBH₄ have certain disadvantages. NaBH₄ is a potential source of contamination, which may limit the detection power;¹⁰ it is expensive; and its aqueous solution is unstable and should, therefore, be prepared freshly each working day.¹¹ Furthermore, this system is prone to interferences from coexisting ions.¹²⁻¹⁵

More recently, the electrochemical hydride generation (Ec-HG) has been introduced as a suitable alternative to common chemical hydride generation by NaBH₄ (NaBH₄-CHG).^{13,16-21} Ec-HG benefits several advantages compared to chemical methods. It alleviates the use of NaBH₄, and has been shown to

provide an equally sensitive but potentially cleaner approach to CHG, together with the ease of operation. The most often reported construction of the electrolytic cell consists of two-half cells, the anodic and cathodic ones, usually separated by an ion exchange membrane or a porous glass frit. Several cathode materials have been proposed for Ec-HG. The most useful materials seem to be carbon in its different forms and Pb.²²

There are few studies on the use of Ec-HG for elemental speciation. Schaumlöffel and Neidhart²³ introduced an automatic pre-reduction system to determine As(III) and As(V) with electrochemical hydride generation and atomic absorption detection. Pyell *et al.*¹⁷ reported that, the selectivity could be changed by variation of the cathode material, opening the possibility to circumvent a pre-reduction step. Li *et al.*²⁴ developed a method for speciation of inorganic arsenic by controlling the electrolytic currents.

The aim of this study is to develop a simple, sensitive and reliable method for direct determination of traces of As(III) and As(V) by a batch electrochemical hydride generation spectrophotometry system without pre-reduction of As(V). The speciation of inorganic arsenic using the proposed method was based on using different cathodic materials in the analysis. At first, the per activated graphite cathode was used to perform the reduction of As(III) to AsH₃ and then after its completion, the graphite cathode was replaced with a tin-lead (Sn/Pb) alloy wire cathode in order to reduce As(V) to AsH₃. Subsequently each species was determined by reaction of AsH₃ with silver diethyldithiocarbamate (SDDC) to give an absorbing complex at 510 nm.

Experimental

Reagents and chemicals

All reagents used were analytical grade. The standard stock solution of As(III) (1000 µg ml⁻¹) was prepared by dissolving

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0.1320 g of As_2O_3 (Merck) in 10 ml of 0.1 mol l^{-1} NaOH (Merck) solution, followed by neutralization with 0.2 mol l^{-1} H_2SO_4 (Aldrich) and diluting to 100 ml with distilled water. The As(V) standard stock solution of 1000 $\mu\text{g ml}^{-1}$ was prepared by dissolving 0.4165 g of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (BDH) in 0.1 mol l^{-1} HCl (Merck) and diluting to 100 ml with distilled water. Working standard solutions were prepared daily by further dilution with appropriate concentrations of H_2SO_4 . The SDDC solution was prepared by dissolving 5 ml morpholine (Fluka) in 200 ml chloroform (Merck), followed by adding 1.000 g SDDC (Merck) and diluting to 250 ml with chloroform. This solution was filtered and stored in the dark.²⁵ Nitrogen of high purity was used as the carrier gas (Sabalan, Iran). For interference studies, solutions (1000 $\mu\text{g ml}^{-1}$) of sulfate or chloride salts were used.

Apparatus

All spectrophotometric measurements were made with an Agilent 8453 spectrophotometer equipped with a 1-cm path length glass cell. The spectrophotometer was interfaced to a personal computer furnished with the G1115A software.

The electrochemical hydride generation system was similar to that described by Arbab-Zavar and Hashemi.²⁵ The hydride generator consists of a cathodic cell immersed in the electrolyte of the anodic cell. A porous glass frit separates the anode and the cathode, and allows electrical conduction between them. A coil of platinum wire having a surface area of 1.0 cm^2 served as the anode and graphite rod (4 cm long and 0.5 cm in diameter) or a coil of Sn/Pb alloy wire (Sn:Pb 63:37, 10 cm long and 1 mm diameter) were used as the cathode for determination of As(III) and As(V), respectively. A power supply (ADAK-302 PS, Iran) with a coupled current controller provided a constant current for electrolysis. In this system, nitrogen carrier gas passes through vanadium(II) perchlorate solution to remove oxygen impurities and then enters the cathodic compartment. Immediately after the electrochemical hydride generation, the gaseous products are swept off through the sodium hydroxide pellets to remove acid and water vapors, and then introduced into the SDDC absorber U-tube, containing 2 mm diameter glass beads and a lead acetate scrubber.

Procedure

One hundred milliliters of 1 mol l^{-1} H_2SO_4 were transferred to the anodic cell, and 10 ml of sample or standard solution was transferred into the cathodic cell. The absorber U-tube was filled with 5 ml SDDC solution. The cathode (graphite or Sn/Pb alloy) was then mounted and the cell was operated with a constant direct current. The AsH_3 formed at the cathode was purged by a stream of N_2 gas and transported into the absorber U-tube, in which AsH_3 reacts with SDDC to form a colored absorbing complex at 510 nm. After 15 or 25 min, for As(III) or As(V) respectively, the SDDC solution was then removed, diluted to 5 ml with chloroform and its absorbance was measured at 510 nm. When the graphite cathode was used, pretreatment of the cathode was required. The surface of the graphite cathode was polished with fine sandpaper and was then washed successively with 0.1 M HNO_3 , acetone, ethanol (95%) and distilled water. Finally, the electrode was anodically activated at a constant current of 2 mA in 0.1 M H_2SO_4 for 20 min and stored in 0.1 M H_2SO_4 before use.²⁵ Also, when the Sn/Pb alloy cathode was used, changing of the cathode was required, due to alternation of the surface structure of the cathode. Replacement of the old cathode with a new one provided a reproducible cathode surface, avoiding the necessity of conditioning the cathode surface. The new cathode surface

Table 1 Effect of cathode materials on measured absorbance of 2 $\mu\text{g ml}^{-1}$ As(III) and 2 $\mu\text{g ml}^{-1}$ As(V)

Cathode material	Analyte	
	As(III)	As(V)
Pt	0.08 ^a	0.02
Pb	0.35	0.15
Sn/Pb	0.38	0.24
Graphite	0.39	0.02
Activated graphite	0.54	0.01

a. Measured absorbance value (mean of three replicates).

Conditions: catholyte, 1 mol l^{-1} HCl; electrolytic current, 100 mA; electrolysis time, 15 min for As(III) and 20 min for As(V); N_2 flow rate, 100 ml min^{-1} .

area was set by adjustment of susceptible wire length. For determination of arsenic in samples containing As(III) and As(V), after 15 min, which is needed for reduction of As(III) to AsH_3 on the graphite cathode, the SDDC solution was decanted off, diluted to 5 ml by chloroform and its absorbance was measured. The graphite cathode was then replaced with Sn/Pb alloy cathode and the absorber U-tube was filled with 5 ml new SDDC solution; then electrolysis procedures were carried out for 25 min as mentioned before. In order to indicate that the AsH_3 formation process from As(III) on the graphite cathode was completed; the electrolysis procedures were carried out for 15 min on a sample containing As(III). After 15 min (which is the time needed for completed reduction of As(III) to AsH_3), the graphite cathode was replaced with Sn/Pb alloy cathode, the SDDC solution was removed and the absorber U-tube was filled with 5 ml of new SDDC solution. Again electrolysis procedures were carried out for 10 min. No absorbance was observed. For other runs, the anolyte was degassed for 2 min by N_2 gas for removal of oxygen that is formed at the anode and the procedure was repeated.

Results and Discussion

Cathode material and catholyte solution

Electrodes must be made of a material that would not corrode or contaminate the solution under the applied potential. Since generation of AsH_3 , in acidic and neutral media, occurs with co-evolution of H_2 , a large hydrogen overvoltage is advantageous for the cathode.²⁶ In our primary experiments, various materials such as the untreated shiny wires of Pb, Pt, Sn/Pb alloy, graphite and activated graphite rod were investigated as cathodes for electro reduction of As(III) and As(V) to AsH_3 . Result are shown in Table 1, it should be noted that the blank values for each electrode was measured and no absorbance was observed. The best results were found with the activated graphite and Sn/Pb alloy for As(III) and As(V), respectively. The response related to the use of the activated graphite cathode for As(V) was negligible. Under the constant conditions, the hydrogen overvoltage increases from Pt to Sn/Pb in the following sequence:²⁰ Pt < graphite < Pb < Sn/Pb.

Tin-lead alloy due to its very high hydrogen overpotential, is an ideal choice for generation of AsH_3 from As(V).

HCl, HNO_3 and H_2SO_4 were examined as the catholyte. No absorbance was observed for As(III) and As(V) using HNO_3 which will contribute to the role of NO_3^- as cathodic depolarizer for suppression of AsH_3 from both As(III) and As(V). The

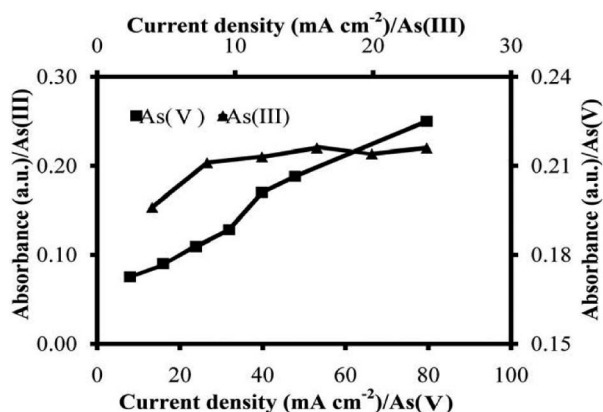


Fig. 1 Effect of applied electrolytic current density on measured absorbance of $1 \mu\text{g ml}^{-1}$ As(III) and $2 \mu\text{g ml}^{-1}$ As(V): electrolysis time, 15 min for As(III) and 20 min for As(V); N_2 flow rate, 200 ml min^{-1} ; cathode, graphite for As(III) and Sn/Pb for As(V); H_2SO_4 concentration, 0.3 mol l^{-1} for As(III) and 0.7 mol l^{-1} for As(V).

suppressing effect of HNO_3 on the NaBH_4 -CHG process is also well known.²⁷ The comparison of measured absorbance due to AsH_3 from As(III) and As(V) at the graphite and Sn/Pb alloy cathode, respectively, showed that there was no significant difference between HCl and H_2SO_4 as the catholyte for the reduction of As(III). However, H_2SO_4 seemed to be a superior electrolyte for generation of AsH_3 from As(V) solution and was chosen as the catholyte in this study.

Concentration of the catholyte

The effects of H_2SO_4 concentration of catholyte on AsH_3 production from As(III) and As(V) by measuring the absorbance of complex related to As(III) and As(V) were investigated in the range of $0.05 - 1.5 \text{ mol l}^{-1}$. The measured absorbance increases when sulfuric acid concentration increased up to 0.3 and 0.7 mol l^{-1} for As(III) and As(V), respectively, and then leveled off with further increase in acidity. The optimum concentration of catholyte was selected to be 1.0 mol l^{-1} H_2SO_4 for simultaneous generation of AsH_3 from As(III) and As(V).

Carrier gas flow rate

The carrier gas, together with the excess of hydrogen produced during the electrochemical reduction, aids in separation of the volatile compound from the liquid phase and transports it *via* the gas-liquid separator into the SDDC absorption cell. The absorbance shows an increase with increasing the carrier gas flow rate up to 200 ml min^{-1} , after which the absorbance decreases with further increase of the flow rate. At higher flow-rates, the decrease in the measured absorbance may be due to the decrease of the efficiency of the complex formation between AsH_3 and SDDC, and also to the significant increase of pressure, which caused some leakage. Therefore, a N_2 flow rate of 200 ml min^{-1} was selected as the optimal rate for further experiments.

Electrolysis current density and electrolysis time

The effects of the electrolysis current density on AsH_3 production from As(III) and As(V) were investigated. The obtained results are shown in Fig. 1. The measured absorbance due to As(III) remained constant at the range of $4 - 24 \text{ mA cm}^{-2}$, but the measured absorbance of As(V) increased linearly with current density up to 80 mA cm^{-2} . The use of higher current

Table 2 The optimized experimental conditions for determination of As(III) and As(V)

Variable	As(III)	As(V)
Anode	Pt ^a	Pt ^a
Anolyte	H_2SO_4^b	H_2SO_4^b
Anolyte concentration/mol l ⁻¹	1 ^b	1 ^b
Cathode	Activated graphite	Sn/Pb alloy
Catholyte	H_2SO_4	H_2SO_4
Catholyte concentration/mol l ⁻¹	≥ 0.3	≥ 0.7
Carrier gas flow rate/ml min ⁻¹	200	200
Current density/ mA cm^{-2}	24	80
Electrolysis/min	15	25
Surface area of cathode/ cm^2	6.3	3.2
Cell temperature/ $^\circ\text{C}^a$	25	25

a. Ref. 25.

b. Ref. 27.

Table 3 Analytical characteristics of As(III) and As(V)

Parameter	As(III)	As(V)
Calibration equation ^a	$A = 0.2582C + 0.0031$	$A = 0.0965C - 0.0071$
R^2 ^b	0.9990	0.9995
Linear range/ $\mu\text{g ml}^{-1}$	0.1 - 5.0	0.5 - 4.0
RSD ^c , %	0.8	7.2
LOD ^d / $\mu\text{g ml}^{-1}$	0.02	0.06

a. A is absorbance and C is the concentration of As(III) or As(V) in $\mu\text{g ml}^{-1}$.

b. Squared correlation coefficient.

c. Relative standard deviation.

d. Limit of detection.

density was restricted due to the considerable overheating of the electrolytic cell. Therefore a current density of 24 and 80 mA cm^{-2} were used for determination and speciation analysis of As(III) and As(V), respectively.

The effects of the electrolysis time were also investigated at current density of 24 mA cm^{-2} (for As(III)) and 80 mA cm^{-2} (for As(V)). The results showed that electrolysis times of more than 15 min for As(III) and 25 min for As(V) were sufficient to obtain the maximum sensitivity.

Cathode surface area

The dependence of AsH_3 from As(III) and As(V) with surface area of graphite and Sn/Pb alloy cathode were investigated in the range of $1.6 - 6.3 \text{ cm}^2$ (for graphite) and $0.6 - 3.2 \text{ cm}^2$ (for Sn/Pb alloy). The maximum sensitivity was observed at 6.3 cm^2 (whole length of rod) of graphite cathode and in the range of $2.4 - 3.2 \text{ cm}^2$ for Sn/Pb alloy cathode.

Analytical figures of merit

Analytical figures of merit, under the optimum conditions (Table 2) were determined for electrochemical hydride generation of AsH_3 from As(III) and As(V). These are summarized in Table 3. The calibration curves were linear in the ranges of $0.1 - 5 \mu\text{g ml}^{-1}$ for As(III) and of $0.5 - 4 \mu\text{g ml}^{-1}$ for As(V). Concentration detection limits based on $3\sigma/m$, where σ is the standard deviation of five measurements of the blank and m is the slope of the calibration curves, were 0.02 and $0.06 \mu\text{g ml}^{-1}$ for As(III) and As(V), respectively. The relative standard deviations (RSD) for five replicate measurements of $3 \mu\text{g ml}^{-1}$ As(III) and As(V) were 0.8 and 7.2% , respectively.

Table 4 Effect of interferences on the determination of 3 $\mu\text{g ml}^{-1}$ As(III) and 3 $\mu\text{g ml}^{-1}$ As(V) in the presence of 1000 $\mu\text{g ml}^{-1}$ foreign ions

Species	Recovery, %		Species	Recovery, %	
	As(III)	As(V)		As(III)	As(V)
Cl ⁻	100	79	Na ⁺	100	108
Br ⁻	100	92	K ⁺	100	102
I ⁻	100	84	Mg ²⁺	100	77
SO ₄ ²⁻	100	99	Al ³⁺	100	31
NO ₃ ⁻	0	0	Fe ²⁺	99	50
NO ₂ ⁻	0	0	Fe ³⁺	37	36

Table 5 Results of speciation of As(III) and As(V) in water samples by the proposed method

Sample	Added/ $\mu\text{g ml}^{-1}$		Found/ $\mu\text{g ml}^{-1}$		Recovery, %	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Tap water	0.00	0.00	ND ^a	ND	—	—
	1.00	1.00	0.99 ± 0.01 ^b	0.95 ± 0.02	99	95
	2.50	2.50	2.55 ± 0.00	2.32 ± 0.02	102	93

a. Not detectable.

b. Mean ± SD (three replicates).

Interferences

The effects of co-existing various ionic species on the determination of 3 $\mu\text{g ml}^{-1}$ As(III) and 3 $\mu\text{g ml}^{-1}$ As(V) were studied in the presence of 1000 $\mu\text{g ml}^{-1}$ of foreign ions. Results are shown in Table 4. The effects of interferences on the determination of As(V) by using Sn/Pb alloy cathode were more serious than of As(III) by using graphite cathode, and the difference may be due to the different mechanisms for electrochemical reduction of arsenic on graphite and on Sn/Pb alloy cathodes.

Validation and application of the proposed method

Accuracy of the proposed method was evaluated by speciation of spiked tap water samples for As(III) and As(V). Obtained results are summarized in Table 5. The good agreement between the obtained results and the known values indicates the successful applicability of the proposed method in real samples.

Conclusions

The Ec-HG system described has proven to constitute an effective approach for speciation and determination of As(III) and As(V). The speciation of inorganic arsenic can be performed using appropriate different cathodic materials without pre-reduction of As(V) in the analysis. At first, the pre-activated graphite cathode was used to perform complete reduction of

As(III) to AsH₃; then, the graphite cathode was replaced with a tin-lead (Sn/Pb) alloy wire cathode in order to reduce As(V) to AsH₃.

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