

Solid Phase Extraction of Zirconium as Arsenazo(III) Complex on Agar and Spectrophotometric Determination

N. Pourreza*, A. Mouradzadegan and S. Mohammadi

Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

(Received 26 May 2010, Accepted 24 February 2011)

A new solid phase extraction method for the separation and determination of zirconium using agar as an adsorbent is described. The method is based on the adsorption of zirconium as arsenazo(III) complex on agar in a mini-column, elution with sulfuric acid-acetone mixture and determination by spectrophotometry. The effect of different parameters such as pH, concentration of the reagent, eluting reagent, and volume of the sample, amount of the adsorbent and interfering ions was investigated. The calibration graph was linear in the range of 5-300 ng ml⁻¹ of zirconium under optimum conditions. The limit of detection based on 3S_b was 1.3 ng ml⁻¹ and the relative standard deviation (R.S.D) for ten replicate measurements of 15 and 200 ng ml⁻¹ of zirconium was 3.7 and 1.8%, respectively. The method was applied to the determination of zirconium in water and soil samples.

Keywords: Zirconium, Arsenazo(III), Agar, Solid phase extraction, Spectrophotometric determination

INTRODUCTION

Zirconium is used in the nuclear industry as a shielding material, in metal alloys, as catalyst in the organic reactions, in manufacture of water repellent textiles, in dyes pigment and ceramics [1]. Zirconium oxychloride has also been used as an antiperspirant. It has high melting point and good chemical stability, therefore, its determination by flame atomic absorption spectrometry (FAAS) is not very sensitive and can not be determined at concentrations less than 8 mg l⁻¹ [2]. Thus, direct determination of trace amounts of zirconium by FAAS is difficult to achieve. Various other methods have also been used for the determination of zirconium including inductively coupled plasma mass spectrometry (ICP-MS) [3], X-ray fluorescence [4], reverse phase liquid chromatographic separation (RP-LC) [5], voltammetry [6], potentiometric

method using ion selective electrodes [7] and spectrophotometric methods [8-10]. The spectrophotometric determination of zirconium can be carried out with alizarin S, pyrocatechol violet, xylenol orange only after separating interfering species [11]. Some of the quantitative determination methods such as chromatography suffer from heavy solvent consumption whose sensitivity is not sufficient for its determination. These deficiencies can be overcome by a preconcentration step prior to its determination.

Different separation and preconcentration procedures, such as liquid-liquid extraction followed by spectrophotometric measurement [12], solid phase extraction [13], flotation [14] and cloud point extraction [15] have been reported for the determination of zirconium. Solid-phase extraction is one of the fastest, economical and clean preconcentration methods to separate and concentrate trace metals from different samples [16]. We recently reported the use of modified agar as an adsorbent for the solid phase extraction and cold vapor

*Corresponding author. E-mail: npourreza@yahoo.com

determination of mercury [17]. Agar-agar powder is a mixture of branched and unbranched polysaccharides with OH functional groups. It has a heavy molecular weight and is insoluble in water at room temperature [18].

In this paper, a new approach for the application of agar as an extractor for solid phase extraction is proposed. The method was developed for the preconcentration of zirconium using agar as an adsorbent. Zirconium as arsenazo(III) complex is retained on a column containing agar. The complex is then eluted by sulfuric acid-acetone mixture (2:1) and its absorbance is measured at 534 nm.

EXPERIMENTAL

Apparatus

A GBC Cintra 101, UV-Vis spectrophotometer (Australia) was used for recording absorption spectra and absorbance measurements using 1 cm glass cells. A digital pH-Meter model 632, Metrohm (Switzerland) with a combined glass electrode was used for pH adjustments. A Tebazma vacuum pump (Iran) was used for pumping the solutions.

Reagents

Analytical reagent-grade chemicals and double distilled water were used throughout this study. A stock solution of 1000 $\mu\text{g ml}^{-1}$ of zirconium was prepared by dissolving 0.3532 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Merck) in water adding a few drops of concentrated HCl (Merck) and diluting to the mark in a 100 ml volumetric flask. More diluted solutions were prepared using this stock solution. 6.4×10^{-4} M solution of arsenazo(III) (Merck) was prepared by dissolving 25 mg of the dye in water and diluting to 500 ml in a volumetric flask. 2 M solution of HCl (Merck) was prepared by diluting 83.3 ml of concentrated HCl to 500 ml in a volumetric flask. 2.5 M solution of H_2SO_4 (Merck) was prepared by diluting 69.5 ml of the acid to 500 ml in a volumetric flask.

General Procedure

A glass tube (7 cm length and 7 mm i.d.) with a very fine bore was used as a preconcentration column. A piece of cotton wool was placed in the column; it was then filled with 0.15 g of agar and slightly pressed with a flat glass rod. An aliquot of zirconium solution to effect concentration in the range of 5-

200 ng ml^{-1} , 2.5 ml of 6.4×10^{-4} M arsenazo(III) and 15 ml of 2 M hydrochloric acid were added to a 200 ml volumetric flask and diluted to the mark with water. The solution was passed through the mini-column at a flow rate of 3.0 ml min^{-1} . The adsorbed complex was eluted with 2.5 ml of 2.5 M of sulfuric acid-acetone mixture (2:1). A blank solution was also run under the same analytical conditions without adding any zirconium. The absorbance of the eluted solution was measured at 534 nm against the blank.

Preparation of the Ore Sample

One gram of powdered ore sample was weighed into a platinum crucible. Three ml of nitric acid was added and gently heated on a hot plate at 50 °C. Then, 3 ml of nitric acid and 10 ml of hydrofluoric acid was added. This solution was gently heated on a hot plate at 50 °C to near dryness. Three ml of nitric acid and 5 ml of perchloric were added to the residue and gently heated again on a hot plate at 50 °C. The residue was heated in 4 ml of aqua regia and evaporated to dryness. Finally, the residue was dissolved in 100 ml of hydrochloric acid (1.0 M). 10 ml of this solution was treated under the general procedure.

RESULTS AND DISCUSSION

Arsenazo(III) or 2,7-bis-(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfuric acid (Fig. 1) react with zirconium(IV) ions in acidic solution to give a colored complex with high molar absorptivity [19]. The zirconium(IV) complex with arsenazo(III) is formed through covalent bonding with AsO_3H_2 group, OH and an azo group [20-21]. This reaction is highly selective and sensitive to Zr(IV) and is generally carried out in 0.1-3.0 M of HCl [22]. It was found that this complex is retained by agar as a solid phase extractor but the blank solution containing no zirconium is only slightly retained. The adsorption of the complex on agar could

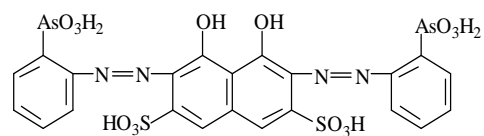


Fig. 1. The structure of arsenazo(III).

Solid Phase Extraction of Zirconium as Arsenazo(III) Complex

probably be through its interaction with OH functional groups on the surface of agar.

In acid solution, the maximum absorption of zirconium(IV) complex with arsenazo(III) in the visible region is at 665 nm while the maximum absorbance of arsenazo(III) in acidic solution is at 540 nm [21]. The absorption spectra of the eluted solution by acetone-sulfuric acid mixture for both the adsorbed complex and the blank are shown in Fig. 2. The spectra indicate that the maximum absorption is at 534 nm. This wavelength is very close to that of arsenazo(III) in acidic solution possibly implying that upon eluting the column with sulfuric acid-acetone mixture, the complex is decomposed. Therefore, absorbance measurements for the eluted solutions were performed at 534 nm. In order to obtain the maximum efficiency, the solid phase extraction conditions were optimized.

Influence of HCl Concentration

As was noted above, and as our preliminary investigation showed, the zirconium(IV)-arsenazo(III) complex is formed in acidic solution. Different acids such as HCl, HNO₃ and sulfuric acid were examined whereby HCl was selected as the acidic media for the formation of the complex because it affords higher absorbances. Accordingly, the effect of hydrochloric acid concentration on the formation of the complex was investigated. As presented in Fig. 3, the highest absorbance occurs at HCl concentration of 0.15 M. At higher HCl concentrations the absorbance is decreased probably because the adsorption of the complex on agar is less effective at higher acid concentrations. Therefore, 0.15 M of HCl was selected as the optimum.

Effect of Arsenazo(III) Concentration

Different solutions containing 100 ng ml⁻¹ of zirconium and various concentrations of arsenazo(III) were subjected to the solid phase extraction process. The results showed that the absorbance of the eluted solution increases up to 1.6 × 10⁻⁶ M and decreases slightly above this concentration. Therefore, concentration of 1.6 × 10⁻⁶ M was chosen as the optimum.

The Effect of Eluent Type and Concentration

Various acids and organic solvents such as ethanol, acetone, nitric acid (2.0 M), hydrochloric acid (2.0 M),

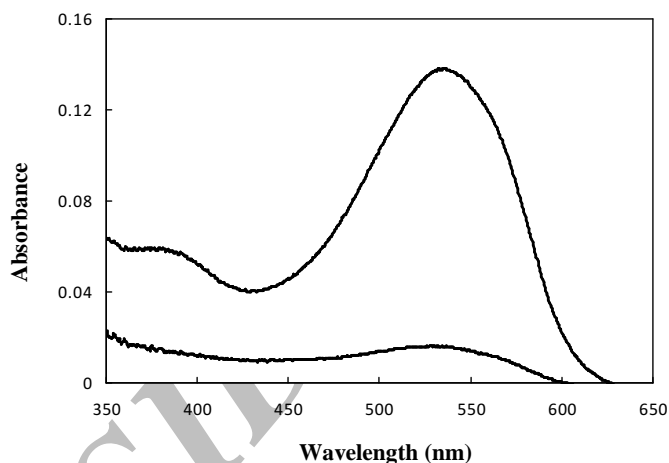


Fig. 2. The absorption spectrum of the (a) blank and (b) eluted solution by sulfuric acid. Conditions: HCl concentration; 0.15 M, arsenazo(III) concentration; 1.6 × 10⁻⁶ M, sample flow rate; 3 ml min⁻¹, sample volume; 200 ml, eluent; 2.5 ml of a mixture of 2:1 H₂SO₄ (2.5 M) and acetone, adsorbent amount 0.15.

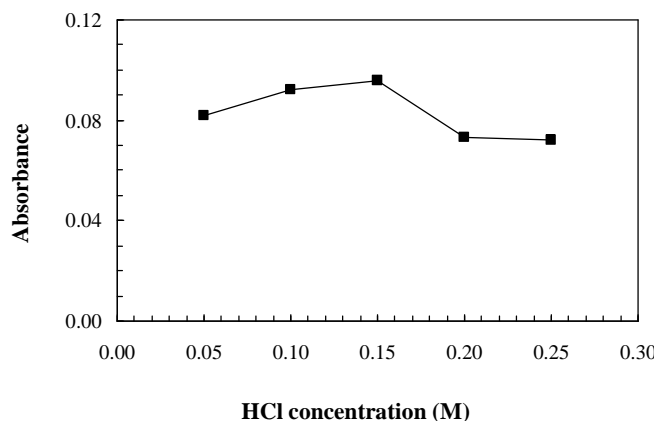


Fig. 3. Influence of hydrochloric acid concentration on the absorbance of the eluted complex. Conditions: arsenazo(III) concentration; 1.6 × 10⁻⁶ M, sample flow rate; 3 ml min⁻¹, sample volume; 200 ml, eluent; 2.5 ml of a mixture of 2:1 H₂SO₄ (2.5 M) and acetone, adsorbent amount 0.15.

sulfuric acid (2.0 M)-acetone mixture (2:1) and sulfuric acid (2.0 M) were used to identify the best eluents for the adsorbed zirconium on the column. The results showed that among the

solvents studied, acetone-sulfuric acid (2.0 M) mixture provided higher efficiency compared to the acids in aqueous and acid solutions and other solvents. Therefore, the concentration of sulfuric acid was optimized. According to the results shown in Fig. 4 concentration of 2.5 M of sulfuric acid affords higher absorbance. In subsequent studies, 2.5 ml of a mixture of 2:1 H₂SO₄ (2.5 M) and acetone were used as the eluent.

Effect of Amounts of Adsorbent

The amount of adsorbent is an important factor in the column studies for the quantitative recovery. In order to estimate the optimum adsorbent quantity different amounts of the adsorbent in the range of 0.05-0.25 g were applied for the preconcentration of zirconium. The results shown in Fig. 5 indicate that the absorbance of the eluted samples was almost constant when the amount of the adsorbent was greater than 0.10 g. Therefore in this procedure, 0.15 g of adsorbent was selected as the optimum. Each column, containing 0.15 g of agar, can be used three times without any loss in the recovery.

Effect of Sample Flow Rate

Flow rate of the sample solution is a measure of the contact time between the sample solutions and the adsorbent. Thus, the effect of sample flow on the adsorption of the complex was investigated. The retention for zirconium (IV)-arsenazo(III) complex was virtually quantitative for sample flow rates up to 3 ml min⁻¹. Consequently a flow rate of 3 ml min⁻¹ was selected as the sample flow rate.

The Effect of Sample Volume

For the preconcentration of trace elements, it is desirable to consider a variety of preconcentration factors. In order to obtain the preconcentration factors, maximum applicable sample volume must be established. For this purpose, preconcentration procedure was adopted for sample volumes of 100-500 ml containing the same amounts of zirconium (10 µg). The absorbance of the eluted solution from the column was constant for sample volumes up to 200 ml. Thus, in this procedure, by using 2.5 ml of elution solution, a preconcentration factor of 80 was determined.

Capacity of the Adsorbent

In order to determine the maximum amount of zirconium

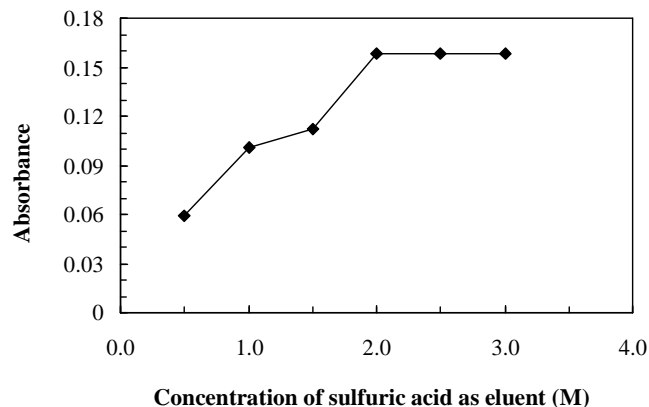


Fig. 4. Effect of sulfuric acid concentration as the eluent on the absorbance of the eluted complex. Conditions: HCl concentration; 0.15 M, arsenazo(III) concentration; 1.6×10^{-6} M, sample flow rate; 3 ml min⁻¹, sample volume; 200 ml, adsorbent amount 0.15.

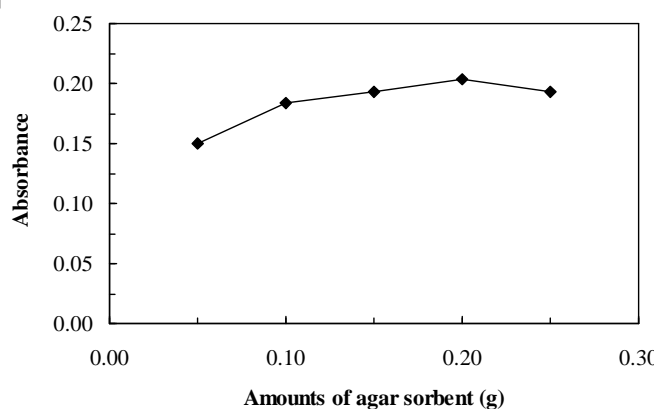


Fig. 5. Effect of amount of sorbent on the absorbance of the eluted complex. Conditions: HCl concentration; 0.15 M, arsenazo(III) concentration; 1.6×10^{-6} M, sample flow rate; 3 ml min⁻¹, sample volume; 200 ml, eluent; 2.5 ml of a mixture of 2:1 H₂SO₄ (2.5 M) and acetone.

as arsenazo(III) complex retained on the adsorbent, 200 ml of 5.0 µg ml⁻¹ of zirconium solution as arsenazo(III) complex was passed through the column containing 0.15 g of the adsorbent under optimized conditions. The column was then

washed with water and the amount of zirconium as arsenazo(III) complex, retained by the adsorbent, was measured using the general procedure. The calculated adsorption capacity was found to be 527 μg of zirconium as the complex per gram of the adsorbent.

Analytical Performance

A linear calibration graph was drawn for the determination of zirconium under the proposed experimental conditions. The data yielded a good linearity in the range of 5-300 ng ml^{-1} zirconium. The equation of the line was $A = 0.0044C + 0.0496$ with a regression coefficient of $r = 0.9988$ ($n = 9$). The limit of detection (LOD) defined as the concentration of the analyte giving signals equivalent to three standard deviations of the blank ($3S_b$) was 1.3 ng ml^{-1} and the relative standard deviations (R.S.D) for ten replicate measurements of 15 and 200 ng ml^{-1} of zirconium was 3.7 and 1.8%, respectively.

Interference Studies

In order to evaluate the selectivity of the method, the effects of different ions on the solid phase extraction and determination of zirconium were investigated. A constant concentration of zirconium (100 ng l^{-1}) was taken with different concentrations of ions and the general procedure was followed. Any deviation of $\pm 5\%$ or more from the absorbance value of the standard solution was considered as an interference. Results given in Table 1 indicate that the proposed method is relatively selective for the determination of zirconium.

Applications

The proposed solid phase extraction procedure was applied to the determination of trace zirconium in water and ore samples. Different amounts of zirconium were spiked to the tap, spring and wastewater samples and the resulting solutions were submitted to the preconcentration procedure. The results are given in Table 2. Good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery value for the analyte ions was in the range of 99-104%. In order to estimate the accuracy of the procedure, an ore sample was also analyzed by both this method and ICP-Mass method. The values obtained by using ICP-Mass ($90.0 \mu\text{g g}^{-1}$) and this method ($92.6 \mu\text{g g}^{-1}$) show that there is a good agreement between the results of the two methods and that there was no significant difference between them as performing a t-test at 95% confidence limit reveals.

CONCLUSIONS

The capability of agar for the adsorption of zirconium arsenazo(III) complex was used to develop a simple preconcentration method for the spectrophotometric determination of zirconium. To the best of our knowledge, this is the first application of unmodified agar as a sorbent. Agar is an eco-friendly adsorbent and can be used at least three times without any loss in the recovery. The method is sensitive compared to similar methods and does not need any sophisticated instrumentation [3,4]. A comparison with some of the previously reported methods is given in Table 3. An

Table 1. Effect of Diverse Ions on the Determination of 100 ng ml^{-1} of Zr(IV)

Ions	Tolerance ratio
Ca^{2+} , Na^+ , K^+ , I^- , Al^{3+} , Zn^{2+} , NH_4^+	1000
NO_3^- , NO_2^- , SO_4^{2-}	
Ni^{2+} , Co^{2+}	700
Mg^{2+} , CO_3^{2-}	500
$^a\text{Fe}^{3+}$, Cu^{2+} , Fe^{2+} , Pb^{2+} , Br^-	100
Cd^{2+}	10
Th^{4+} , F^-	1

^aThe interference of Fe^{3+} up to 100-fold was overcome by the addition of 1.0 ml of 1000 mg l^{-1} of EDTA solution.

Table 2. Determination of Zr(IV) in Water Samples

Sample	Zr(IV) added (ng ml ⁻¹)	Zr(IV) found ^a (ng ml ⁻¹)	Recovery (%)
Spring water	-	ND ^b	
	15.0	14.9 ± 0.5	99.0
	25.0	26.2 ± 0.6	104.9
Tap water	-	ND	
	25.0	25.8 ± 0.6	103.0
	50.0	51.9 ± 0.6	103.8
Waste water	-	ND	
	25.0	25.8 ± 0.6	103.0
	50.0	51.4 ± 0.6	102.8

^a $\bar{x} \pm ts / \sqrt{n}$ at 95 % confidence (n = 5). ^bNot detected.

Table 3. Comparison of the Proposed Method with some of the Methods Reported in Literature

Method	DL (ng ml ⁻¹)	RSD (%)	Enrichment factor	Ref.
Extraction-transport	5.0	1.1	5.0	[1]
Solid phase extraction and Chromatography	50.0	7.0	100.0	[5]
PVC membrane-electrode	55.0	-	-	[8]
Flotation-spectrophotometry	5.8	4.4	40.0	[14]
Cloud point extraction-ICP-OES	0.26	2.9	38.9	[15]
Solid phase extraction on agar	1.3	3.7	80.0	This work

enrichment factor of 80 was achieved. The method was verified by real samples and it was proven to be satisfactory for the determination of trace levels of zirconium in a variety of water matrixes and also an ore sample.

ACKNOWLEDGEMENTS

The authors wish to thank Shahid Chamran University, Ahvaz, Iran, for the financial support of this project (Grant 1388). The authors also express their sincere gratitude to Dr. A.R. Zarasvandi (Geology Department, Shahid Chamran University) for kindly providing the ore sample and ICP-MS analysis.

REFERENCES

- [1] Y.K. Agrawal, S. Sudhakar, *Sep. Purif. Technol.* 27 (2002) 111.
- [2] Y.K. Agrawal, M. Sanyal, P. Shrivastav, S.K. Menon, *Talanta* 46 (1998) 1041.
- [3] X.J. Yang, C. Pin, *Anal. Chim. Acta* 458 (2002) 375.
- [4] P. Peralta-Zamora, L. Cornejo-Ponce, M.I. Maretti, S. Bueno, J.W. Martins, *Talanta* 44 (1997) 811.
- [5] S. Oszwaldowski, J. Jakubowska, *Talanta* 60 (2003) 643.
- [6] J. Wang, P. Tuzhi, K. Varughese, *Talanta* 34 (1987) 561.

Solid Phase Extraction of Zirconium as Arsenazo(III) Complex

- [7] H.A. Arida, *Talanta* 76 (2008) 40.
- [8] S. Obarsk, N. Ku, Z. Marczenko, *Anal. Sci.* 8 (1992) 213.
- [9] Y. Shigetomi, T. Kojima, *Bull. Chem. Soc. Jpn.* 54 (1981) 1887.
- [10] I.P. Alimarin, V.I. Fadeeva, G.V. Kudryavtsev, I.M. Lokutova, T.I. Tikhomirova, *Talanta* 34 (1987) 103.
- [11] Z. Marczenko, *Spectrophotometric Determination of Elements*, Wiley, New York, London, Sidney, Toronto, 1976, p. 501.
- [12] Z.P. Wang, L.L. Shi, G.S. Chen, K.L. Cheng, *Talanta* 51 (2000) 315.
- [13] M.L. Firdaus, K. Norisuye, T. Sato, S. Urushihara, Y. Nakagawa, S. Umetani, Y. Sohrin, *Anal. Chim. Acta* 583 (2007) 296.
- [14] N. Pourreza, H. Parham, S. Shiri, *J. Korean. Chem. Soc.* 54 (2010) 283.
- [15] S. Shariati, Y. Yamini, *J. Colloid. Interf. Sci.* 298 (2006) 419.
- [16] G. Khayatian, S. Pouzesh, *J. Iran. Chem. Soc.* 4 (2007) 490.
- [17] N. Pourreza, K. Ghanemi, *J. Hazard. Mater.* 161 (2009) 982.
- [18] M. Fuchigami, A. Teramoto, Y. Jibu, *Food Hydrocolloids* 20 (2006) 160.
- [19] K. Burger, *Organic Reagents in Metal Analysis*, Pergamon Press, Toronto, Canada, 1973, p.134.
- [20] S.B. Savvin, *Talanta* 8 (1961) 673.
- [21] S.B. Savvin, *Talanta* 11 (1964) 7.
- [22] A.A. Huseyinli, K.F. Koseoglu, U.D. Uysali, *Anal. Sci.* 17 (2001) 1793.

Archive of SID