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Effect of cathodic electrolyte on the performance of electrochemical hydride generation from graphite cathode

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Abstract

The classic silver diethyldithiocarbamate (SDDC) spectrophotometric procedure for arsenic determination has been used for investigation of the effect of cathodic electrolyte on the performance of electrochemical hydride generation (HG) from graphite cathode. The results of this study show that the presence of a soft metal ion such as Cd(II), Sn(II) and/or Zn(II) in the acidic cathodic electrolyte can increase effectively the efficiency of electrochemical hydride generation and decrease the effect of interferences. The possible mechanisms of these effects have been discussed in detail. The parameters related to the electrochemical hydride generation were investigated. Also the characteristic data of the electrochemical hydride generation and common hydride generation by $NaBH_4$ were compared. Under optimised conditions, the system is selective to As(III) and total inorganic analyses can be performed after a pre-reduction stage prior to electrochemical hydride generation. This will allow the differential determination of inorganic arsenic species. The method is appropriate to the determination of 4–40 μg of each arsenic species.

Keywords: Electrochemical hydride generation; Arsenic; Spectrophotometry; Silver diethyldithiocarbamate

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1. Introduction

Hydride generation (HG) is undoubtedly the most sensitive and competitive technique for determination and speciation of arsenic (As) in a wide range of the samples, as has been highlighted by several reviews [1–4]. The $NaBH_4$–acid reduction system has been widely used for HG. However, this system has certain disadvantages. $NaBH_4$ is a potential source of contamination, which may limit detection power [5], is expensive and its aqueous solution is unstable and should, therefore, be prepared freshly on each working day [6]. Also, the rapid reaction between $NaBH_4$ and HCl may generate a troublesome foam, particularly when undigested biological fluids are being analysed [1]. Furthermore, this system is prone to interferences from coexisting ions [7–11]. More recently, the electrochemical hydride generation (EC-HG) has been introduced as a suitable alternative to common hydride generation by $NaBH_4$ ($NaBH_4$-HG) [12–20]. It has been shown that the EC-HG provides an equally sensitive but potentially cleaner approach to HG than the $NaBH_4$-HG, together with ease of operation. However, only a few studies have been reported in the literature concerning this method and there is much work left to be done to understand this technique better, before it could become fully established. The electrochemical hydride generator consists of a cathode cell separated from the anode cell. Generally, the acidic media (H_2SO_4 and/or HCl) is used as cathodic electrolyte for EC-HG process with different cathode materials. To date, no data have been given concerning the effect of the other possible cathodic electrolytes on the performance of EC-HG process. The graphite has been introduced as a likely choice for cathode material in EC-HG, especially when interference elimination is attempted by electrochemical means and/or increasing the acidity [13–16]. However, the efficiency of the hydride production onto the graphite cathode is relatively low (∼40% for arsine). The pretreatment of graphite cathode by anodic activation in acidic media [13] and/or chemical activation [16] may serve to increase the efficiency of EC-HG. However, the pretreatment of the electrode is time-consuming

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and the lifetime of such a pretreated electrode is a potential problem.

In the continuation of our pervious work, in this study, the silver diethyldithiocarbamate (SDDC) spectrophotometric procedure for arsenic determination has been used to demonstrate the effect of composition of cathodic electrolyte on the performance of EC-HG onto the graphite cathode. Also, the method is modified for inorganic arsenic speciation. The results of this study show that the presence of a soft metal ion such as Cd(II), Sn(II) and/or Zn(II) in acidic media as cathodic electrolyte has a catalytic effect on the EC-HG process and effectively decreases the interference effects. Also, the possible mechanisms of these effects have been discussed in detail.

2. Experimental

2.1. Apparatus

The basic EC-HG system and associated parts (Fig. 1) have been described in detail in our pervious publication on the spectrophotometric determination of As(III) [13]. This system was used without any modification. The electrochemical hydride generator was powered by a dc power supply (Leybold–Heraeus). All spectrophotometric measurements were made with Beckman DU-6 spectrometer.

2.2. Reagents

Analytical grade reagents and doubly distilled water were used throughout the study. Stock solutions (1.000 g l^{-1}) of As(III) and As(V) were prepared by dissolution of As_2O_3 in 0.1 M NaOH and Na_3AsO_4 in 0.1 M HCl. Stock solution of Sn(II), Cd(II) and Zn(II) (1 mol l^{-1}) were prepared by dissolving the respective chloride salts in 1 M HCl. The absorbing SDDC solution and $NaBH_4$ solution were prepared as described previously [12].

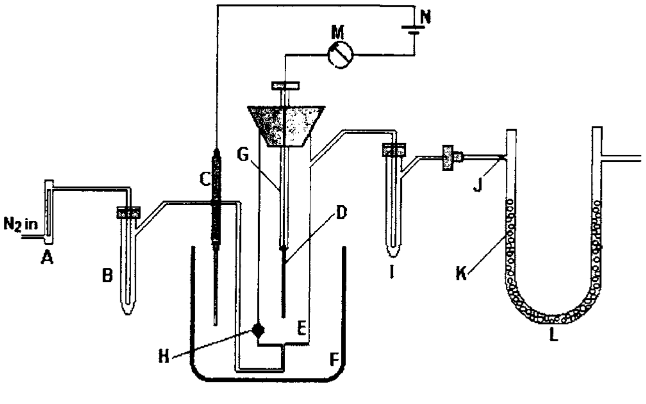

Fig. 1. The schematic diagram of the analytical system. (A) flowmeter; (B) vanadium perchlorate; (C) Pt anode; (D) graphite cathode; (F) anode cell; (G) cathode holder; (H) glass fit; (I) NaOH trap; (J) lead acetate scrubber; (K) glass beads; and (L) SDDC absorbing cell.

2.3. Procedure

All determinations were completed using in situ collection of the electrochemically generated hydrides in SDDC absorbing solution followed by spectrophotometric measurement of the formed red complex at 525 nm. The anode cell was filled with H_2SO_4 (0.1 M) as anodic electrolyte. Ten millilters of sample solution containing analyte and cathodic electrolyte were transferred into the cathode cell and the absorber U-tube was filled with 4 ml SDDC solution. The graphite cathode was then mounted and the cell was operated with a constant direct current of 60 mA, unless otherwise stated. The arsine formed at the cathode was purged by a stream of N_2 gas at a flow-rate of 6 ml min^{-1} and transported into the absorber U-tube. For other runs, the sample solution was decanted off and the procedure was repeated with new sample. The common hydride generation with $NaBH_4$ was performed by the procedure described in [9].

3. Results and discussion

The parameters related to SDDC spectrophotometric method were as described by pervious publication [13]. No additional optimisation was undertaken and only the parameters related to the EC-HG were investigated. In the context of this study, the efficiency of hydride generation is defined as the ratio (%) of the measured absorbance of a given mass of As by EC-HG to that by $NaBH_4$-HG.

3.1. Effect of electrolyte

The EC-HG consists of at least three sequential events: reduction and deposition of the aqueous analyte onto the surface of the cathode (or at specific active surface sites); stepwise reaction of the deposited analyte with nascent hydrogen ($H^\bullet$) generated on the surface of the cathode; and subsequent desorption of the analyte hydride [17]. The EC-HG process requires an excess electrolyte for increasing of electrical conduction of the sample solution. The electrolyte used should not interfere with hydride generation and/or hydride release efficiency. A solution of H_2SO_4 (0.1 mol l^{-1}) was used as anodic electrolyte and the effectiveness of several electrolytes were compared as cathodic electrolyte. Results are shown in Table 1. With KNO_3 and HNO_3, the efficiency of arsine generation was zero. Nitrate ion may act as cathodic depolariser and suppresses hydrogen and arsine evolution. Also, the oxidising property of NO_3^- or reduced nitrogen oxide species such as NO_2^- or $NO_{(g)}$ can decrease the hydride release efficiency. The suppressing effect of HNO_3 on the $NaBH_4$-HG process is also well known [1]. From comparison of results, it is revolved that the efficiency of arsine generation was significantly increased in the presence of Cd, Zn and/or Sn ions. During our investigations, we observed that a layer of these metals was formed on the cathode surface, which easily was anodically stripped. For providing the

Table 1
The effect of different electrolyte on the measured absorbance of 30 μg of As(III) and As(V)

Cathodic electrolyte	Measured absorbance[a]	
	As(III)	As(V)
HCl (0.4 M[b])	0.336 ± 0.014	ND
H_2SO_4 (0.4 M)	0.321 ± 0.020	ND
HNO_3 (0.4 M)	ND	ND
KCl (0.4 M)	0.155 ± 0.040	ND
KNO_3 (0.4 M)	ND	ND
$SnCl_2$ (0.001 M in 0.4 M HCl)	0.671 ± 0.010	ND
$CdCl_2$ (0.001 M in 0.4 M HCl)	0.675 ± 0.009	ND
$ZnCl_2$ (0.001 M in 0.4 M HCl)	0.656 ± 0.014	ND

Conditions: current, 100 mA; electrolysis time, 20 min; N_2 flow-rate, 6 ml min^{-1}; anodic electrolyte, 0.1 M H_2SO_4.

[a] All results: mean ± standard deviation based on three replicate analyses.

[b] Concentration of cathodic electrolyte. ND: not detectable.

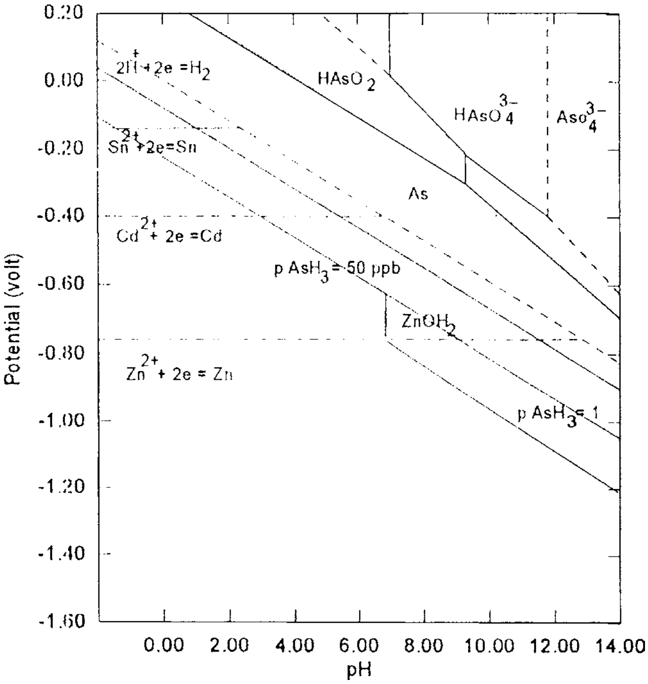

Fig. 2. Potential–pH equilibrium diagram for the arsenic–water system at 25 °C, showing voltage–pH ranges capable of giving rise to arsine generation in excess of the threshold limit value.

same surface activity of the cathode surface for all investigations, and also in order to avoid the electrode fouling or the memory interference effects, it is necessary to clean the cathode surface for each sample run. In order to implement this, the cathode polarity was reversed after each sample run and the electrode surface was anodically cleaned for a period of 5 s. Fig. 2 shows the potential–pH diagram for arsine evolution in the presence of these soft metal ions. It is clear that the codeposition of As with these soft metals in certain pH range does not preclude the evolution of arsine. A possible explanation for catalytic effects of these species on arsine production is that the codeposition of these soft metals with As on the graphite surface increases the hydrogen overpotential of the surface and provides a means of continuous generation of nascent hydrogen for the deposited As to form arsine. Additionally, Fig. 2 shows that the deposited species can reduce As to arsine. Reducing property of Zn, Cd or Sn species in acidic media is well known. Although this behaviour is desirable from thermodynamic aspects (Fig. 2), our experimental data show that this behaviour is slow kinetically. When the graphite cathode was previously coated with a layer of these species and then was mounted in the cell, when no voltage was applied; only after 30 min, the efficiency of arsine production reached to 25%. Due to smaller standard half-cell reduction potentials of these ions relative to the As(III), the possibility of hydride generation with open circuit was also investigated. The efficiency of hydride generation in each three cases was zero. These studies show that the formation of a layer of these species and dissolution of them in acidic media during EC-HG process generates continuously an active site on the electrode surface for the production of nascent hydrogen. This is in line with finding of Ding and Sturgeon who demonstrated that the active sites on the lead cathode surface may be operative in the electrochemical generation of stibine [15]. The presence of such metal ions in acidic media can overcome the potential problem with the use of soft metals as cathode material in acidic media. These cathode materials have a large hydrogen overpotential, however, dissolved unfavourably in acidic media under applied potentials. Due to catalytic effect of these species on EC-HG process, the effect of their concentration on the absorbance of 30 μg As(III) was examined in the range 10^{-6} to 10^{-3} M. The maximum sensitivity was observed in the range 10^{-4} to 10^{-3} M for all measurements. It is likely that a minimum concentration of 10^{-4} M is sufficient for the formation of a uniform coverage over the entire geometric area of the cathode surface. For investigation of the possible error introduced via the cathodic electrolyte, the blank absorbance was also examined. The results showed that the amounts of increase in blank absorbance were nearly zero. Because of the low concentration of the added electrolyte, the possible errors introduced via the traces of the analyte in the blank can be made very low. When As(V) solution was used in place of As(III) solution, no discernible absorbance was observed in the investigated electrolytes. This may suggest that the rate controlling step for the EC-HG process is the reduction of As species onto the electrode surface. However, As(V) can be detected after pre-reduction prior to EC-HG. With the conventional $NaBH_4$-HG KI, L-cysteine, KI–ascorbic acid and KI–$SnCl_2$ are generally used for reduction of As(V) to As(III) prior to HG. In presented study, the effect of these reagents on electrochemical arsine generation form 30 μg As(V) and AS(III) in 0.4 M HCl were examined. Addition of different concentration of KI, L-cysteine and KI–ascorbic acid to the As(V) solution with a pre-reduction time of 10 min were found ineffective. Furthermore, the measured absorbance of

30 μg As(III) in the presence of 5% (m/v) L-cysteine and 10% (m/v) KI decreased by 12 and 20%, respectively. Also, a sever memory interference was observed for subsequent determination of free As(III) solution with that electrode was previously exposed to solutions containing the reducing agent. These observations suggest that the major action of these interferences occurs on the cathode surface. Probably, adsorbing of this reducing agent on the cathode surface destroys the favourable nature of the cathode surface for the EC-HG. Investigation of KI–$SnCl_2$ showed that this mixture had beneficial effects. With use of 10^{-4} mol l^{-1} $SnCl_2$, the optimum amount of KI and pre-reduction time were investigated. Our results showed that a 2% (m/v) KI and a pre-reduction time of 10 min is sufficient for ratio of the measured absorbance of 30 μg As(V) to that of 30 μg As(III) reach to unite. Since Sn(II) can be useful for pre-reduction stage, it was selected for further studies.

3.2. *Acidity and acid of sample solution*

Form thermodynamic aspects, the arsine evolution depends on the sample acidity [21]:

$$E = -0.225 - 0.059\,\mathrm{pH} + 0.0197 \log p(\mathrm{AsH_3})$$

As shown in Fig. 2, with increasing of acidity, the potential of arsine generation shifts to more positive values, and therefore, efficiency of arsine evolution increases. Furthermore, only in a certain range of acidity, the codeposition of As with Cd, Zn and Sn cannot preclude the arsine evolution. Also, it can be seen that this range becomes wider when the As concentration (or $P^{\mathrm{AsH_3}}$) decreases. The effect of HCl, HNO_3 and H_2SO_4 was examined on the performance of EC-HG process. As expected, HNO_3 suppressed arsine generation completely. This is due to oxidising property of NO_3^- and/or reduced nitrogen oxide species. The effect of HCl and H_2SO_4 concentrations on the measured absorbance of 30 μg As(III) is shown in Fig. 3. The measured absorbance increased with increasing acidity up to 0.4 M for HCl and 0.55 M for H_2SO_4 and then levelled off with further increases in acidity. The R.S.D. of replicate measurements ($n = 5$) is less than 2% in 0.4–1 M for HCl and 0.55–1 M for H_2SO_4. The F-test shows no significant difference between analytical performance of two acids ($P = 0.05$). However, HCl is preferred due to better performance at lower concentrations.

3.3. *Cell current*

The effect of cell current was investigated in the range 20–120 mA. The measured absorbance increased up to 60 mA and then it levelled off with further increases in current indicating that the EC-HG process was complete. In the absence of Sn(II), the measured absorbance of 30 μg As(III) with a current of 60 mA was 40% of that in the presence of Sn(II). This supports this idea that Sn(II) has a catalytic effect on the EC-HG process.

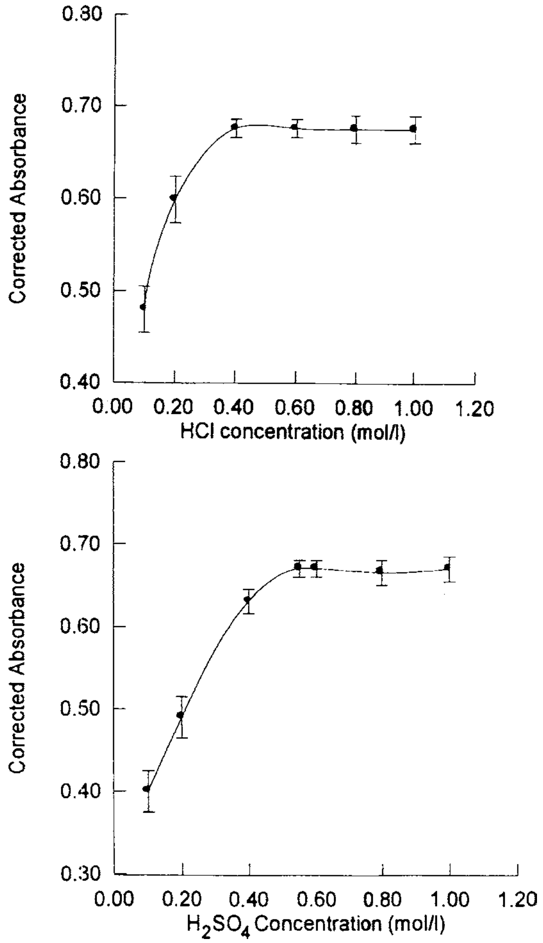

Fig. 3. The effect of sample acidity on the measured absorbance of 30 μg of As(III).

3.4. *Sample volume and N_2 gas flow-rate*

The effect of sample volume was investigated in the range 4–10 ml. The maximum sensitivity was observed in the range 7–10 ml. At lower sample volumes, the surface of the electrode in contact with the solution decreases resulting in a reduction in the efficiency of HG process. This is in line with the finding of Huang and co-workers who demonstrated that the efficiency of EC-HG for the same applied current increased with increasing electrode area [20]. The optimum N_2 flow-rate was found to be 6 ml min^{-1}. This flow-rate was sufficient to ensure that sample carry-over did not occur. At higher flow-rates the pressure increased significantly and caused leakage.

3.5. *The efficiency of hydride generation*

The high efficiency of $NaBH_4$-HG is one of the advantages of this method. The efficiency of arsine generation by EC-HG and $NaBH_4$-HG was compared with replicate measurements ($n = 5$) of absorbance of 30 μg As(III) by two techniques. There was no significant difference ($P = 0.05$)

Table 2
Comparison of analytical data

	EC-HG	$NaBH_4$-HG
Detection limit ($3S_b$, μg)	0.5	0.5
Dynamic range (μg)	4–40	4–40
Precision (30 μg As(III); $n = 5$) (%R.S.D.)	1.48	1.50
Sensitivity (slope of calibration graph, μg^{-1})	0.0224	0.0205

between corrected absorbances and therefore hydride generation efficiency of the two methods.

3.6. Analytical figures of merit

A linear calibration graph was obtained over the range 4–40 μg of As(III) with linear regression equation $A = 0.02240C + 0.00855$ (C, μg As) and correlation coefficient $r = 0.9995$. An absolute detection limit ($3s_b$) of 0.5 μg and concentration detection limit of 0.05 $\mu g\,ml^{-1}$ were obtained using a 10 ml sample volume. The precision (R.S.D.) for five replicate determination of 30 μg As(III) was 1.48%. The characteristic data of the EC-HG and $NaBH_4$-HG methods were compared for spectrophotometric determination of As(III). The results are presented in Table 2. The F-test shows no significant difference between precision of the two methods ($P = 0.05$). The results show that the analytical performances of the two methods are same.

3.7. Speciation study

As discussed above, As(III) can be directly converted to arsine by electrolytic reduction, however As(V) require a pre-reduction prior to EC-HG. Therefore, As(III) can be detected selectively and total inorganic analysis can be performed with a pre-reduction stage. At first, this appears to be a disadvantage but it offers the possibility of chemical speciation. Speciation information can be obtained by subtracting the concentration of As(III) obtained on one aliquot of sample without a pre-reduction stage from total inorganic As concentration obtained on a second aliquot. Table 3 shows the results of selective determination of As(III) and As(V) in standard solutions. The average recoveries of As(III) and As(V) in mixture of standard solutions were found to be 101 and 94.3%, respectively.

3.8. Interference effects

In pervious publication [13], we had shown that the ions of copper group elements and noble metals have severe suppressing effects on the EC-HG process with acidic electrolyte. It is generally believed that the interferences of these metal ions are due to electrochemical reduction of these species on the cathode surface during the EC-HG process, which decreases the current efficiency for arsine production. Also, the deposition of interfering metal ions on the cathode surface can destroy the favourable nature of the cathode electrode for the EC-HG process. Additionally, it is possible that the electrochemically reduced metal ions subsequently disperse in the cathode cell and decompose or scavenge the generated arsine. As the EC-HG efficiency was found to increase in the presence of soft metal ions in cathodic electrolyte, it was resonated that the presence of soft metal ions may have beneficial effect on suppressing the interference effects. Since Pt(IV), Au(III) and Cu(II) are among the ions known to produce the most sever interference effects in the EC-HG process [13,18], they were selected and the usefulness of Sn(II) ($10^{-4}\,mol\,l^{-1}$) in reducing the interferences by 1000 μg of Pt(IV), Au(III) and Cu(II) on determination of 30 μg As(III) was examined. In the presence of Sn(II), the complete suppressing effect (100%) of Pt(IV), Au(III) and Cu(II) reduced, respectively, to 24, 20 and 15% suppression as compared to an interferent-free solution. As mentioned above, the EC-HG of arsine takes place during reduction of interfering metal ions to metals on the electrode surface. If deposition of interfering metal ions during the EC-HG process can be avoided, the suppressing effects of interfering ions can be reduced. The standard half-cell potential for Au(III)–Au, Pt(IV)–Pt, Cu(II)–Cu and Sn(II)–Sn systems are +1.5, +0.75, +0.337 and −0.136, respectively, relative to the NHE [22]. Due to higher standard potential of the interfering ions relative to the Sn(II), it is possible that the interfering metal ions are reduced to metallic form and dispersed in solution phase prior to the EC-HG process. The relatively low observed interferences may relate to scavenging of the formed arsine by metallic form of these ions. This suggests that the main action of interferences may be on the electrode surface.

The simultaneous generation of hydrides from other hydride forming elements may also affect the performance of

Table 3
Selective determination of As(III) and As(V) in standard mixture

Mixture (μg As(III) + μg As(V))	Determined concentration (μg)			Recovery (%)	
	As_T[a]	As(III)	As(V)	As(III)	As(V)
30 + 0	–	29.5 ± 0.4	–	98 ± 1	–
20 + 10	29.5 ± 0.4	20.2 ± 0.4	9.3 ± 0.6	101 ± 2	92 ± 6
10 + 20	29.2 ± 0.4	10.3 ± 0.4	18.9 ± 0.4	103 ± 4	94 ± 3
0 + 30	–	–	29.1 ± 0.4	–	97 ± 1

All results: mean ± standard deviation based on five replicate analyses.

[a] Total arsenic concentration.

the EC-HG of arsine. Since the use of EC-HG is also reported for Se(IV) and Sb(III), they were selected for this investigation. Presence of 10, 100 and 500 μg of Se(IV) had no effects on the efficiency of arsine generation from 30 μg As(III). However, presence of 50 μg Sb(III) enhanced the apparent absorbance of 30 μg As(III) by 61%. The positive interference of Sb(III) is due to reduction of Sb(III) to stibine (SbH_3) under the experimental conditions and reaction of stibine with SDDC to give a coloured absorbing complex at 525 nm that increases the apparent As absorbance [13]. Investigation of possible suppression effect of antimony requires an experimental approach that can be remarkably free from spectral interferences such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and is the subject of further research projects.

4. Conclusion

The efficiency of EC-HG from graphite cathode with acidic electrolyte is relatively low. The electrochemical activation or chemical activation of graphite cathode can increase the EC-HG efficiency. However, the lifetime of such a pretreated electrode is a potential problem. The presence of soft metal ions in the acidic media, as cathodic electrolyte, can increase the EC-HG efficiency and decrease the interference effects. Deposition of soft metal ions on the electrode surface increases the hydrogen overpotential of the electrode surface and provides a means of continuous generation of nascent hydrogen atoms for deposited As to form arsine. Also Sn(II) can prevent reduction of interfering ions on the electrode surface during the EC-HG process and therefore decrease the electrode surface interferences. As(III) can selectively convert to arsine and As(V) requires a pre-reduction stage prior to EC-HG. This will allow differential determination of As(III) and As(V). The $SnCl_2$–KI reducing system is found as the best reagent for pre-reduction stage. This research will be continued to extend the application area of EC-HG.

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