Bull. Chem. Soc. Ethiop. **2011**, 25(2), 295-298.
Printed in Ethiopia

ISSN 1011-3924

SHORT COMMUNICATION

POLYPROPYLENE BASED ANION EXCHANGE FIBER FOR ENRICHMENT AND DETERMINATION OF TRACE INDIUM BY GFAAS

Xiao-ling Wei*, Qi Gong, Kai Ouyang and Xin Hong

Department of Chemistry and Chemical Engineering, Guangxi University, Nanning, 530004, China

(Received January 4, 2010; revised October 4, 2010)

ABSTRACT. Indium was enriched and separated by a new polypropylene based anion exchange fiber before determined by graphite furnace atomic absorption spectrometry (GFAAS). Indium can be enriched quantitatively by 0.1 g of fiber at the flow rate within 6 mL·min^{-1} in the pH 4 and can be desorbed quantitatively with 10 mL of 1.0 M nitric acid from the fiber column. The fibers were soaked in 2 M sodium hydroxide sodium hydroxide solution for activation and were washed with distilled water at least thirty times until neutral for regeneration, The saturated capacity of the fiber for In(III) was 1.32 mg·g^{-1}. The activation energy (E_a) of the fiber adsorption In(III) was 89.3 kJ·mol^{-1}.The method was used to enrich trace In(III) in artificial samples solution and zinc concentrate solution before determination. The method detection limit was 0.08 ng·mL^{-1}, the recoveries were 96.8-101%, and the relative standard deviations (RSD) were 0.1-2.1%.

KEY WORDS: Anion exchange fiber, Separation, Enrichment, Indium, GFAAS

INTRODUCTION

Indium is a rare element, its abundance in the earth's crust is very low, estimated as 0.11 μg·g^{-1} [1]. It is a very important and typical dispersed element which is used in semiconductor and electronic industry [2-3]. As it enters into the composition of many rock-forming minerals, so it was obtained mainly by refining from residues generated during zinc ore processing [4]. Because of its content of rare in minerals, the direct determination by GFAAS was difficult. In order to determine trace indium in mineral, suitable preconcentration and separation methods were required before determination. At present, several determination and enrichment and separation method of trace indium have been reported, such as nanometer-size titanium dioxide adsorption [5], solid phase extraction [6], electrothermal atomic absorption spectrometry [7], spectrophotometry [8], and differential pulse polarography [9]. But these methods there have still some shortcomings such as complex operation, slower separation, and so on. In recent years, a number of solid phase extraction method for separation and enrichment of the metal ions have been reported. This approach was increasingly being recognized because of its high separation efficiency and easy operation [10-13]. However, solid-phase extraction for separation and enrichment of indium was still rare. In this paper, a method was developed for concentration and separation of trace indium by polypropylene based anion exchange fiber, and this fiber was used for enrichment of trace In(III) has not been report. The conditions of enrichment and separation with the fiber column, including acidity of adsorption and elution, flow rate, saturation adsorption capacity, reuse, interferences and adsorbing mechanism were studied in detail. The precision and the accuracy of the proposed method are achieved by analysis of real samples with satisfactory results.

EXPERIMENTAL

Apparatus. An Z-8000 atomic absorption spectrometer (Hitachi, Japan) with an indium hollow-cathode lamp at a wavelength of 325.6 nm was used. All experiments with the graphite furnace

---

*Corresponding author. E-mail: wxl1651@163.com

were injected with 10 μL samples. Tungsten coated graphite tubes were used throughout. The instrumental parameters are summarized in Table 1.

Table 1. Temperature program for the graphite furnace.

Step	Start temperature (^{o}C)	End temperature (^{o}C)	Time (s)	Ar flow (mL·min^{-1})
Drying	80	120	15	200
Pyrolysis	600	600	15	200
Atomization	2000	2000	5	30
Cleaning	2400	2400	3	200

Reagents. Polypropylene based anion exchange fiber was supplied by Guilin Zhenghan Science & Technology Developing Co. Ltd. (China). Reagents of analytical purity were used for all the experiments. The stock solution of 1.00 mg·mL^{-1} In(III) was prepared by dissolving indium in dilute nitric acid. It is diluted to give standard solution of 1.00 μg·mL^{-1} In(III) to used for experiments.

Fiber pretreatment. The polypropylene based anion exchange fiber was washed with alcohol and distilled water in order to remove organic and inorganic contaminants [6], and dried under 40 ^{o}C.

Fiber column preparation. 0.1 g of dry fiber was added to 2 M sodium hydroxide about 20 min, and washed with water until neutral, then loaded into a filler with some cotton in the bottom. The end of the filler was connected to a rubber tube with a screw clip to adjust the flow rate.

Analytical procedure. The standard solutions of indium or real samples were prepared in cleaned beaker and adjusted to pH 4 with diluted aqueous ammonia and hydrobromic acid. Pass through the column packed with 0.1 g of fiber at flow rate < 6 mL·min^{-1}. After eluting the indium from the column with 10 mL of 1.0 M nitric acid at the same flow rate and the contents of In(III) was determined by the GFAAS.

Determination of indium in artificial samples. 0.8 mg of aluminum, 5.0 mg of copper and 8.0 mg of zinc as the matrix was added to 25 mL solutions which contain 5.00 μg In(III), respectively. The pH was adjusted to 3, and the analytical procedure was followed to enrich and determine the indium.

Determination of indium in zinc concentrate. Accurately weighed 0.5000 g of zinc concentrate was taken into a digest container. A few drops of water were added to wet, and 10 mL of concentrated nitric acid was added followed by addition of 5 mL of hydrofluoric acid. The container was heated for 40 min at 70 ^{o}C, and it was placed in the microwave digest instrument to digest 15 min, then heated until evaporation of the acidic residue, keeping the temperature between 60-70 ^{o}C. Finally, small amount of water was added to dissolve the salts and the solution was transferred into a 50 mL calibrate flask, the solution was diluted to the mark with distilled water. The concentration of the zinc concentrate was 10 mg·mL^{-1}. 10 mL of sample was taken into a beaker and the pH was adjusted to 3, and the analytical procedure was followed.

RESULTS AND DISCUSSION

Effect of acidity on adsorption. Equal concentrations of indium standards solution were diluted to equal volumes with distilled water. Following the analytical procedure, the In(III) was enriched by the fiber column at pH 1-6 and then analyzed. The results showed that the recovery of trace In(III) was > 95% after enrichment by the fiber columns at pH 4. The pH 4 was selected as the enrichment acidity.

Effect of test solution flow rate on enrichment. According to the above procedure, when pre-enrichment of In(III) the test solution flow rate on fiber column at pH 4 were controlled in the range 2.0-10.0 mL·min^{-1}. The results show that In(III) can be enriched quantitatively at flow rate within 6 mL·min^{-1} with the recoveries > 95%.

Acidity and volume of eluent. After the trace In(III) is enriched on the fiber column following the analytical procedure, each column is eluted with 10 mL of 0.2-1.6 M nitric acid. The results show that 0.6-1.6 M HNO_3 can desorb In(III) from column quantitatively. However, the higher acidity of the eluent, the more serious influence on the determination of In(III) by GFAAS. So, 10 mL 1.0 M HNO_3 is selected.

Adsorption capacity, adsorption rate constant and activation energy. 0.1 g fiber was placed in a conical flask, 150 μg In(III) and 50 mL distilled water were added to the flask. The acidity was adjusted to pH 4 and shaken on a mechanical shaker. The concentration of In(III) was measured by GFAAS at certain time intervals until equilibrium was reached. The saturated adsorption capacity of the fiber for indium was calculated to be 1.32 mg·g^{-1}. The adsorption rate constant can be calculated on the basis of equation $-\ln(1-F) = k \cdot t$, where $F = Q_t/Q_e$ (Q_t is the adsorbance at moment t, and Q_e is the adsorbance at equilibrium). Followng the process describe above, the adsorption rate constants of the feber for In(III) were measured at 303, 313 and 323 K to be respectively $k_{303K} = 1.80 \times 10^{-3}$ s^{-1}, $k_{313K} = 5.87 \times 10^{-3}$ s^{-1} and $k_{313K} = 1.72 \times 10^{-2}$ s^{-1}.According to Arrhenius equation $\log k = -E_a/2.303RT + \log A$, from the slope of the plot of log k versus 1/T, the activation energy (E_a) of the process for the fiber adsorption In(III) was 89.3 kJ·mol^{-1}.

Interference of other ions. Different interfering ions were added to 25 mL solutions which contains 5.00 μg In(III) respectively. The analytes were enriched and analyzed according to the analytical procedure. The results show that the weight (mg) of the following ions cause little interference with the enrichment of indium: Mg^{2+}, Ca^{2+}, K^+, Na^+ (100); Ba^{2+}, Zn^{2+}, W(VI), Cr^{3+}, Al^{3+}, Pb^{2+}, Fe^{3+} (10); Cu^{2+}, Se(IV), Mn(II), Ge(IV), Ni^{2+} (5).

Reuse of the fiber. After the indium was desorbed from the fiber with 10 mL of 1.0 M HNO_3, the fiber column was washed with distilled water, then treated with 100 mL of 2 M NaOH, and washed with distilled water until neutral. The fiber which was repeatedly used at least thirty times according to the analytical procedure, could still enrich quantitatively trace of indium at pH 4 with recoveries > 90%.

Analytical precision and accuracy. Under the selected conditions, the recoveries of 5.00 μg In(III) in 25 mL of solutions enriched and determined five times were in the range of 98-103%. The relative standard deviation (RSD) was 2.3 %. The accuracy of the method was studied by the analytical recoveries of artificial samples and standard additions of zinc concentrates. In all cases, good recoveries were obtained (Table 2 and 3).

Application. The method was applied to enrichment and determination of indium in different artificial samples and zinc concentrate. The results obtained are given in Table 2 and 3.

Table 2. Results for indium determination in artificial samples.

Artificial samples	Matrix added (mg)	In(III) added (μg)	Found[a] (μg)	Recovery (%)	RSD (%)
Aluminum sample	0.8	5.00	4.86	97.2	2.3
Copper sample	5.0	5.00	4.95	99.0	1.0
Zinc sample	8.0	5.00	5.03	101	1.3

[a] Average of five determinations.

Table 3. Results for indium determination in zinc concentrate.

Sample	Found [a] (μg)	Added (μg)	Sum (μg)	Recovery (%)
Zinc concentrate	2.86	1.00	3.77	97.7
		2.00	4.85	99.8
		3.00	5.87	100

[a] Average of five determinations.

CONCLUSIONS

The polypropylene based anion exchange fiber can quickly and conveniently be used for concentration and separation of trace indium form sample solutions. This process combine with GFAAS was proved to be efficient and feasible for the determination of trace indium in some real samples. It offers satisfactory recoveries with sufficient precision and accuracy. The fiber can be reused efficiently.

REFERENCES

1. Sinclair, W.D.; Kooiman, G.J.A.; Martin, D.A.; Kjarsgaard, I.M. *Ore Geology Reviews*, **2006**, 28, 123.
2. Ferreira, E.D.; Morelli, M.T.; Moreira, I.M.N.S.; Carvalho, M.S. *J. Braz. Chem. Soc.* **2004**, 15, 563.
3. Acar, O.; Kilic, Z.; Turker, A.R. *Anal. Chim. Acta* **1999**, 382, 329.
4. Liu, S.Y. *Colored metal.* **1999**, 2, 30.
5. Zhang, L. Wang, Y.N.; Guo, X.J.; Zhu, Y.; Zhao, Z.Y. *Hydrometallurgy* **2009**, 95, 92.
6. Tuzen, M.; Soylak, M. *J. Hazard. Mater.* **2006**, 129, 179.
7. Dash, K.; Thangavel, S.; Chaurasia, S.C.; Arunachalam, J. *Talanta* **2006**, 70, 602.
8. Huseyinli, A.A.; Alieva, R.; Haciyeva, S.; Güray, T. *J. Hazard. Mater.* **2009**, 163, 1001.
9. Mohammad, A.T. *Talanta* **2000**, 52, 301.
10. Ghaedi, M.; Asadpour, E.; Vafaie, A. *Bull. Chem. Soc. Jpn.* **2006**, 79, 432.
11. Ghaedi, M.; Karami, B.; Ehsani, Sh.; Marahel, F.; Soylak, M. *J. Hazard. Mater.* **2009**, 172, 802.
12. Ghaedi, M.; Fathi, M.R.; Marahel, F.; Ahmadi, F. *Fresenius Environ. Bull.* **2005**, 14, 1158.
13. Ghaedi, M.; Ahmadi, F.; Tavakoli, Z.; Montazerozohori, M.; Khanmohammadi, A.; Soylak, M. *J. Hazard. Mater.* **2008**, 152, 1248.