



Separation of Silver by Ion-Exchange Resin and Its Determination by Electrothermal Atomic Absorption Spectrometry

M. CHAMSAZ* and M.M. RIAZI

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

*Corresponding author: E-mail: mchamsaz@gmail.com; mahdi.riazy@gmail.com

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In this investigation a novel and extremely sensitive method for separation and determination of silver in aqueous samples by ion-exchange resin combined with electrothermal atomic absorption spectrometry is described. In this method 100 mL of Ag^+ in pH 4.5 at room temperature is separated with Chelex-100 ion-exchange resin. After separation, the resin is washed by a solution inclusive of 0.5 M HNO_3 concurrent with 0.4 % (w/v) thiourea and 20 μL of washing solution is directly transferred into a graphite tube together with coinjection of 20 μL Cu^{2+} 0.2 % (w/v) as matrix modifier. In this investigation the type of washing solution, concentration of washing solution, pH of sample solution, concentration of thiourea, rate of sample solution and ionic strength were optimized. Using 100 mL sample solution, an enrichment factor of 10 was obtained. The detection limit was calculated to be 0.2 ng mL^{-1} based on $3S_b$ and relative standard deviation for five replicate analysis of $1.00 \text{ ng mL}^{-1} \text{Ag}^+$ was 5.1 %. The calibration curve was linear in the range of 0.2 ng mL^{-1} to 3.0 ng mL^{-1} with a sensitivity of 20.0 pg mL^{-1} . This method was used for determination of silver in tap water, waste water, sea water and soil sample.

Key Words: Silver, Electrothermal atomic absorption spectrometry, Ion-exchange resin, Chelex-100, Matrix modifier, Thiourea.

INTRODUCTION

Selective enrichment and separation of metal ions are important research fields. These metallic ions mainly include toxic heavy metal ions in water^{1,2}, low contents of rare metal ions in the earth crust as well as some precious metals. Owing to its excellent properties of electrical and thermal conductivity and ductility, silver has been widely applied in fields of aerospace, communications, chemical industry, medical equipment, electroplating, photographic materials, electronic industries, etc. The silver resources in the world are extremely scant and mainly associated with lead, copper and antimony deposits. In addition, there are considerable waste solutions, containing silver ions, produced by electroplating wastewater, waste fixative as well as the Ag-containing wastewater in laboratory. Therefore, silver recovery from waste solutions becomes more and more important with developing society. However, due to the low concentration, it is necessary to enrich and separate silver ions before recovery. There are some traditional techniques to recover silver from waste solutions such as electrolysis, replacement, precipitation and ion exchange in industry. Recently, Donia *et al.*³ have studied a chemically modified chitosan with magnetic properties, which can be used in silver recovery from aqueous solutions. Silver from thiosulfate and

thiocyanate leach solutions can be recovered by anion exchange resins and activated carbon⁴. Instead of columns filled with particles, membranes have become increasingly attractive for efficient separation due to their promising properties of ease and low energy of operation⁵. The membrane has wide application in metal enrichment and separation and membrane technology is an established part of several industrial processes⁶. While, the common membrane does not perform well on selective enrichment and separation of the target metal ions and the problem can be effectively solved by the technique of molecular imprinting, which is a convenient and powerful technique recognizing the imprinted molecule selectively by preparing polymeric materials with artificial receptor-like binding sites for various substances⁷⁻¹⁰. As a branch of molecular imprinting, ion imprinting has the character as well. Furthermore, ion imprinted polymers have been applied in solid phase extraction, sensors and membrane separations of inorganics¹¹. There are few reports on ion imprinted membrane used to recover silver in waste solutions¹². Overall, combining the technique of ion imprinting with membrane, metal ion imprinted membrane has extensive prospect in metal ion recovery.

In this investigation, Chelex-100 ion-exchange resin was used for separation and preconcentration of silver ion followed by its determination by electrothermal atomic absorption spectro-

metry in real samples. In order to increase the separation efficiency, thiourea was used in washing solution for desorption of silver ions from ion-exchange resin.

EXPERIMENTAL

All reagents were of analytical reagent grade and triply distilled water was used throughout: A shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer and D₂ lamp for background correction was used. Silver hollow cathode lamp was used as radiation source adjusted at 4 mA. An atomic absorption signal at 328.1 nm line was recorded on a graphic printed PR-4 with peak height and gas stop mode for quantification. The temperature program for the furnace is as follows (Table-1):

Stage	Furnace temperature (°C)	Mode	Time (s)	Argon flow rate (L min ⁻¹)
Drying	150	Ramp	15	1.5
Ashing	500	Step	15	1.5
Atomization	1800	Step	3	0 (gas stop)
Cleaning up	2300	Step	2	1.5

Determination of silver *via* preconcentration using ion-exchange resin: 100 mL of Ag (I) solution was adjusted at pH 4.5 and transferred into a column (L:20 cm and I.D:0.5 cm) containing 6 gr Chelex-100 ion-exchange resin (mesh: 50-100 μm) at 1 mL min⁻¹ rate. The column was maintained at room temperature and Ag (I) was extracted from resin. After separation of silver ion, the resin was washed by 8 mL of 0.5 M HNO₃ concurrent with 0.4 % (w/v) thiourea at a rate of 1 mL min⁻¹. The wash solution was then made up to 10 mL and 20 μL of this solution was injected into the graphite tube with coinjection of 20 μL of 0.2 % (w/v) Cu²⁺ as matrix modifier.

RESULTS AND DISCUSSION

Optimizing the parameters for separation: In order to investigate the effects of different parameters on silver separation by ion exchange resin, 100 mL solution of 1 ng mL⁻¹ silver was used at all the following stages.

Effect of pH of sample solution: Different pHs were tested for sample solution and the optimum pH was 4.5. At lower pH, there is a competition between Ag⁺ and H⁺ for adsorption on the resin and at high pHs hydroxide ion complexes with silver ion and hence the absorbance is decreased (Fig. 1).

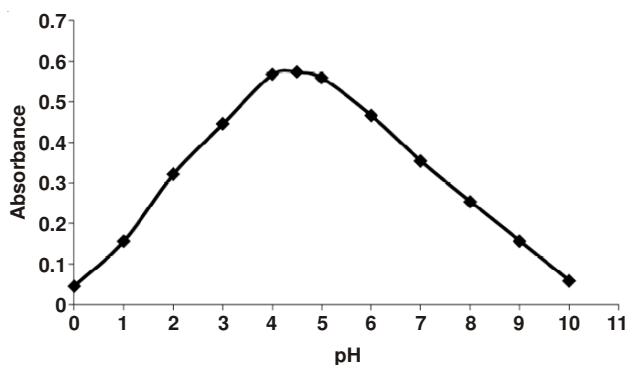


Fig. 1. Effect of pH of sample solution

Type of washing solution: The extraction efficiency of the method was tested at different washing solutions at 0.5 M concentration concurrent with 0.4 % (w/v) thiourea. As can be seen from Fig. 2, the best solution was HNO₃.

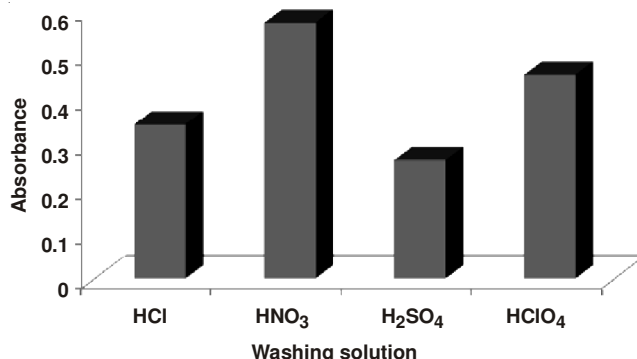


Fig. 2. Effect of washing solution

Effect of thiourea concentration: The thiourea concentration in washing solution was varied from 0.2 to 1.0 % (w/v). The separation efficiency was increased with increasing of thiourea concentration up to 0.4 % (w/v) and then leveled off at higher concentrations (Fig. 3). As the results show the optimum concentration of thiourea is 0.4 % (w/v).

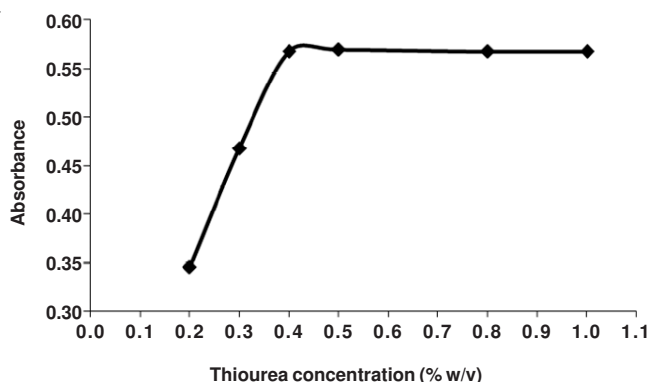


Fig. 3. Effect of thiourea concentration

Effect of washing solution concentration: The separation of Ag (I) was performed with HNO₃ at concentrated ranging from 0.05 M to 2 M as washing solution and the results showed maximum efficiency at the optimum concentration of 0.5 M (Fig. 4).

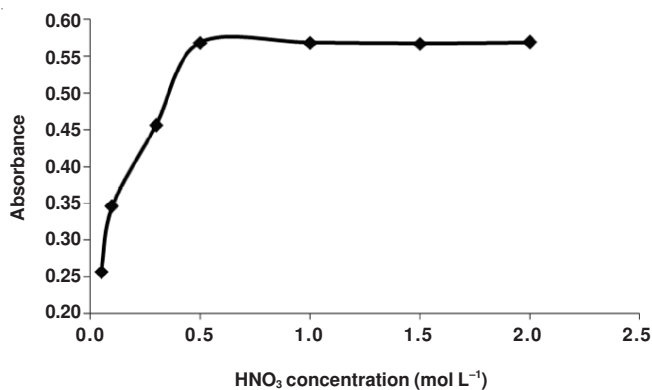


Fig. 4. Effect of washing solution concentration

Effect of rate of sample solution: The rate of sample solution through the resin was varied from 0.25 to 4 mL min⁻¹. By decreasing the rate, the retainment of silver onto the resin is increased and becomes leveled off at rates greater than 1 mL min⁻¹. However at lower rate than 1 mL min⁻¹ the retainment of silver ions is decreased (Fig. 5). As the results show the optimum rate of sample solution is 1 mL min⁻¹.

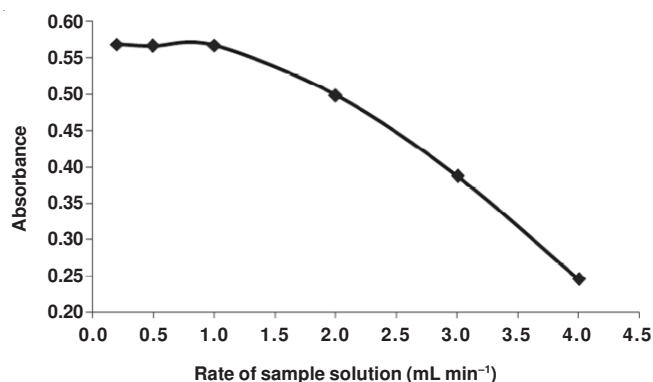


Fig. 5. Effect of rate of sample solution

Effect of ionic strength and salt concentration: The effect of ionic strength was tested using potassium chloride in the concentration range of 0.02 to 0.25 mol L⁻¹ in the sample solution (Fig. 6).

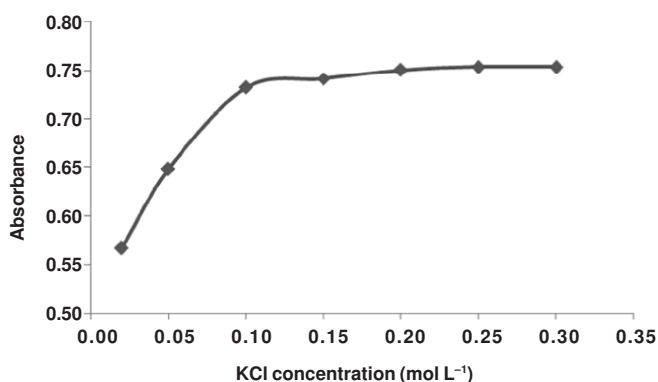


Fig. 6. Effect of ionic strength

At high concentrations of salt, solvent molecules are in contact with salt ions and Ag(I) ions are relatively free in the solution for adsorption. The efficiency of extraction is increased but higher concentration of salt than 0.1 mol L⁻¹ decreases this effect and the extraction efficiency becomes constant.

Effect of interferences: Interfering species at 100 fold excess were added to Ag(I) solution and the extraction was followed at the optimized conditions. Table-2 indicated that the serious interferences are due to Bi³⁺, Hg²⁺, Sb³⁺, Au³⁺, SCN⁻ and Cd²⁺, which could be effectively removed by using separate solutions of 0.1 M KCN for Au³⁺, Hg²⁺ and Cd²⁺, 0.1 M NaF for Bi³⁺ and 0.1 M tartaric acid for Sb³⁺.

Analytical figures of merit: Calibration curve was constructed at the optimized conditions and was linear in the range of 0.2 ng mL⁻¹ to 3.0 ng mL⁻¹ silver with a correlation coefficient of 0.9989 and sensitivity of 20.0 pg mL⁻¹. The detection limit was calculated to be 0.2 ng mL⁻¹ based on 3S_b. The relative

standard deviation (RSD) for five replicate analysis of 1.00 ng mL⁻¹ silver was 5.1 %. Recovery test was performed using tap water, waste water, sea water with 1.0 ng mL⁻¹ silver and 0.10 µg gr⁻¹ silver for spiked soil sample. The results show recovery of 96-104 % for the technique.

TABLE-2
EFFECT OF INTERFERING IONS

Interfering ion*	Relative error in absorbance (%)
Cl ⁻	-3.9
SCN ⁻	-8.3
PO ₄ ³⁻	-2.1
SO ₄ ²⁻	-1.6
AsO ₃ ³⁻	-0.8
SiO ₃ ²⁻	-3.0
Na ⁺	2.1
K ⁺	1.9
Mg ²⁺	-0.6
Ca ²⁺	1.2
Bi ³⁺	-13.6
Ba ²⁺	-1.9
Al ³⁺	1.0
Sn ⁴⁺	0.6
Sb ³⁺	-12.3
Cr ³⁺	1.1
Cu ²⁺	2.7
Hg ²⁺	-7.3
Pb ²⁺	0.6
Fe ³⁺	2.7
Zn ²⁺	-1.5
Au ³⁺	-11.4
Mn ²⁺	0.8
Co ²⁺	-0.5
Ni ²⁺	0.2
Cd ²⁺	-11.1

*Solutions for cations was prepared from the chloride salts and anions from the sodium salts

Analysis of real sample: In order to evaluate the capability of the method different real samples were analyzed according to the method described earlier. The results are given in Table-3.

TABLE-3
RESULT OF DETERMINATION SILVER IN REAL SAMPLES

Sample	Ag added (ng mL ⁻¹)	Ag found (ng mL ⁻¹)	Recovery (%)
Tap water	0	0	-
	1.00	1.04 ± 0.07	104
Waste water	0	0.48 ± 0.06	-
	1.00	1.49 ± 0.08	101
Sea water	0	0	-
	1.00	0.96 ± 0.05	96
Soil sample	0	0.22 µg gr ⁻¹ ± 0.08	-
	0.10	0.33 µg gr ⁻¹ ± 0.07	103

Conclusion

The results show a promising technique for determination of silver in a variety of samples at ng mL⁻¹ and pg mL⁻¹ levels without the needs for any sophisticated device. Apart from having extremely high sensitivity, the procedure is very simple, nearly fast and benefits a very low detection limit. By the use of a preliminary separation step using a resin, the method could be relatively free from interferences. The experimental parameter such as pH of sample solution, rate of sample solution,

type of washing solution, concentration of washing solution, concentration of thiourea in washing solution and ionic strength have great effects on the sensitivity of method and should be optimized. The results show that the silver could be determined with high sensitivity and relatively good reproducibility in aqueous samples such as tap water, sea water, waste water and solid samples.

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REFERENCES

1. A.H. Chen, C.Y. Yang, C.Y. Chen, C. Yu and C.W. Chen, *J. Hazard. Mater.*, **163**, 1068 (2009).
2. Q. Li, H.J. Su and T.W. Tan, *Biochem. Eng. J.*, **38**, 212 (2008).
3. A.M. Donia, A.A. Atia and K.Z. Elwakeel, *Hydrometallurgy*, **87**, 197 (2007).
4. O.N. Kononova, A.G. Kholmogorov, N.V. Danilenko, N.G. Goryaeva, K.A. Shatnykh and S.V. Kachin, *Hydrometallurgy*, **88**, 189 (2007).
5. Y.H. Zhai, Y.W. Liu, X.J. Chang, X.F. Ruan and J.L. Liu, *React. Funct. Polym.*, **68**, 284 (2008).
6. S.P. Nunes and K.V. Peinemann, *Membrane Technology in the Chemical Industry*, Wiley-VCH Verlag GmbH (2001).
7. X.J. Xu, L.L. Zhu and L.R. Chen, *J. Chromatogr. B*, **804**, 61 (2004).
8. J.F. Yin, G.L. Yang and Y. Chen, *J. Chromatogr.*, **1090**, 68 (2005).
9. Z.S. Liu, Y.L. Xu, C. Yan and R.Y. Gao, *J. Chromatogr.*, **1087**, 20 (2005).
10. T.Y. Guo, Y.Q. Xia, J. Wang, M.D. Song and B.H. Zhang, *Biomaterials*, **26**, 5737 (2005).
11. T.P. Rao, R. Kala and S. Daniel, *Anal. Chim. Acta*, **578**, 105 (2006).
12. H.A. Shawky, *J. Appl. Polym. Sci.*, **114**, 2608 (2009).