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High Sensitive Spectrophotometric Determination Method of Arsenic from Water

VU VAN TIEN[1], DAO VAN BAY[1], DANG XUAN THU[1] and TRAN VAN CHUNG[2,*]

[1]Hanoi National University of Education, 136 Xuan Thuy Street, Cau Giay District, Hanoi, Vietnam
[2]Department of Analysis, Institute of Chemistry and Materials, Hanoi, Vietnam

*Corresponding author: E-mail: tranchunghhvl@gmail.com

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Arsenic present in water may be determined by many methods such as atomic adsorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, electrochemistry and spectrophotometry with silver diethyldithiocarbamate. This study presents the determination of arsenic present in water by spectrophotometric method based on molybdate reagent. This method is highly sensitive and selective but has not been studied in detail. The obtained results exhibited the experimental optimum conditions for arsenic determination by spectrophotometric method using molybdate reagent. The method consists of two steps (i) arsinization producing AsH_3, (ii) $AgNO_3$, H_2O_2 oxidized AsH_3 reacting with molybdate reagent to produce molybdenum blue. The absorbance of molybdenum blue at the wavelength of λ = 878 nm has been used for arsenic determination. The limit of detection and limit of quantitation of the method are 2 and 7 ppb respectively

Keywords: Aresenic, Arsine, Arsenomolybdate blue.

INTRODUCTION

The arsenic of groundwater consumed of millions of people in the developing countries has become a major health concern. Because arsenic concentrations in drinking water far exceeding the guideline value of the World Health Organization (WHO) pose a serious health hazard to tens of millions peoples[1-3]. Symptom of acute poisoning usually occur within 1 h of ingestion, particularly in presence of food but be delayed for up to 12 h. Intake of 70 to 300 mg of arsenic trioxide may be fatal[4,5]. Arsenic present in water may be determined by many methods such as atomic adsorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), electrochemistry, spectrophotometry with silver diethyldithiocarbamate and molybdate reagent[6,7]. Arsenate in the water sample reacts with molybdate and a suitable reducing reagent gives blue colour due to formation of heteropoly species containing both Mo(V) and Mo(VI). This method is influenced by the phosphate species and other metallic ions present in water sample that give the colour with molybdate reagent. The influence of these chemical compounds may be overcome by conversion of arsenic species to arsine (arsinization), evolved and trapped in solutions containing $AgNO_3$ and H_2O_2 to convert arsine into arsenate. The arsenate compound then reacts with molybdate reagent and a suitable reducing reagent to form arsenomolybdate blue compound. This compound may be used for determining arsenic content by spectrophotometric measurement at the maximum wave length of 878 nm[8,9]. Present study, presents an investigation of high sensitive spectrophotometric method for arsenic determination present in water. The method consists of the arsinization of sample, oxidation of arsine and the formation of arsenomolybdate blue compound.

EXPERIMENTAL

All chemical reagents imported from Germany Merck company include: H_3AsO_4, $NaBH_4$, H_2O_2 30 %, $AgNO_3$, H_2SO_4, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The following stocks were prepared: As(V) solution of 1000 mg/L, $AgNO_3$ (0.01 M) and combined reagent (CR). The combined reagent was prepared according to the literature[5] as follows:

Sulfuric acid solution 2.5 M: Dilute 70 mL of sulfuric acid H_2SO_4 to 500 mL distilled water, denotes R_1.

Antimony potassium tartrate solution: Dissolve 0.270 g of antimony potassium tartrate $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ in 100 mL distilled water, denotes R_2.

Ammonuim molybdate solution: Dissolve 10 g of ammonuim molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 250 mL distilled water and store in plastic botlle at 4 °C, denotes R_3.

Ascorbic acid 0.1 M: Dissolve 4.4 g of acsorbic acid $C_6H_8O_6$ in 250 mL of distilled water, denotes R_4.

Above reagents are mixed in the following proportions for 100 mL, 50 mL, 2.5 M of R_1 + 5 mL R_2 + 15 mL of R_3 + 30 mL of R_4.

Experimental procedure

Arsinization and arsine oxidation: The arsinization (producing AsH_3) was carried out from arsenic species in the sample based on the reaction with $NaBH_4$ (solid) in the reaction vessel with stirred in the presence of acid solution HCl. The arsine gas with the N_2 carrier gas stream were filtered through a cotton layer impregnated with $Pb(CH_3COO)_2$ to enter the absorption part containing $AgNO_3$ and H_2O solutions. Here the AsH_3 was oxidized to produce As(V) (Fig. 1).

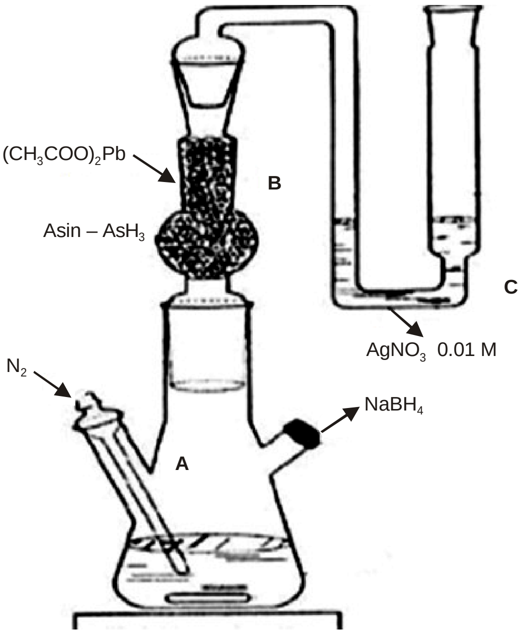

Fig. 1. Kits for arsinization; (A) Reaction vessel containing arsenic sample, $NaBH_4$, N_2 gas placed on magnetic stirrer (B) Filter of arsine gas by $(CH_3COO)_2Pb$; Part of absorption and oxidation of AsH_3 gas

Preparation of molybdenum blue: The obtained As(V) will react with the combined reagent solution in the other reactor vessel to producing arsenomolybdate and molybdenum blue compound. This compound was used to determination of arsenic concentration in the sample.

Determination of arsenic concentration: Arsenic concentration was determined based on the measurement of absorbance of molybdenum blue compound at the wavelength of 878 nm using spectroscopy UV-Vis Biochrom Libra (USA).

Determination of factors influencing onarsinization process: According to the reaction pathway in Fig. 1, all chemicals of oxidation ($AgNO_3$, H_2O_2), combined reagents (CR) (5.0 mg) were kept constant. The absorbance of the arsenomolybdate blue compound, depending on V_{HCl}, V_{HCl} + $NaBH_4$ and blowing time of N_2 was measured at the wavelength of 878 nm.

Influence of V_{HCl}: The experiments were carried out in the conditions such as arsenic solution of 50 mL (0.10 mg/L), $NaBH_4$ solution, 15 mL (1 %), the HCl (2 M) acid volume was added into the reaction vessel varying from 7 to 13 mL. The experimental sample presented in the Table-1.

Influence of ratio of $(HCl+NaBH_4)$/As: The experimental data of the samples are presented in the Table-2.

Influence of arsenic concentrations: The experimental data of the samples are presented in the Table-3.

Influence of the N_2-blowing: The experimental data of the samples are presented in the Table-4.

Experiments determining the optimum conditions of molybdenum blue formation: For all experiments, the absorbance of the arsenomolybdate blue compound was measured at the wavelength of 878 nm.

Influence of pH: The experimental data of the samples are presented in the Table-5.

Influence of the ratio (V_{CR}/V_{As}): The experimental data of the samples are presented in the Table-6.

Influence of the stability of arsenomolybdate blue: The experiments were carried out in the 50 mL volumetric flask

TABLE-1
EXPERIMENTAL DATA OF SAMPLES

No.	V_{As} (0.1 mg/L) (mL)	$V_{HCl\ 2\ M}$ (mL)	V_{H_2O} (mL)	V_{NaBH_4} 1 % (mL)	V_{CR} (mL)	n_{HCl} (mmol)	n_{NaBH_4} (mmol)	pH
1	50	7	13	15	5	14	3.965	2.32
2	50	8	12	15	5	16	3.965	1.38
3	50	9	11	15	5	18	3.965	1.14
4	50	10	10	15	5	20	3.965	0.95
5	50	11	9	15	5	22	3.965	0.82
6	50	12	8	15	5	24	3.965	0.73
7	50	13	7	15	5	26	3.965	0.65

TABLE-2
EXPERIMENTAL DATA OF SAMPLES

No.	V_{As} (0.3 mg/L) (mL)	$V_{HCl\ 2\ M}$ (mL)	V_{NaBH_4} 1 % (mL)	V_{HCl} + V_{NaBH_4} (mL)	V_{CR} (mL)	n_{HCl} + n_{NaBH_4} (mmol)	n_{As} (mmol)	pH
1	50	7	10.5	17.5	5	16.775	2.0×10^{-4}	1.14
2	50	8	12.0	20.0	5	19.172	2.0×10^{-4}	1.05
3	50	9	13.5	22.5	5	21.568	2.0×10^{-4}	0.99
4	50	10	15.0	25.0	5	23.965	2.0×10^{-4}	0.96
5	50	11	16.5	27.5	5	26.361	2.0×10^{-4}	0.91
6	50	12	18.0	30.0	5	28.758	2.0×10^{-4}	0.87
7	50	13	19.5	32.5	5	31.154	2.0×10^{-4}	0.82

TABLE-3
EXPERIMENTAL DATA OF SAMPLES

No.	V_{As} (0.01 mg/L) (mL)	$V_{HCl\ 2\ M}$ (mL)	$V_{NaBH_4\ 1\ \%}$ (mL)	V_{CR} (mL)	pH
1	50	10	15	5	0.96
2	70	10	15	5	0.98
3	100	10	15	5	1.00
4	250	10	15	5	1.05
5	350	10	15	5	1.07
6	500	10	15	5	1.10
7	750	10	15	5	1.13

TABLE-4
EXPERIMENTAL DATA OF SAMPLES

No.	V_{As} (0.1 mg/L) (mL)	$V_{HCl\ 2\ M}$ (mL)	$V_{NaBH_4\ 1\ \%}$ (mL)	V_{CR} (mL)	N_2 blowing (min)
1	50	10	15	5	10
2	50	10	15	5	15
3	50	10	15	5	20
4	50	10	15	5	25
5	50	10	15	5	30
6	50	10	15	5	35
7	50	10	15	5	40

TABLE-5
EXPERIMENTAL DATA OF SAMPLES

No.	V_{As} (2 mg/L) (mL)	V_{CR} (mL)	V_{total} (mL)	pH
1	0	5	50	0.8
2	5	5	50	0.2
3	5	5	50	0.4
4	5	5	50	0.6
5	5	5	50	0.8

TABLE-6
EXPERIMENTAL DATA OF SAMPLES

No.	V_{As} (2 mg/L) (mL)	V_{CR} (mL)	V_{CR}/V_{As} (mL/mL)	V_{Total} (mL)	pH
1	0	5	/	50	0.8
2	5	2	2/5	50	0.8
3	5	3	3/5	50	0.8
4	5	4	4/5	50	0.8
4	5	5	5/5	50	0.8
6	5	6	6/5	50	0.8
7	5	7	7/5	50	0.8

containing the As(V) solution of 5 mL (2 mg/L) and combined reagent solution of 3 mL, pH = 0.8.The absorbance of the arsenomolybdate blue were measured during the time from 0 to 120 min.

RESULTS AND DISCUSSION

Factors influence on arsinization process: The factors influencing on the arsinization is determined by the absorbance of the arsenomolybdate blue.

Dependence of absorbance on V_{HCl}: The dependence of absorbance of the arsenomolydate blue on V_{HCl} is presented in the Fig. 2. The results indicate that the absorbance of sample increases with the HCl-amount increasing and reaches a constant value. This is due to the formation of arsenomolybdate compound increased. The H^+ role may be explained by the following reactions:

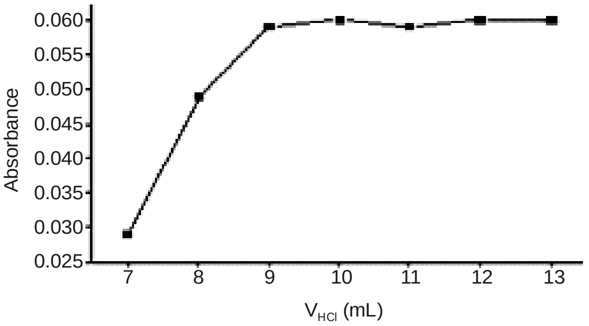

Fig. 2. Dependence of absorbance on V_{HCl} volume

$$4H_3AsO_4 + BH_4^- + H^+ \longrightarrow 4\ H_3AsO_3 + HBO_3 + H_2O$$

$$4H_3AsO_3 + 3BH_4^- + 3H^+ \longrightarrow 4\ AsH_3 + 3HBO_3 + 3H_2O$$

The obtained arsine gas can be oxidized by $AgNO_3$ and H_2O_2 to form As(V) compound then reacts with combined reagent solution to producing arsenomolybdate blue. Table-1 indicated that the optimum conditions for the arsinization process are: pH from 0.65 to 1.14 ratio of $V_{HCl}/V_{NaBH_4} = 10/15$.

Dependence of absorbance on the ratio of (HCl + $NaBH_4$): The dependence of $V_{HCl\ +\ NaBH_4}$ is presented in the Fig. 3.

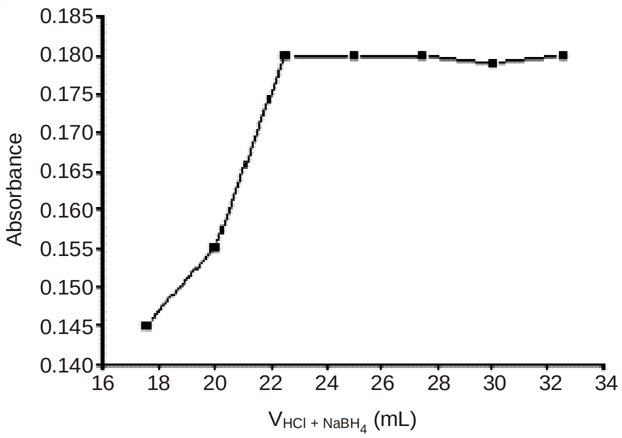

Fig. 3. Dependence of absorbance on $V_{HCl\ +\ NaBH_4}$

These experimental results indicate that when the arsenic amount is kept constant, the absorbance of arsenomolybdate blue increases with the $V_{HCl\ +\ NaBH_4}$ increasing then reaches constant value. Table-2 indicated that in this case, the optimum conditions for the arsinization process are: ratio of $V_{HCl} + V_{NaBH_4}$ = 25 mL and the ratio of $(n_{HCl} + n_{NaBH_4})/n_{As} = 23.965/2.0 \times 10^{-4} \sim 1.2 \times 10^5$, pH = 0.96. These conditions may be applied in practice for producing AsH_3.

Dependence of absorbance on arsenic concentrations: The dependence of absorbance of arsenomolydate blue on the arsenic concentrations or volume of arsenic solutions, 0.01 mg/L respectively is presented on Fig. 4.

The experimental results indicated that the absorbance of the arsenomolybdate blue is proportional to the added arsenic solutions in the range of volume of 50 to 750 mL (0.01 mg/L) or from arsenic concentrations of 6.66×10^{-3} to 9.67×10^{-3}, respectively. This is a good base for establishing the standard plot for the arsenic determination.

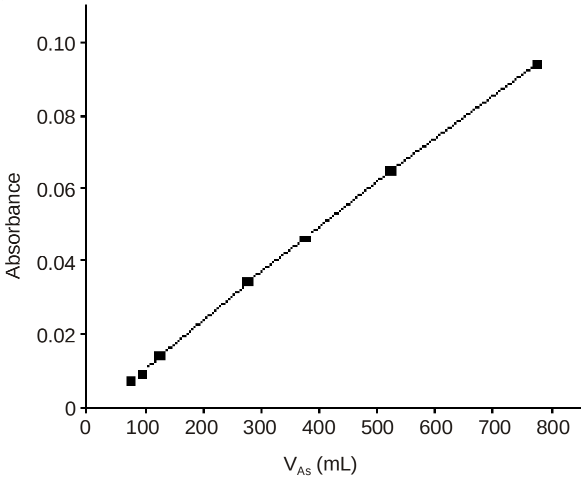

Fig. 4. Dependence of absorbance on the added volume of arsenic solutions

Dependence of absorbance on the N_2-blowing time: The dependence of absorbance of the arsenomolydbate blue on the N_2-blowing time was presented in Fig. 5.

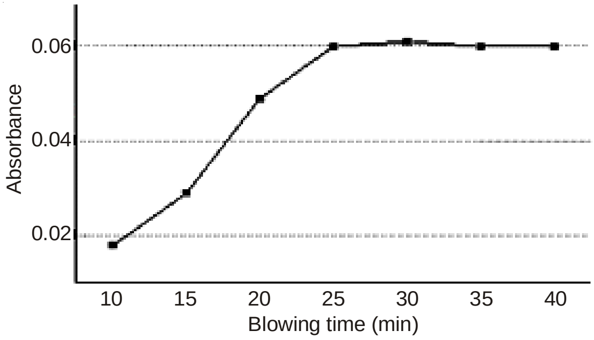

Fig. 5. Dependence of absorbance on the N_2-blowing time

The experimental results have indicated that the sufficient time of N_2-blowing in this case is 0.5 h.

Results determining the optimum conditions of molybdenum blue formation: The optimum conditions of molybdenum blue formation were determined by the dependence of its absorbance on the pH, ratio of V_{CR}/V_{As} and the stability of arsenomolybdate blue.

Dependence of absorbance on pH of solution: The results of dependence of absorbence on pH is presented by the UV-visible spectroscopy (Fig. 6).

The results have showed that the pH value of 0.8 may be selected for the experiments as the optimum value.

Dependence of absorbance on the volume of V_{CR}: The experiments were carried out with 5 mL of arsenic solution, 2 mg/L; pH = 0.8; the volume of combined reagent solution varying from 2 to 7 mL, reaction time of 0.5 h. The dependence of absorbance of arsenomolybdate blue on combined reagent volume is presented in Fig. 7.

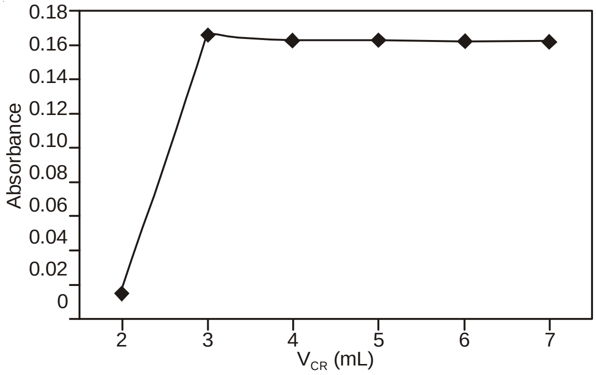

Fig. 7. Dependence of absorbance on volume of combined reagent

The experimental results have showed that the absorbance in the samples increases with volume of combined reagent increased then reached the constant when the volume ratio of V_{CR}/V_{As} 3/5. In this case the $V_{CR}/V_{As} = 3/5$ is selected as the optimum condition for the experiments

Stability of arsenomolybdate blue: The results of experiments (not showed here) indicated that the asrenomolybdate blue can be stable for 0.5 h.

Standard plot of the dependence of absorbance asrenomolybdate blue on the As(V) concentration: The standard plot was implemented in the selected optimum conditions is presented in Fig. 8.

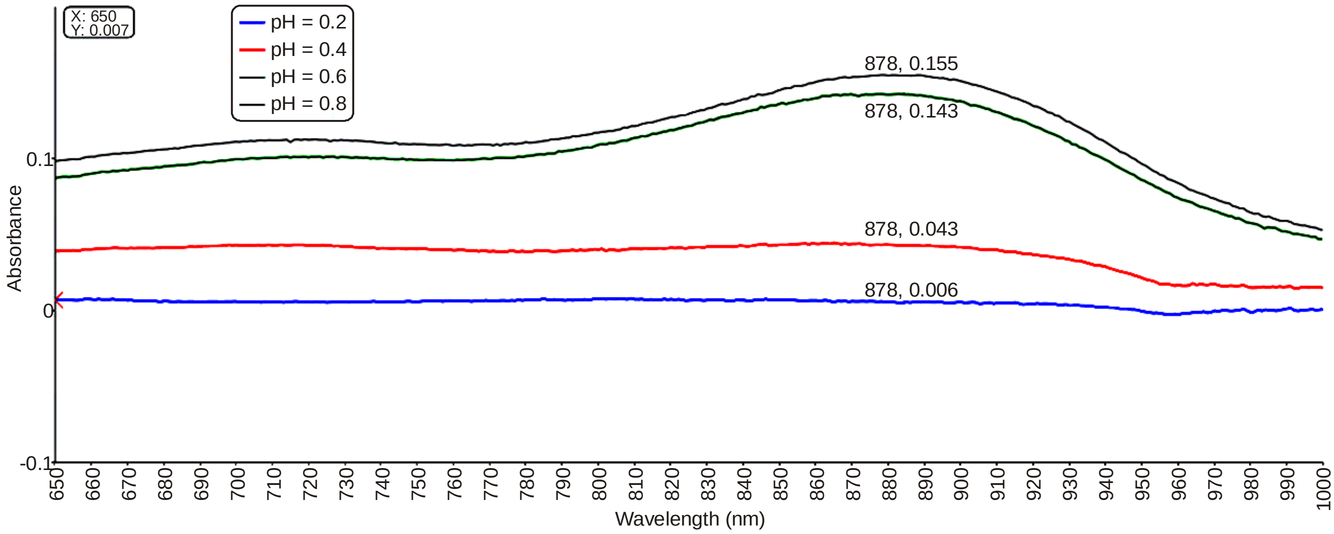

Fig. 6. UV-visible spectroscopy, sample consisting of 5 mL solution As(V), 2 mg/L; 5 mL solution of combined reagent, reaction time of 0.5 h, pH varying from 0.2 to 0.8

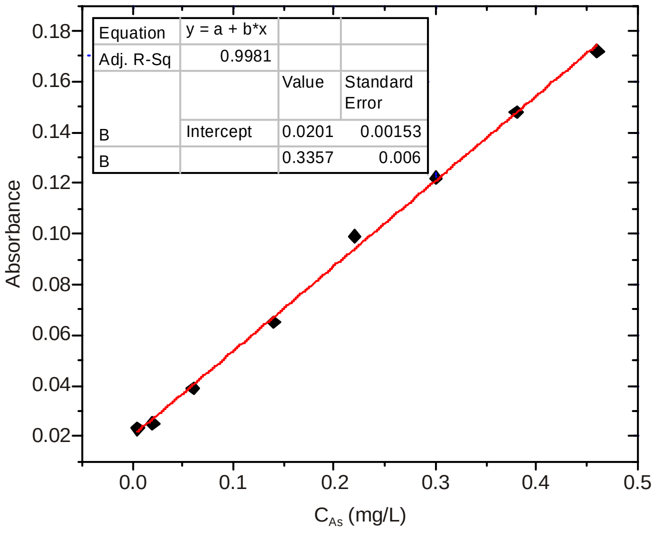

Fig. 8. Standard plot for determination of arsenic concentration

Basing on the standard plot, the values of limit of detection (LOD) and limit of quantitation (LOQ) were determined and are 2 ppb, 7 ppb, respectively

Conclusion

A high sensitive spectrophotometric method for arsenic determination from water has been established systematically. The method consists of two steps (i) arsinization producing AsH_3, (ii) $AgNO_3$, H_2O_2 oxidized AsH_3 reacting with molybdate reagent and conbined reagent to produce molybdenum blue. The absorbance of molybdenum blue at the wave length of λ = 878 nm has been used for arsenic determination. The LOD and LOQ of the method are 2 and 7 ppb, respectively.

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