



## Solid phase extraction of ultra traces silver(I) using octadecyl silica membrane disks modified by 1,3-bis(2-cyanobenzene) triazene (CBT) ligand prior to determination by flame atomic absorption

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### ARTICLE INFO

#### Article history:

Received 30 August 2008

Received in revised form 25 January 2009

Accepted 14 February 2009

Available online 11 March 2009

#### Keywords:

Silver(I)

SPE

Octadecyl silica disks

C<sub>18</sub>

1,3-bis(2-cyanobenzene) triazene

AAS

### ABSTRACT

A simple, reliable and rapid method for preconcentration and determination of the ultra trace amount of silver using octadecyl silica membrane disk modified by a recently synthesized triazene ligand, 1,3-bis(2-cyanobenzene)triazene (CBT), and flame atomic absorption spectrometry is presented. Various parameters including pH of aqueous solution, flow rates, the amount of ligand and the type of stripping solvents were optimized. The breakthrough volume was greater than 1800 ml with an enrichment factor of more than 360 and 6.0 ng l<sup>-1</sup> detection limit. The capacity of the membrane disks modified by 5 mg of the ligand was found to be 1070 μg of silver. The effects of various cationic interferences on the percent recovery of silver ion were studied. The method was successfully applied to the determination of silver ion in different samples, especially determination of ultra trace amount of silver in the presence of large amount of lead.

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### 1. Introduction

Analysis of trace heavy metals is difficult because of both their low abundance levels in samples and high complexity of sample matrices. Hence, preliminary concentration and matrix-removal steps are frequently required to guarantee the accuracy and precision of the analytical results [1]. Various preconcentration techniques including solvent extraction, coprecipitation, cloud point extraction, ion-exchange, solid phase extraction and electroanalytical techniques [2–6] have been levels in various environmental samples around the world.

Solid phase extraction (SPE) is an attractive separation preconcentration technique for heavy metal ions with some important advantages (simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment friendly). Various (SPE) materials have been successfully used for preconcentration and separation of heavy metal ions at trace levels [7–11]. The basic principle of SPE is the transfer of the analyte from the aqueous phase to bind to active site of the adjacent solid

phase. It has several advantages over other techniques, including stability and reusability of the solid phase, reach of high preconcentration factors, easiness of separation and enrichment under dynamic conditions, no need for organic solvents which may be toxic and minimal costs due to low consumption of reagents.

Silver is a useful element in many respects and the determination of low levels of silver is important. Recently, the solid phase extraction approach has gained rapid acceptance because of its simplicity, its amenability to automation, and the availability of a wide variety of sorbent phases. The typical sorbents used for silver separation contain organic agents with sulfhydryl groups which form stable complexes with silver [12]. Thus, separation, preconcentration and sensitive determination of silver ion is of increasing interest.

Space exploration by human requires maintenance of an adequate drinking water supply. At present, shuttle missions and the International Space Station (ISS) employ iodine (up to 3 mg/l) or silver(I) (up to 0.5 mg/l) as bacterial growth inhibitors. Periodic monitoring of these compounds is therefore required to confirm that their concentrations are held at levels that are sufficient for effective biocidal action, but below those which may affect crew health. Long term exposure to high silver levels can cause argyria, whereas extended exposure to high iodine levels may induce

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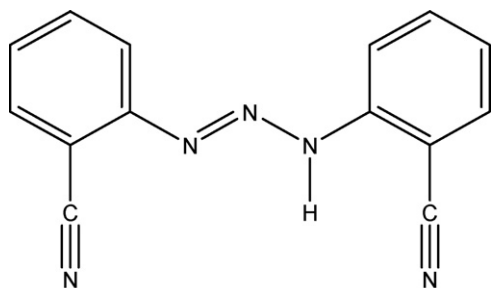


Fig. 1. Chemical structure of 1,3-bis(2-cyanobenzene)triazene (CBT).

thyroid dysfunction. To these ends, the testing method must be simple, rapid, and operable in microgravity [13].

Recently, solid phase extraction cartridges and disks were successfully utilized for the preconcentration and separation of trace metal ions from different matrices [14–19]. This method is an attractive technique that reduces consumption of and exposure to solvent, disposal costs and extraction time. The synthesis and crystal structures of the new triazene ligands, 1,3-bis(2-methoxybenzene)triazene and 1,3-bis(2-cyanobenzene)triazene (CBT) (Fig. 1), and the related structures have been reported [20,21]. Solution studies with triazene derivative ligands show that their complex formation with  $\text{Ag}^+$  [22] is very strong. In the present study a simple separation–preconcentration method for atomic absorption spectrometric determination of  $\text{Ag}^+$  by SPE with 1,3-bis(2-cyanobenzene)triazene an octadecyl silica ( $\text{C}_{18}$ ) disk has been established. The effect of different parameters such as sample matrix, amount of ligand, type of eluent for elution of analyte from disk, flow rates of sample solution and eluent and breakthrough volume have been evaluated. The method has also been extended the extraction of  $\text{Ag}^+$  in the presence of a large amount of other ions and from some real samples.

## 2. Experimental

### 2.1. Instrumentation

The  $\text{Ag}^+$  determination was performed on a Philips Pye Unicam 9100X atomic absorption spectrometer with Hollow Cathode Lamp (HCL) and equipped with a deuterium background corrector. The absorbance wavelength was set at 328.1 nm, and the spectral bandwidth at 0.5 nm. The determination of all other ions was carried out with the same atomic absorption spectrometer under the recommended conditions for each metal ion. A model 3510 digital Jenway pH meter equipped with a combined glass–calomel electrode was used for the pH adjustments.

### 2.2. Chemicals and reagents

Methanol, acetonitrile, and other organic solvents used in this work, were of spectroscopic grade, and all acids and water were of pro analysis from Merck. Analytical grade silver nitrate, sodium hydroxide, and nitrate or chloride salts of copper, magnesium, manganese, zinc, cobalt, lead, nickel, barium, sodium, potassium, calcium, iron, and chromium (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over  $\text{P}_2\text{O}_5$ . The new synthesized 1,3-bis(2-cyanobenzene)triazene with the highest purity was used as a chelating ligand. The standard stock of silver(I) nitrate was prepared by dissolving an appropriate amount of salt in pro analysis water (from Merck). Working standards were prepared by appropriate dilution of the stock solution with pro analysis water.

### 2.3. Sample extraction

Extraction were performed with a 47 mm diameter  $\times$  0.5 mm thickness, Empore high performance extraction membrane disk containing octadecyl-bonded silica (8  $\mu\text{m}$  particles, 6 nm pore size) from 3 M company. The disks were used in conjunction with a standard Schott Duran 47 mm filtration apparatus.

After placing the membrane in the filtration apparatus it was washed with 10 ml methanol and then with 10 ml acetonitrile to remove all contaminations arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, a solution of 5 mg 1,3-bis(2-cyanobenzene)triazene dissolved in 5 ml methanol was introduced to the reservoir of the apparatus and was drawn slowly through the disk by applying a slight vacuum. Then 2 ml water was added to the test tube and the resulting solution was again introduced to the reservoir and pass through the disk slowly. The filtration step was repeated until the passed solution was completely clear. Finally, the disk was washed with 25 ml water and dried by passing the air through it. The membrane disk modified by the triazene ligand was then ready for sample extraction.

The modified disk was first washed with 2 ml methanol followed by 25 ml water. This step prewets the surface of the disk prior to the extraction of the  $\text{Ag}^+$  ions from water. It is important to note that the surface of the disk was not left to become dry from the time the methanol was added until the extraction of  $\text{Ag}^+$  ions from water was completed [22]. Then 500 ml of the sample solution containing 2  $\mu\text{g}$   $\text{Ag}^+$  was passed through the membrane (flow rate = 25 ml/min). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted silver was stripped from the membrane disk using appropriate amounts of suitable eluent (the best eluent was 2 M ammonium thiocyanate). This step was done with 5 ml eluent solution and the  $\text{Ag}^+$  was determined with atomic absorption spectrometer.

## 3. Results and discussion

### 3.1. Choice of effluent

In order to choose the most effective eluent for quantitative stripping of the retained ions from the modified disk after extraction of 2  $\mu\text{g}$   $\text{Ag}^+$  from 500 ml sample (in the presence of 5 mg ligand), the  $\text{Ag}^+$  ions were stripped with 2–10 ml of different inorganic effluent, and with 5 ml of the effluent the recovery is 100%, and in all experiments this volume of stripping solution was used. The resulting data are listed in Table 1.

From the data given in Table 1, it is immediately obvious that among the different solutions, 5 ml 2 M ammonium thiocyanate can accomplish the quantitative elution of silver from the membrane disk, while other solutions are ineffective for the complete elution of silver. On the other hand, since negligible stripping of the  $\text{Ag}^+$  takes place in the presence of inorganic acids, these solutions can

**Table 1**  
Percent recovery of silver from the modified membrane disk using 5 ml of different stripping solutions.

Stripping solution	Recovery (%)
$\text{HNO}_3$ (0.1 M)	0.0
HCl (0.1 M)	0.0
$\text{HClO}_4$ (0.1 M)	2.8
$\text{H}_2\text{SO}_4$ (0.1 M)	0.0
$\text{NH}_3$ (0.1 M)	11.9
EDTA (0.1 M)	4.2
$\text{CH}_3\text{COOH}$ (0.1 M)	0.0
$\text{NH}_4\text{SCN}$ (0.1 M)	45.5
$\text{NH}_4\text{SCN}$ (1.0 M)	85.7
$\text{NH}_4\text{SCN}$ (2.0 M)	100.3

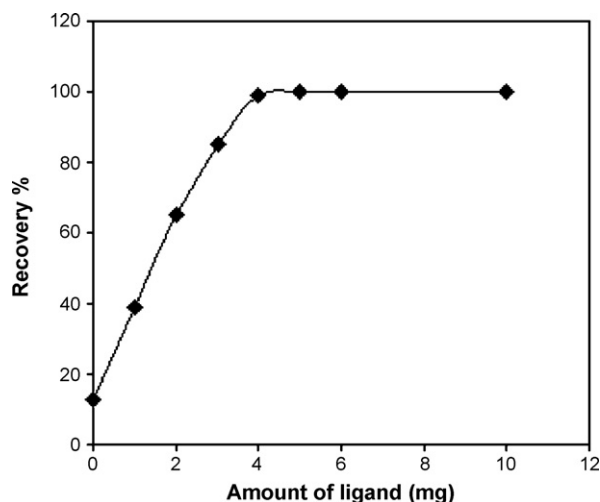


Fig. 2. Ligand amount effect on extraction efficiency of silver ion.

be used for the solution of some interfering ions, which may be co-extracted with the  $\text{Ag}^+$  ions by the membrane disk.

The influence of  $\text{NH}_4\text{SCN}$  concentration on the stripping efficiency is also included in Table 1. As can be seen, stripping of silver ion does not quantitatively occur at ammonium thiocyanate concentration of 0.1 M.

### 3.2. Effect of ligand amount

The optimum amount of the ligand for the membrane disks was studied. The results showed that the amount of ligand play an important role in obtaining quantitative recoveries of metal ions, because in its absence, the disk does not retain the metal ions. Therefore, the influence of the amount of ligand on recovery of the silver ion was examined in the range of 1–10 mg using 250 ml solution containing  $10 \mu\text{g}$  silver ions. The recoveries of silver ion increased by increasing the amount of the ligand and reached to 100% with at least 5 mg of the ligand (Fig. 2). On this basis, all studies were carried out with 5 mg of 1,3-bis(2-cyanobenzene) ligand.

### 3.3. Effect of flow rate and pH

The effect of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of silver ion was investigated. It was found that, in the range of 5 to  $70 \text{ ml min}^{-1}$ , the retention of silver by the membrane disk is not affected by the sample solution flow rate considerably. Similar results for extraction of organic materials [23,24], and metal ions have already been reported [25]. On the other hand, quantitative stripping of silver ion from the disk was achieved in a flow rate of  $1.0\text{--}8.0 \text{ ml min}^{-1}$ , using 5 ml of 2 M ammonium thiocyanate. At higher flow rates (up to  $20 \text{ ml min}^{-1}$ ), quantitative stripping of silver needed larger volumes of 2 M ammonium thiocyanate.

In order to investigate the effect of pH on the SPE of silver ion, the pH of aqueous samples was varied from 1 to 7. The pH was adjusted by using either diluted nitric acid or diluted sodium hydroxide. It is found that the percentage recovery is nearly independent of pH. Higher pH values ( $>7$ ) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

## 4. Analytical performance

### 4.1. Sorption capacity

The maximum capacity of the disk was determined by passing 500 ml portions of an aqueous solution containing

$2000 \mu\text{g}$  silver ion, through the modified disk with 1,3-bis(2-cyanobenzene)triazene ligand, followed by determination of the retained ions using atomic absorption spectrometry. The maximum capacity of the disk was found to be  $1070 (\pm 12) \mu\text{g}$  silver ion per 5 mg of ligand.

### 4.2. Breakthrough volume

The breakthrough volume ( $VB$ ) refers to the maximum sample volume that passes through a given mass of sorbent until analyte retention is no longer quantitative [26].  $VB$  depends on the nature of the sorbent material and the type and concentration of sample constituents. The break through volume of sample solution was tested by dissolving  $10 \mu\text{g}$  silver in 250, 500, 1000, 1500, 1800 and 2000 ml water and the recommended procedure was followed under optimal experimental conditions. In all cases to 1800 ml the extraction by the membrane disk was found to be quantitative. Thus, the break through volume for the method should be greater than 1800 ml. Consequently, by considering the final elution volume of 5.0 ml and the break through volume of 1800 ml, an enrichment factor of 360 was easily achievable.

### 4.3. Limit of detection

The limit of detection (LOD) of the proposed method for the determination of silver ion was studied under the optimal experimental conditions. The LOD obtained from  $C_{\text{LOD}} = K_b S_b \text{ m}^{-1}$  for a numerical factor  $K_b = 3$  is 6 ng per 1000 ml.

### 4.4. Effect of diverse ions on sorption of silver

In order to investigate the selective separation and determination of silver ion from its binary mixtures with diverse metal ions, a 500 ml aliquot solution containing  $10 \mu\text{g}$   $\text{Ag}^+$  and given amounts of other cations (Table 2) was taken and the recommended procedure was followed. The results are summarized in Table 2. The results show that the silver ion in the binary mixtures are retained almost completely by the modified membrane disk, even in the presence of up to about 100 mg of the diverse ions. It is interesting to note that retention of other cations by the disk is negligible and they can be separated completely from the silver ion. However, in the case of  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , their retention by the disk is low, but it is found that the interference of these ions can be avoided by washing the membrane disk by 20 ml (or higher) aliquots of 1 M nitric acid, before the final elution of the silver ion by ammonium thiocyanate solution.

Table 2  
Effect of diverse ions on the recovery of  $10 \mu\text{g}$  silver ion.

Ion	Amount taken (mg)	Recovery of $\text{Ag}^+$ (%)	Recovery of interfere ions (%)
$\text{Na}^+$	100	99.5	0.5
$\text{K}^+$	100	99.6	0.5
$\text{Mg}^{2+}$	24.5	93.5	3.3
$\text{Ca}^{2+}$	39.9	98.4	0.3
$\text{Ba}^{2+}$	5.2	99.0	0.3
$\text{Cu}^{2+}$	4.2	95.8	21.5
$\text{Co}^{2+}$	3.1	100.2	0.1
$\text{Ni}^{2+}$	3.0	100.2	0.1
$\text{Mn}^{2+}$	3.8	100.0	0.1
$\text{Zn}^{2+}$	3.8	100.0	0.1
$\text{Pb}^{2+}$	3.6	98.7	0.6
$\text{Fe}^{2+}$	3.0	100.0	0.1
$\text{Cd}^{2+}$	2.6	95.5	1.8

**Table 3**  
Recovery of 2 µg silver added to 500 ml solution of the synthetic samples.

Samples	Recovery of silver ion (%)
Synthetic sample 1 (Na <sup>+</sup> , K <sup>+</sup> 100 mg of each ion, Mg <sup>2+</sup> , Ca <sup>2+</sup> 25 mg of each ion)	99.4
Synthetic sample 2: (Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , and Ca <sup>2+</sup> , 25 mg of each ion, and Co <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>2+</sup> , Pb <sup>2+</sup> , Mn <sup>2+</sup> and Cd <sup>2+</sup> , 3.0 mg of each ion)	98.7
Lead oxide from Merck	90.0
Lead acetate from Merck	90.0

#### 4.5. Analysis of real and natural water samples

In order to assess the applicability of the method to real samples with different matrices containing varying amounts of variety ions, it was applied to the separation and recovery of silver ions from two different synthetic samples as well as two artificial samples (lead oxide and lead acetate from Merck). The amount of silver in lead oxide and lead acetate of Merck (according to package label) are  $5 \times 10^{-5}$  and  $1 \times 10^{-4}$ %, respectively, and we determined  $4.5 \times 10^{-5}$  and  $9 \times 10^{-5}$ %, respectively. The results are summarized in Table 3. As seen, the results of all sample analysis show that, in all cases, the silver recovery is quantitative.

We have analyzed a lead ore sample of Duna mine in central Alborz of Iran too. The analysis of this sample with ICP-AES has been shown 165 ppm (g/ton) of silver and with our method this amount is  $161 \pm 2$  ppm (g/ton). The fire assay method is used universally for the determination of silver in ores and concentrator products. This method is subject to a loss of silver during cupellation, and corrections for this loss, if made, must be on an empirical basis depending on the conditions of cupellation. The atomic absorption technique was free from interelement effects and required the minimum amount of manipulation, thus it is an advantage of our method for determination of silver in lead ores concentrates and tails of lead mines.

#### 5. Conclusion

A simple, precise and accurate method was developed for selective separation, preconcentration and determination of silver from various complex matrices. The method was to use octadecyl silica membrane disks which modified by 1,3-bis(2-cyanobenzene) triazene ligand for separation of Ag ions by solid phase extraction. The results showed that retention of other cations by the modified disk is negligible and they can be separated completely from the silver ion. The method can determine silver ion in the presence of large amount of lead.

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