

A NEW ION SELECTIVE SYSTEM FOR ARSENIC DETERMINATION USING HYDRIDE GENERATION

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Abstract

A potentiometric procedure for the determination of inorganic arsenic species (As(III) and As(V)) using hydride generation is described. Optimised operation conditions were investigated. Interferences were observed in the presence of nickel(II), antimony(III), selenium(IV), tin(II) bismuth(III), mercury(II), fluoride, nitrate and sulfate ions, these interferences can be eliminated by suitable masking agents and extraction procedures. By controlling the pH of the solution, the differential determination of arsenic(III) and arsenic(V) was performed. The technique can be employed for analysis of samples containing 0.75-8 µg/ml arsenic(III) or arsenic(V) with relative standard deviation 2.8% for 2µg/ml arsenic.

Introduction

Arsenic is a relatively common element existing in natural system in a variety of chemical forms including arsenic(III) arsenic(V), methyl arsenic and ethyl arsenic [1]. In recent years, much attention has been focused of the determination on different forms of arsenic in the environment due to the high toxicity of some of its compounds [2].

A number of procedures have been reported that are suitable for the determination of arsenic in environmental samples. Although many techniques have been applied for the analysis of arsenic [3], the procedures for the determination of arsenic in low levels have largely focused on spectro photometric [4-6] and microwave absorption spectroscopy methods [7]. Hydride generation coupled with atomic absorption spectroscopy have been widely used for the determination of arsenic compounds in low levels in the µg/L range [8-10]. In spite of the merits of using hydride generation various techniques, atomic spectroscopy [11-13],

gas liquid chromatography [14] and chromatography mass spectroscopy, no work has been published on the use of hydride generation with potentiometric methods.

This paper describes a new sensitive and simple hydride generation potentiometric technique for the determination of microgram arsenic in real samples. Information about the oxidation state of arsenic in a sample is obtained by exploiting the pH dependence of sodium tetrahydroborate(III) reduction step.

Experimental Section

Reagents and Glasswares

All chemicals were analytical-reagent grade unless otherwise stated. All glasswares were cleaned by soaking in a 10% solution of nitric acid and were then rinsed with distilled water before use. Stock solutions of arsenic (1000 Mg/L) were prepared from arsenic trioxide (As₂O₃) and disodium hydrogen arsenate (Na₂HASO₄ · 7H₂O). Standard solutions were prepared by dilution of the stock solution on the day of use. Analytical reagent grade sodium tetrahydroborate(III)

Keywords: Arsenic determination; Hydride generation; Ion selective systems; Potentiometry

was used to prepare sodium tetrahydroborate(III) solution in distilled water (optimised condition, 1% m/v). These solutions were stable for the course of the working day. Mercury(II) chloride ($HgCl_2$) solution (0.025%) was prepared by dissolution in distilled water and was diluted with ethanol ($C_2H_5OH:H_2O$ 80:20 v/v). The pH of the solutions was adjusted by orthophosphoric acid (0.1M)-sodium dihydrogen phosphate (0.1M) for pH 1-3, sodium acetate (0.025, M-acetic acid (0.025 M) for pH 4-7 and borax (0.025 M) for adjusting the pH values between 8-11.

Apparatus

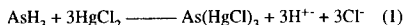
The apparatus used in these studies consisted of a hydride generator, a reaction chamber and Methrohm-632 pH meter with Orion Research pH electrode as a detection system (Fig. 1). The generator chamber was

connected to the rest of the apparatus via a plastic tube. The hydrides were generated in the hydride generator chamber by the introduction of 1 ml of 1% sodium tetrahydroborate(III) into the acidic sample. A flow of nitrogen transfers the arsines to the reaction chamber which contains a solution of mercury(II) chloride and the pH electrode. The potential was read after 10 minutes.

Results and Discussion

Optimisation of Experimental Conditions

The reaction between arsines and mercury(II) chloride is one of the oldest methods used for the determination of arsenic [16]. In this method, arsines react with mercury(II) chloride to form yellow spots (As($HgCl_3$))



Since the hydrogen ion is generated in this reaction, it is possible to use a glass membrane electrode as a detection system. Various experiments were carried out in aqueous solutions with different concentrations of $HgCl_2$ and the potentials were read after 10 minutes after which the potential did not change significantly with time. Those experiments were repeated with $2\mu g/ml^{-1}$ of arsenic and using a 4% m/v solution of $HgCl_2$ in a different composition of ethanol and water. The results are shown in Figure 2.

The adsorption of arsine in solution containing 1-10% (v/v) ethanol was very low and the reaction of arsines with mercury(II) chloride did not occur to a significant extent. The adsorption of arsine was increased by increasing the concentration of ethanol, and maximum adsorption was observed at 80% of ethanol concentration (Fig. 2).

The effect of mercury(II) chloride concentration

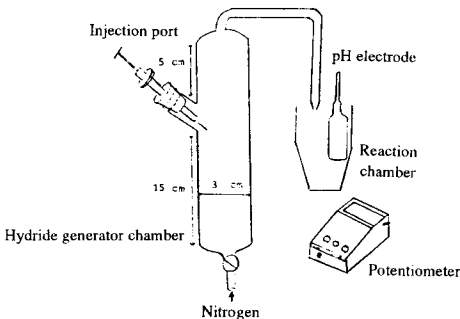


Figure 1. The arsene generation and apparatus for determination of arsenic by ion selective electrode

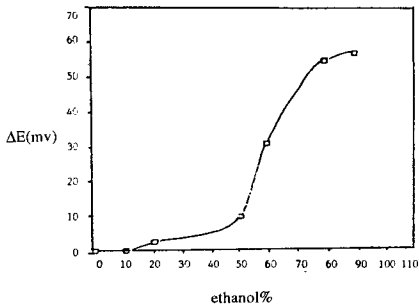


Figure 2. Percentage of ethanol on arsine reaction with mercury (II) chloride

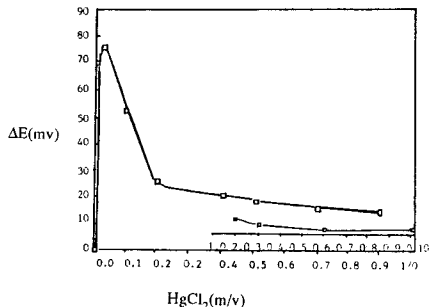


Figure 3. Effect of mercury(II) chloride on potential change obtained for 20 g arsenic(III)

(in 80:20 ethanol; water) was investigated by using various concentrations of mercury(II) chloride (in 80-20 ethanol; water). The results are presented in Figure 3. The suitable mercury(II) chloride concentration was in the range of 0.01-0.03% (m/v) and at this range maximum potential was obtained for hydrogen glass membrane electrode.

The optimisation of experimental conditions was investigated based on the potential change of hydrogen glass membrane electrode $E=E$ (after addition of NaBH_4) -E (before the addition of NaBH_4) from arsenic(III) standard solution $2\mu\text{g/ml}$. The effects of varying the hydrochloric acid concentration, mercury(II) chloride concentration, carrier gas flow rate, sample volume and reduction time are shown in Figure 4. Table 1 shows the optimised conditions used throughout the work.

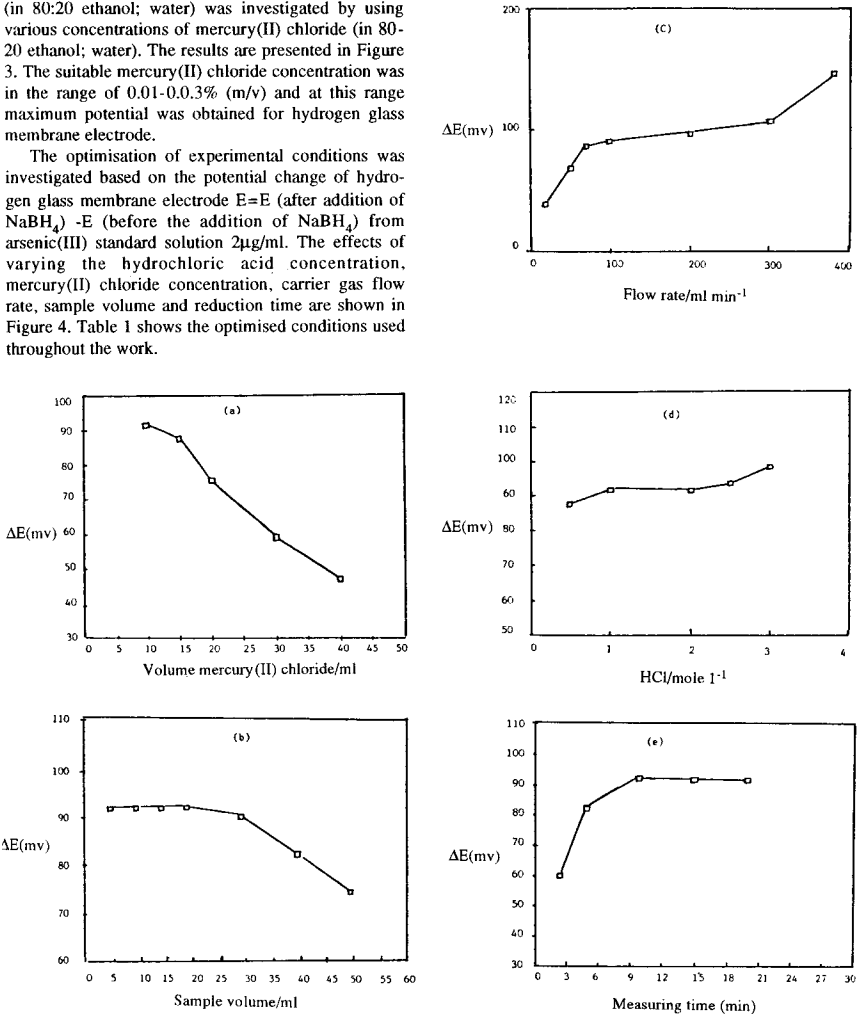


Figure 4. Optimisation of experimental conditions. Effect changing (a) mercury(II) chloride volume; (b) sample volume; (c) carrier gas flow rate; (d) hydrochloric acid concentration; (e) potential measuring time

Table 1. Experimentally optimised conditions

Mercury(II) chloride concentration	0.025% m/v (80-20 ethanol/H ₂ O)
Hydrochloric acid concentration	1 mol l ⁻¹
Sodium tetrahydroborate(III) concentration	1% m/v
Sample volume	10 ml
Carrier flow rate	100 ml/min
Reading time	10 minutes

Interferences

A number of ions such as Ag(I), Bi(III), Br⁻, CH₃COO⁻, Cl⁻, Co(II), Cu(II), F⁻, Fe(II), Hg(II), I⁻, K(I), Mg(II), Mn(II), Na(I), NH₄⁺, Ni(II), NO₃⁻, Pb(II), PO₄³⁻, Sb(III), Se(IV), Sn(II), SO₄²⁻ and tartarate were tested for interferences effects by determination of 2µg/ml of arsenic(III) in the presence of 1000 µg/ml of the potentials interferants. The results are shown in Table 2 and Figure 5. Bi(III), F⁻, Hg(II), Ni(II), NO₃⁻, Pb(II), Sb(III), Se(IV), Sn(II) and SO₄²⁻ are interferences for this method and can be removed by the following procedures:

Bi(III): By extraction of 5 ml of sample at pH 2:0 with 5 ml of dithizone (0.01M in chloroform).

Sb(III): By adding 5 ml of 0.05M 1-2-3 hydroxybenzene in 0.1M sodium tartarate to 10 ml of sample.

Se(IV), Hg(II), SO₄²⁻, F⁻ and NO₃⁻: By making the sample solution 9M in hydrochloric acid and extracting the sample with benzene and subsequently the back extraction of As(III) as AsCl₃ to aqueous phase.

Ni(II): By adding 1 ml of 2x10⁻⁴M EDTA to 10 ml of sample solution as a masking agent.

The efficiency of these treatments was assessed by analysis of solutions containing 2µg/ml of arsenic(III)

Table 2. Assessment of interferences

Ions	As(III)	Ions	As(III)
Ag ⁺	-	Mg ²⁺	-
Bi ³⁺	+	Mn ²⁺	-
Br ⁻	-	Na ⁺	-
CH ₃ COO ⁻	-	NH ₄ ⁺	-
Cl ⁻	-	Ni ²⁺	+
Co ²⁺	-	NO ₃ ⁻	+
Cu ²⁺	-	Pb ²⁺	+
F ⁻	+	PO ₄ ³⁻	-
Fe ²⁺	+	Sb ³⁺	+
Hg ²⁺	+	Se ⁴⁺	+
I ⁻	-	Sn ²⁺	+
K ⁺	-	SO ₄ ²⁻	+
		tartarate	-

"presence of interference effect indicated by "IN"

together with 1000µg/ml⁻¹ of interfering ions and the effect of interferences could be overcome without significant decrease in sensitivity of the method.

The calibration graph was obtained by plotting the electrode potential as a function of the logarithm of the arsenic concentration (Fig. 6). The calibration graph had the slope of 58.959mv which suggests a Nernstian behaviour of electrode systems. Based on 10

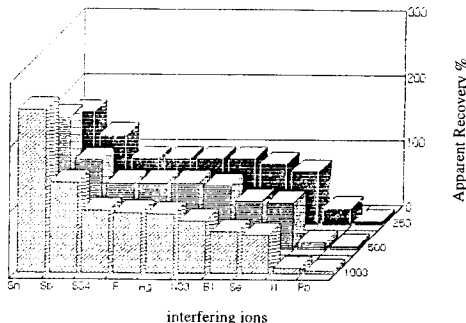


Figure 5. Apparent recovery of arsenic in presence of interfering ions

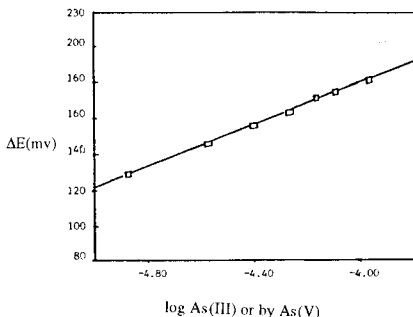


Figure 6. Calibration graph for arsenic(III) and arsenic(V)

replicated analyses, the relative standard deviation of technique was 2.8% for $2\mu\text{g}/\text{ml}^{-1}$ of arsenic.

Speciation of Arsenic (III) and Arsenic (V) by Controlling pH

It is believed that the reduction of arsenic(III) and arsenic(V) to arsine is a function of pH [17]. Therefore, a series of experiments was carried out using standard solutions containing $2\mu\text{g}/\text{ml}$ of arsenic(III) and arsenic(V) adjusting in the pH range of 1 to 9. The results are shown in Figure 7. It is believed that at

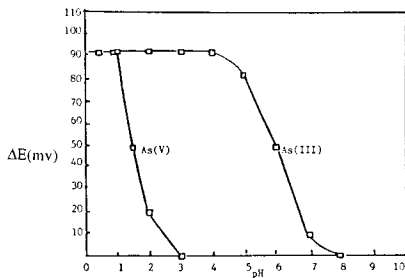


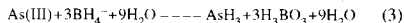
Figure 7. Effect of reduction pH on arsine generation

pH 1-2 the preliminary reduction of arsenic(III) is favourable.



while at pH 1-4 the reduction of arsenic(III) to arsine

is possible.



Reaction (2) is a function of pH at higher pH and is slower than reaction 3 [17]. Therefore, arsenic(III) and arsenic(V) can be determined separately in one analysis by controlling the pH of the solution. For speciation analysis of arsenic(III) and arsenic(V), the sample pH was adjusted to pH 4 and then treated with sodium tetrahydroborate. After 10 minutes, the potential was read and then using fresh mercury(II) chloride solution the pH of the solution was adjusted to pH 1.00 and then 1 ml of sodium tetrahydroborate(III) solution was added to the sample solution and the potential was measured after 10 minutes. The percent of recovery was found to be 103 ± 3 and 91 ± 3 for arsenic(III) and arsenic(V), respectively, using this method.

Conclusion

A new ion selective system using a glass membrane electrode was developed for the determination of a small amount of arsenic based on arsine generation and its selective reaction with HgCl_2 in $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ (80%) solution. The effect of important parameters such as reagent concentration, pH, sample volume and carrier gas flow rate was investigated and optimised conditions were obtained for determination of As(III) and As(V). Speciation analysis of As(III) and As(V) with control of pH is possible using this method. The interference effect of some cations and anions was also investigated and the interfering species were removed. This technique is an accurate, simple, sensitive and inexpensive method for determining arsenic in real samples.

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