Scientific Paper

Solid Phase Extraction of Arsenic by Sorption on Naphthalene-Methyltrioctyl Ammonium Chloride and Spectrophotometric Determination

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Abstract

A simple, sensitive, rapid and reliable preconcentration method has been developed for spectrophotometric determination of trace amounts of arsenic. Arsenic was retained on a minicolumn of adsorbent naphthalene, as an ion associate of arsenomolybdate and methyltrioctylammonium ions. The contents of column was dissolved in a small volume of *N*,*N*-dimethylformamide (DMF) having stannous chloride ($SnCl_2$) as a solvent. To take advantage of the procedure the reagent concentration and reaction condition must be optimized.

Effects of different parameters such as molybdate percent, hydrochlorice acid concentration in aqueous solution, the flow rate of the sample solution through the minicolumn, selection of a suitable solvent to dissolve the adsorbent and also various salts and metal ions as interferences were investigated. Recording the variation in absorbance at a wavelength of 715 nm at room temperature completes the determination of arsenic concentration. The method allows determination of arsenic in the range of 1–8 ng mL^{-1} in the initial solution with r=0.999 (n=6). The relative standard deviation for 15 replicate measurements of 6.0 ng mL^{-1} of arsenic was 1.3% and the 3s detection limit was 0.067 ng mL^{-1}. The preconcentration factors of 100 and 167 could be achieved when using a 5 and 3 mL DMF for dissolving adsorbent, respectively. The optimized method was successfully applied to determination of arsenic in natural water, synthetic sample and fish.

Keywords: Arsenic, solid phase, extraction, spectrophotometric determination

Introduction

The real toxicity of arsenic to the human body usually comes from several ways such as, water and foods. Arsenic contamination in natural water is a worldwide problem. In water, the most common valence states of arsenic are As(V) (arsenate), which is more prevalent in aerobic surface waters and As(III) (arsenite), which is more likely to occur in aerobic ground waters.[1,2]

The amount of arsenic allowed in drinking water has been set at 0.01 mg L^{-1} by the World Health Organization (WHO), but in the most drinking water of the world it is more than this.[3] Many scientists are trying to find the best method to clean the water from arsenic contamination.[4–6] Different methods were used for arsenic determination. Some examples are titrimetry,[7] chemiluminescence,[8] polarography,[9] Hydrid generation atomic absorption spectrometry,[10] electrothermal atomic absorption spectroscopy,[11] HPLC-HGAAS,[12] and HPLC-HGAES.[13]

Many methods for the spectrophotometric determination of trace amounts of arsenic are based on the formation of an ion-pair between arseno-molybdate and a large dye cation.[14,15] These methods, however, have not enough sensitivity and selectivity to establish the arsenic amounts of natural waters without using a preconcentration step.[16] A preconcentration step be able not only concentrate the analyte but also simplify the matrix of the sample that is usually strongly desired. There are many kinds of preconcentration methods, such as liquid-liquid extraction[17] and ion exchange[18] that have been used for the separation and enrichment of trace amounts of arsenic from aqueous solutions. These classical preconcentration methods are usually time consuming and tedious. Furthermore, these methods usually require large amounts of high purity organic solvents, which are harmful to health and creates environmental problems. Since the introduction of the concept of the solid-phase extraction (SPE) technique about 20 years ago, there has been sustained interest in the application of this method to various contaminants in complex matrix environmental samples. This preconcentration technique has the advantage of high recovery, short analysis time, high enrichment factor, low cost and consumption of organic solvents.[19] Up to now, several kinds of sorbent, such as activated alumina,[19] chelating resins,[20] activated carbon,[21] polymeric support,[22] and C-18 bonded silica have been used for the preconcentration of metal ions.[23]

In this paper, a sensitive and highly selective preconcentration method for the determination of arsenic is reported. Arsenic is reacted in a suitable acid solution with ammonium molybdate to form the practically colorless molybdoarsenic heteropoly acid.[24] Then the column contents dissolved in *N*,*N*-dimethyl-formamide (DMF) having $SnCl_2$ as a solvent and reducing agent respectively. $SnCl_2$ reduced the molybdoarsenic acid to arsenomolybdenium blue,[24] therefore absorption and sensitivity are increased because arsenomolybdenium blue has higher molar absorption coefficient that molybdoarsenic acid.

Effects of different parameters are investigated and optimized. The optimized parameters then were utilized for the trace determination of arsenic in various standard solutions of some kinds of fishes and natural waters. The method is economical, rapid, reliable and sensitive.

Results and Discussions

Spectral Characteristics

The absorption spectrum of the ion associate of arsenomolybdate and methyltrioctyl ammonium ions in DMF having $SnCl_2$ against a reagent blank prepared under general procedure was recorded. The most absorbance was at wavelength of 715 nm. All absorbance then were determined at this wavelength.

Effect of Variables

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to obtain the optimized system. These optimized parameters were used for all the experiments.

The effect of molybdate percent in aqueous solution in the range of 0.01%–0.07% was investigated. Absorbance is maximum at 0.04–0.05% molybdate as shown in Figure1.

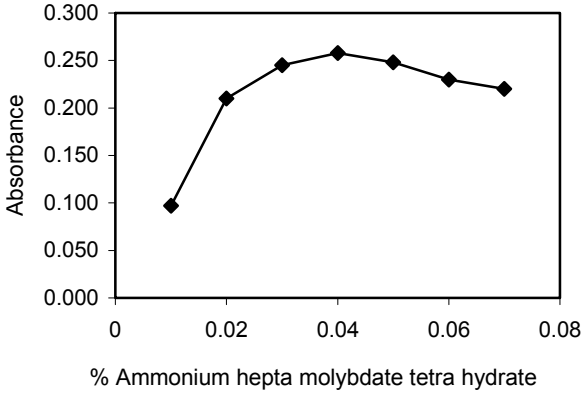

Figure1. Effect of % of ammonium hepta molybdate tetra hydrate on the absorbance.

The influence of hydrochloric acid concentration in aqueous solution also was studied in the range of 0.015–0.308 M. The results showed maximum absorbance is at 0.08 M HCl (Figure2).

The flow rate of the sample solution through the minicolumn is also very important, since it is not only affects the recovery of arsenic but also control the time of analysis.

It is always expected that sample solution can be pumped through the column at a higher flow rate without sacrificing the recoveries, because a large volume of sample solution is needed in the preconcentration. The effect of the flow rate of the sample solutions on the recoveries of arsenic on a minicolumn placed was examined in the range of 1–20 mL min^{-1}. It was found that in the range chosen for our experiments the flow rate of the sample solutions had no obvious influence on the quantitative recoveries of arsenic on the minicolumn. These experimental results show that the adsorption in this system is a rapid kinetic process. A flow rate of 2 mL min^{-1} was used for small volume solution and 10–15 mL min^{-1} used for large volume solution.

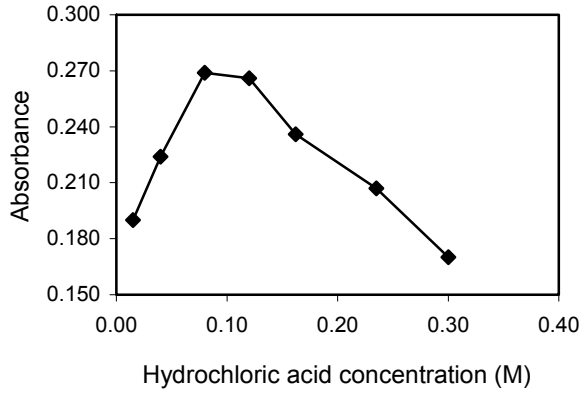

Figure 2. Effect of hydrochloric acid concentration on the absorbance.

Effect of consistency of absorbance with time was also studied from 2–30 minutes. It was found that the absorbance of arsenomolybdenioum blue was constant from 2–20 minutes.

The effect of ionic strength was studied by using sodium chloride solution in the range of 0.1–1 M. It was found that in this method ionic strength had no interference for determination of desired ion in real samples.

Preconcentration Factor of Method

The influence of sample volume on the retention of arsenic on the column was studied in order to obtain the preconcentration factor. The absorbance of 4 μg arsenic was constant as long as the sample volume did not exceed 400 mL. Therefore, a preconcentration factor of 100 is obtained when using 5 mL DMF solvent

for dissolving solid phase. If 3 mL DMF is used a preconcentration factor of 167 could be achieved.

Retention Capacity of the Adsorbent

A funnel-tipped glass tube was used to determine the retention capacity of the adsorbent. The funnel was filled with the adsorbent slurry to a height of 2 cm (about 1 mL of slurry adsorbent) and slightly pressed with a flat glass rod. A solution of 1000 μg arsenic (more than amount of adsorbed by adsorbent) in optimum condition was passed through the column. The amount of undesorbed arsenic by column collected in suitable volumetric flask and determined by spectrophotometric method. The solid mass in the column was filtered through a filter paper, aspirating and dried in room temperature. The adsorbent was weighted to determine its mass. For determination of retention capacity of the adsorbent, by calculating amount of arsenic adsorbed on the column divided to mass of adsorbent. The result showed retention capacity of the adsorbent was 14.6 mg of arsenic per gram of adsorbent.

Choice of Solvent

It was essential to select a proper solvent because $SnCl_2$ should be dissolved in it. Therefore a number of solvents were studied to dissolve the adsorbent. $SnCl_2$ is insoluble in normal organic solvents such as acetone, tetrahydrofuran, methanol and ethanol but it is soluble in DMF and acetonitrile. DMF having $SnCl_2$ was preferred due to high solubility (of solid mass) and stability. It was found that 3 – 5 mL of this solvent was sufficient to dissolve whole column thus enhancing the sensitivity of method. Acetonitrile having $SnCl_2$ dissolved whole the column but absorbance of this solution was unstable.

Calibration Curve

The calibration curve for determination of arsenic was prepared according to the general procedure under the optimum conditions. A linear calibration graph was obtained in the range 1–8 ng mL^{-1} arsenic in the initial solution with r=0.999 (n=6). The 3s detection limit was 0.067 ng mL^{-1} and relative standard deviation for 15 replicate measurements of 6.0 ng mL^{-1} of arsenic was 1.3%.

Effect of Diverse Ions

Various salts and metal ions were added individually to a solution containing of 0.4 μg As and the general procedure was applied. An error of ±3% was considered tolerable. The results are given in Table1. Many of the ions that examined have not shown any interference up to 250-tolerance ratio (w/w), but PO_4^{3-}, SO_4^{2-} and SiO_3^{-2} have shown interferences. PO_4^{3-} and SO_4^{2-} were masked with 1 mL of 0.8% $Ca(NO_3)_2$ solution at pH 8.5–9 and 1 mL of 0.6% $Ba(NO_3)_2$ solution respectively. To reduce SiO_3^{-2} interference added F^- to solution mentioned above and after formation of $(SiF_6)^{2-}$ the solution passed from the minicolumn and then washed with 5 mL boric acid (2%) solution. Therefore, SiO_3^{-2} eliminated from the minicolumn, without any effect on elution of arsenic.

Table 1. Effect of interfering on the determination of 4 μg arsenic.

Ion tested	Tolerance ratio (w/w)
Na^+, K^+,Ca^{2+}, Mg^{2+}	250
Co^{2+},Al^{3+}, Bi^{3+}, Zn^{2+}	250
Pb^{2+}, Ni^{2+}, Cl^-, F^-	250
Br^-,NO_3^-,$C_2O_2^{2-}$	250
Cr^{3+}, SCN^-, CN^-, ClO_4^-	220
Cu^{2+}, Cd^{2+}, Fe^{3+}, Tl^+	125
SO_4^{2-},	15, 125[a]
PO_4^{3-}	10, 125[b]
SiO_3^{2-}	10, 125[c]

[a] Masked with $Ba(NO_3)_2$ 0.6% W/V, [b] Masked with $Ca(NO_3)_2$ 0.8% W/V, [C] Masked with F^- and desorbed column with 5 mL boric acid 2% W/V.

Applications

In order to test the applicability of the method, it was applied to the determination of arsenic in Dez river water, Ravand drinking water, synthetic sample and fish. The samples were acidified with nitric acid to the pH of about 2 immediately after collection to prevent any loss of arsenic and were stored in glass bottle until analyzed. The sample fish from Dez river, Iran is prepared by dried 10 g sample at 50 °C for 24 hours in oven, then 0.1 g of sample decomposed by heating with 10 mL of concentrate nitric acid at 40 ºC for 16 hours, then 2 mL of 3% hydrogen peroxide was added to the solution and heated until became dried and this solution diluted to 100 mL in volumetric flask. An aliquot of this solution and water samples quantified by a standard addition method and using the general procedure and hydrid generation AAS for determination of arsenic. The results are presented in Table 2 showed acceptable accuracy and precision.

Table 2. Determination of Arsenic in river water, drinking water, fish and synthetic samples.

Sample	arsenic added	arsenic found[a]
Ravand drinking water	–	Nil[c]
Dez river water[b]	–	Nil[c]
Fish without skin[b]	–	1.164±0.14 µg/g
Fish with skin[b]	–	1.646±0.17 µg/g
Synthetic sample Containing: I^-, Br^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Ba^{2+}, Na^+ and K^+ 100 µg each	4 µg/mL	4.1±0.02 µg/g

[a] Mean ± standard deviation (n=3), [b] Standared addition method used, [c] Very close to detection limit.

Conclusions

The used method provided a simple, reliable, sensitive and selective for the determining trace amounts of arsenic since a preconcentration factor of 100–167 can easily be achieved by using different volume of solvent for dissolved solid phase. Therefore, the proposed preconcentration method could be used to determine of arsenic at very low concentration. A few interferences were observed that by masking agent their interferences eliminated. As a result even in presence of many ions, good precision and accuracy were obtained. The method can be applied to the analysis of different sample such as river water, drinking water and fish. Since the proposed method requires only simple glassware and a small volume of organic solvent for dissolution of the complex, it is very economical.

Experimental

Apparatus

Absorbance-wavelength graphs were recorded on a UV-Visible recording spectrophotometer (Perkin-Elmer, Germany). Absorbance was measured with a spectra 162 (Sanjesh, Iran) spectrophotometer with 1 cm quartz cell. A funnel-tipped glass (50 mm×6 mm i.d) with naphthalene was used as preconcentration column. The column loaded with adsorbent was lightly pressed with the flat end of a glass rod so that its height would be about 2.0 cm.

Reagents

All the chemicals used were of analytical-reagent grade or of the highest purity available. Standard arsenic(V) solution (1mg mL^{-1}) 0.132 g of arsenioum oxide dissolved in 2 mL NaOH 2 M and the solution diluted with water, and added 1 g potassium proxy disulfate to oxidized arsenic to arsenate. The solution then was diluted with water in a 100 mL volumetric flask. The solution then became standard and more dilute solutions were prepared daily from this stock solution. Molybdate (Merck) 0.2% reagent solution and hydrochloric acid (Merck) 0.8 M were prepared by dissolving appropriate amount of each compound in water. For interference study, prepared of cations solution used their nitrate salts and for anions solution used alkali metal salts (1 mg mL^{-1}).

Adsorbent Preparation

A solution of adsorbent was prepared by dissolving 20 g naphthalene (Merck) and 1 g methyltrioctylammonium chloride (MTOA) in 40 mL of aceton (Merck) on a hot-plate stirrer at ~40 °C. This solution was transferred into a beaker containing 1500 mL water in a fast stream with continuous stirring at room temperature. It was stirred for about 30 min. and allowed to stand for other 30 min. at ambient temperature. The supernatant solution of naphthalene coprecipitated with MTOA was washed twice by water. The adsorbent in the form of a slurry was stored in a polyethylene bottle for subsequent use.

General Procedure

A suitable aliquot of standard sample solution containing of 1–7 μg As(V) was transferred into a 20 mL beaker. Then 1 mL of 0.2% molybdate reagent solution and 0.5 mL of 0.8 M HCl solution was added (these parameters should be optimized) then the solution was diluted to about 10 mL by water.

The column loaded with the MTOA-Naphthalene adsorbent and arsenomolybdate was passed through the column at a flow rate of 2 mL min^{-1}. The column packing was washed with a small volume of water and the aspirated strongly for a few seconds. The naphthalene material pushed down with a flat glass rod to eliminate the excess of water attached to naphthalene. The contents of column then were dissolved in DMF having $SnCl_2$ as a solvent and reducing agent. The variation in absorbance of this solution was recorded at a wavelength of 715 nm. After the optimized parameters the absorbance for standard amounts of arsenic were measured and a calibration curve was constructed against a reagent blank prepared in a similar manner.

Acknowledgements

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References

1. Z. Slejkovec, J. T. Vanelteren, *Talanta* **1999**, *49*, 619–627.
2. C. K. Jain and I. Ali, *Wat. Res*. **2000**, *34*, *17*, 4304–3412.
3. M. D. Masud Karim, *Wat. Res*. **2000**, *34*, *1*, 304–310.
4. F. N. Robertson, Environmental Geochemistry and Health **1989**, *11*, 171–185.
5. F. Frost, D. Frank, K. Pierson, L. Woodruff, B. Roosina, R. Davies, J. Davies, *Environmental Geochemistry and Health* **1993**, *15*, 209–214.
6. A. Chatterjee, D. Das, B. K. Mandal, T. R. Chowdhury, G. Samanta, D. Chekaborty, *Analyst* **1995**, *120*, 643–650.
7. S. A. El-Shatoury, M. Tharwat, M. M. Girgis, A. Hassan, *Monatsh. Chem*. **1998**, *119*, 1357–1363.
8. H. Sakai, T. Fujiwara, T. Kumamura, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2317–2319.
9. F. T. Henry, T. M. Thrope, *Anal. Chem*. **1980**, *52*, 80–83.
10. S. Karthikeyn, T. P. Rao, C. S. P. Iyer, *Talanta* **1999**, *49*, 523–530.

11. N. Hata, H. Yamada, I. Kasahara, S. Tagachi, *Analyst* **1999**, *124*, 23–26.
12. C. T. Tye, S. J. Haswell, P. O. Neill, K. C. C. Bancroft, *Anal. Chim. Acta* **1985**, *169*, 195–200.
13. G. Rauvet, R. Rubio, A. Padro, Fresenius, *J. Anal. Chem.* **1991**, *340*, 157–160.
14. C. Matsubara, Y. Yamamoto, K. Takomura, *Analyst* **1987**, *112*, 1257–1260.
15. T. Nasu, M. Kan, *Analyst* **1988**, *113*, 1683–1686.
16. K. Palanivelu, N. Balasubramaniam, T. V. Ramakrishna, *Talanta* **1992**, *39*, 5, 555–561.
17. J. Chappell, B. Chiswell, H. Olszowy, *Talanta* **1995**, *42*, 3, 323–329.
18. G. P. Miller, D. I. Norman, P. L. Frisch, Wat. *Res*. **2000**, *34*, 4, 1397–1400.
19. N. Pourreza, M. Behpour, *Microchemical Journal* **1999**, *63*, 250–256.
20. R. K. Sharma, Analyst **1995**, *120*, 2203–2205.
21. S. Smith, J. Nelissen, R. E. Vangrieken, *Anal. Chem*. Acta **1979**, *111*, 215–226.
22. A. S. Khan, A. Chow, Talanta **1986**, *33*, 182–184.
23. N. Pourreza, M. Behpour, *Anal. Chem. Acta* **2003**, *481*, 23–28.
24. Z. Marczenko, Spectrophotometric determination of Elements, Ellis Horwood, 1976, pp. 131–141.

Povzetek

Razvili smo enostavno, občutljivo in zanesljivo metodo predkoncentracije za spektrofotometrično določevanje arzena v sledovih. Sprva arzen v obliki arzenomolibdata zadržimo na predkoncentracijski kolonici z adsorbentom naftalenom z dodatkom metiltrioktilamonijevih ionov. Vsebino kolonice raztopimo v majhni količini *N,N*-dimetilformamida (DMF), v kateri je raztopljen $SnCl_2$.
Preučili smo učinke različnih dejavnikov, kot sta koncentraciji molibdata ter klorovodikove kisline, pretok raztopine analita ter topilo. Prav tako smo določili moteče ione in soli. Z meritvijo absorbance raztopine pri 715 nm končamo postopek. Območje linearnosti je 1–8 ng mL^{-1} ($R = 0{,}999$, $N = 6$). Relativni standardni odmik za 15 zaporednih določitev znane koncentracije raztopine arzena (6,0 ng mL^{-1}) je 1,3%, medtem ko je meja določitve 0,067 ng mL^{-1}. Dosegli smo predkoncentracijska količnika 100 in 167, z uporabo 5 oz. 3 mL DMF za raztapljanje. Optimizirano metodo smo uporabili za določitev arzena v vodi, sintetičnem vzorcu ter v vzorcu rib.