USE OF DIFFERENT INORGANIC COMPLEXANTS AS ELUENTS FOR CATION-EXCHANGE SEPARATION OF SILVER FROM LEAD

Zenovia Moldovan *, Eleonora-Ana Neagu and Rodica Paraschivoiu

In order to separate silver from lead by cation exchange chromatography, different complexants, namely Na_2SO_3, KSCN, CH_3COONH_4 were examined as eluents. The best results were obtained for 5% Na_2SO_3. Thus, trace and milligram amounts of silver were separated from lead by elution of the first with 5% Na_2SO_3 solution from a column with DOWEX 50 (H^+ form). Lead was then eluted with 2M-HNO_3. The eluted metal ions were analysed by AAS technique. The separation was fairly sharp and quantitative and the method was used to analyse synthetic mixtures.

Introduction

Silver is a widely distributed metal that is mined throughout the world. The majority of silver is associated with base metal ores (for example lead), usually as disseminated sulphides within the ore body. Most of silver is obtained in the refining processes of copper and gold but the mining of silver is also an alternative for silver production.

In the base lead ores, silver is typically found in the concentration range of 0.1÷1%. An important analytical task is the separation of silver on the one hand for its recovery [1÷5] from ores or waste waters and on the other hand for preconcentration of silver [6÷12] prior to its determination by a certain technique. Methods, which are applicable for these purposes, have been carried out mainly by using ion exchange chromatography [13÷17], solvent extraction [16÷22], precipitation and co-precipitation [23÷24] and electrodeposition [1,3,4].

This paper completes the series of investigations aimed at finding a simple method for the silver recovery from real or synthetic samples. The experiments performed were concerned with the choice of an appropriate reagent for silver elution from a cation exchanger in presence of lead. Best results were obtained for 5% Na_2SO_3 solution which enables the elution of silver as $[Ag(SO_3)_2]^{3-}$. Pb(II) remained within the resin as $PbSO_3$ was then eluted with 2M-HNO_3.

Experimental

Apparatus

A Pye Unicam Atomic Absorption Spectrophotometer Model SP 192 (Pye Unicam Ltd) equipped with air-acetylene flame burner and deuterium continuum source background

*   Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest,
     2-14 Bv. Regina Elisabeta, 70346 Bucharest, Romania

corrector was used for quantitative determination of metal ions. All absorption measurements were performed under the following operating conditions: wavelength, 328.1 nm for Ag and 217.0 nm for Pb; window slit, 0.2 mm for Ag and 0.3 mm for Pb; current, 3 mA for Ag and 6 mA for Pb; acetylene flow, 0.8-1.0 L·min⁻¹ for Ag and 1-1.2 L·min⁻¹ for Pb; air flow, 0.8 L·min⁻¹ for Ag and 1.0 L·min⁻¹ for Pb; observation height, 10 mm.

Reagents

All chemicals were of analytical-reagent grade.

DOWEX 50 (Dow-Chemical) in the H^+ ionic form was used as cation exchange resin. The exchange capacity of the resin was found to be 4.8 mEq per g of air-dried resin. The ionic exchange took place in glass column 10 cm long, 0.7 cm in diameter, provided with stopcocks at botttom and funnel with ground joint at top. Known quantities (5 g) of cation exchanger were transferred into columns, purified, converted into H^+ ionic form and washed with water up to negative Cl^- test.

Stock standard silver and lead solutions (10^{-1}M) were prepared by diluting their 1000 ppm atomic absorption standard nitrate solutions (Titrisol, Merck) with 10^{-2}M nitric acid. Solutions of lower concentrations were prepared by dilution of these solutions just before use. The silver solution was stored in a brown bottle.

Solutions of nitric acid (1M, 2M, 10^{-1}M and 10^{-2} M) and hydrochloric acid (4M) were prepared by diluting the reagent solutions (Merck) in distilled water.

Solutions of 2%, 5% and 10% sodium sulphite, 5% potassium thiocyanate, 5% ammonium acetate and 2M nitric acid were used as eluents.

In order to avoid the oxidation of SO_3^{2-} to SO_4^{2-}, the sodium sulphite solutions were prepared by dissolving calculated amounts of $Na_2SO_3 \cdot 3H_2O$ in boiled and cooled distilled water, immediately before the determinations.

Procedure for sorption of metal ions

After fixing a known quantity of metal ion (silver or lead) in the cation exchange resin, 250 mL of one of the proposed elution reagent was passed through the column. The effluent was collected in 25-mL calibrated flasks being used for determination of metal ion by AAS technique. The metal ion concentration in the solution, before and after uptake by the sorbent and after recovery by one of the proposed elution reagent, enabled the evaluation of the eluent efficiency for each experiment. In the second step, the column was rinsed with distilled water up to complete washing of the excess elution reagent, then converted into H^+ ionic form as mentioned above.

Results and Discussion

Silver and lead metal ions have similar chemical properties and therefore it is difficult enough to find specific elution agents for their ion exchange chromatographic separation. However, some inorganic ligands form complexes with the investigated metal ions of

different stabilities. A certain difference between the anionic complexes stability of these metal ions with thiocyanate and acetate was reported [25]. Also, it is known that silver cation reacts with sulphite anion forming a white precipitate, soluble in excess of the reagent:

$$2Ag^+ + SO_3^{2-} \Leftrightarrow Ag_2SO_3; \ Ag_2SO_3 + 3SO_3^{2-} \Leftrightarrow 2[Ag(SO_3)_2]^{3-}.$$
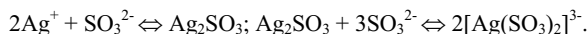
On the contrary, $PbSO_3$ is insoluble in excess of sulphite ions but it is soluble in 2M HNO_3. On the basis of these data, the behaviour of each of the two metal ion fixed in the cation exchange resin toward the mentioned reagents was investigated. It should be mentioned that the experiments were performed with amounts of silver much lower than those of lead with respect to the composition of real samples.

Use of KSCN as eluent

Fig. 1 reports the results obtained for the elution of the investigated metal ions passing through the resin 5% KSCN solution.
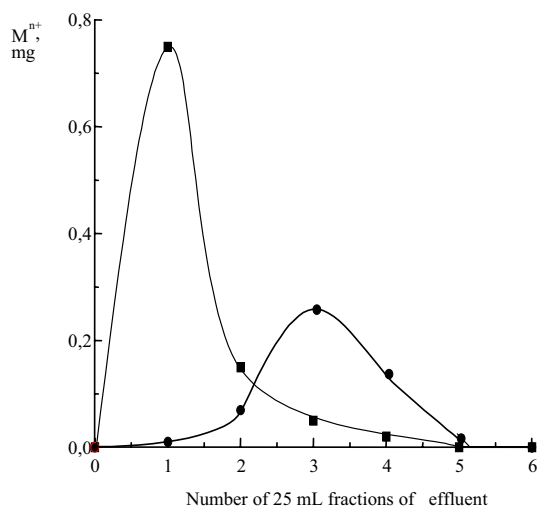

Fig. 1: *Elution of silver and lead retained in the cation exchange resin with 5% KSCN solution; amount of metal ion fixed in the resin:* Pb^{2+} = 37.20 mg; Ag^+ = 2.10 mg; Ag^+(□); Pb^{2+}(■).

It is seen that the experimental behaviour is in agreement with the reported instability constants [25]. Thus, silver is quantitatively eluted from the resin as its anionic thiocyanate complex ($[Ag(SCN)_4]^{3-}$, pK_4 = 9.67). We mention that almost a half of the silver amount was collected in the first portion of 25 mL-effluent (45%). As we expected a very low removal of lead (as $[Pb(SCN)_4]^{2-}$, pK_4 = 0.85), was obtained by using the KSCN solution as eluent (below 10%). Higher concentrations of the ligand were not tested in order to avoid the increase of the amount of lead released from the resin. The elution curves in Fig. 1

suggest that the use of 5% KSCN solution as eluent could not allow a complete separation of silver from lead.

Use of ammonium acetate as eluent

One of the most commonly used reagent for elution of lead fixed on a cationic resin is ammonium acetate [26]. Fig. 2 reports the results obtained for the uptake of the investigated metal ions using 5% ammonium acetate as eluent.

As we observe the two elution curves overlap considerably. On the basis of the instability constant value of $[Ag(CH_3COO)_2]^-$ ($pK_2 = 0.64$) [25], the elution of silver is somewhat higher than that expected. This behaviour may be explained considering the formation of neutral acetate ($pK_1 = 0.73$) which may be released from the resin.
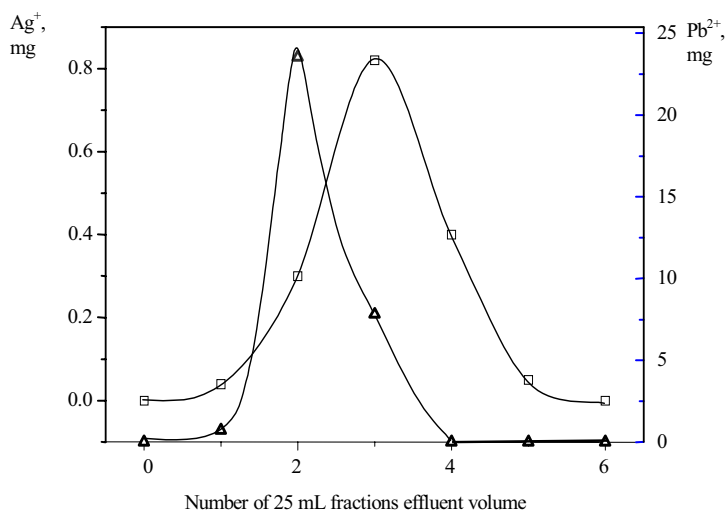

Fig. 2: *Elution of silver (□) and lead (Δ), retained in the cation exchange resin with 5 % ammonium acetate;* amount of Ag^+ fixed in the resin = 2.10 mg; amount of Pb^{2+} fixed in the resin = 37.20 mg.

Use of natrium sulphite as eluent

A complexing agent that seems to be particularly useful for the efficient elution of silver is natrium sulphite. The stability of $[Ag(SO_3)_2]^{3-}$ ($pK_2 = 9.00$) [25] confirms the ability of the complexing agent to release the silver metal ion from the cationic resin. In order to establish the optimal experimental conditions, we studied the influence of the concentration of natrium sulphite solution on the cation exchange behaviour of silver. After fixing a known quantity of silver in the cation exchange resin, 125 mL of 2% Na_2SO_3 solution were passed through the column and then it was washed with water up to complete rinsing of the excess of the reagent. The experiment was repeated using Na_2SO_3 solution of 5% and 10% concentration respectively. The elution curves in Fig. 3 show that the more concentrated the eluent, the more rapidly silver is eluted. It was found that the use of 2% or 5% Na_2SO_3

solution gave the best results for complete recovery of silver. The effluent volume, in which silver was completely recovered from the resin, was observed to be minimal by using 5% Na_2SO_3 as eluent. A slight lowering of silver recovery (around 92%) was observed only in the case of the higher concentration of Na_2SO_3.
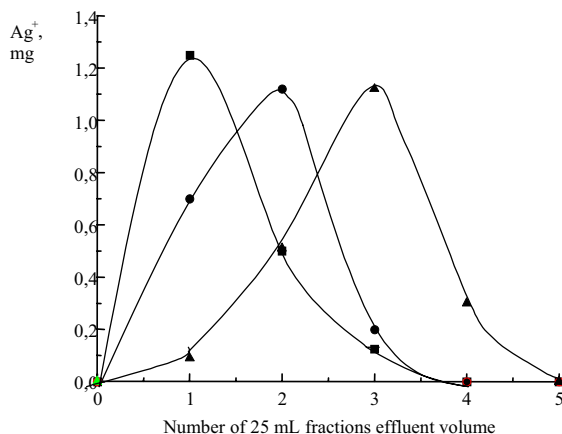

Fig. 3. *Elution curves of silver by using sodium sulphite as eluent agent;* amount of Ag^+ fixed in the resin = 2.10 mg; concentration of sodium sulphite: 10% (▲) ; 5% (●); 2% (■).

It was assumed that the decrease of the silver recovery was due to the following process: in presence of traces of oxygen dissolved in solution, at higher concentration of Na_2SO_3, a small quantity of silver was retained in the resin as silver sulphate. It must be mentioned that a very low recovery of silver was obtained by using 1% Na_2SO_3 as eluent. This may be explained considering that, at lower concentration of the sodium sulphite, the silver initially fixed in the resin is converted into an insoluble species namely silver sulphite which may be retained by the sorbent as well. Moreover it was observed that the colour of the resin changed to black. This behaviour could be due to the decomposition of silver sulphite as follows: $Ag_2SO_3 \rightarrow Ag_2O + SO_2$.

The other investigated metal ion, namely Pb(II) have a high tendency to form, in presence of Na_2SO_3, white insoluble compound. It is retained by the resin in this form. The precipitation of lead as lead sulphite within the resin was proved by the absence of the metal ion in the effluent. Also, the colour of the resin turned into white colour. The lead sulphite was dissolved by passing 2M HNO_3 solution through the column. Thus, the amount of lead (37.2 mg) fixed in the cation exchange resin (see "Procedure for sorption of metal ions") was eluted with 100 mL of 2M HNO_3. The maximum of the elution curve was attained at the first portion of 25 mL-effluent (~60%).

From the above results it can be expected that 5% sodium sulphite solution is especially suitable for selective recovery of silver in the presence of lead. In order to check this assumption, an experiment was performed for separation of silver from lead. After fixing

the two metal ions in the resin, silver was eluted selectively with a 5% Na_2SO_3 solution. After washing the column with distilled water for removing the excess of Na_2SO_3, Pb(II) was eluted with 2M HNO_3. The elution curves in Fig. 4 show good agreement of the quantities taken in the sample with those determined after separation.

On the basis of these results, our study was applied for separation of small quantities of silver from macroamounts of lead.

Table 1 shows that the proposed method can be utilised for recovery of traces of silver in presence of more than 500-fold excess of lead and for elimination of the matrix effect of lead in the determination of silver by conventional analytical methods. Recoveries higher than 97% for silver were found.
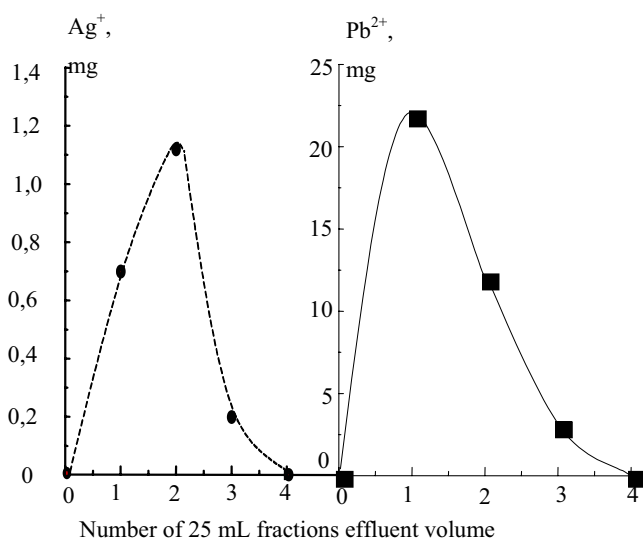

Fig. 4: *Elution curve of silver by using Na$_2$SO$_3$ 5% and of lead by using 2M HNO$_3$ as eluents; amount of Ag$^+$ fixed in the resin = 2.10 mg; ; amount of Ag$^+$ eluted = 2.08 mg; amount of Pb^{2+} fixed in the resin = 37.20 mg; amount of Pb^{2+} eluted = 37.18 mg.*

Table 1. Results of silver separation from lead with cation exchange resin

Silver in sample, %	Silver quantity, mg		Silver recovery, %
	In sample	After elution with 2% Na_2SO_3	
0.16	0.135	0.132	97.77
0.32	0.270	0.264	97.77
0.64	0.540	0.535	99.07
2.80	1.080	1.073	99.35

Conclusion

The results of our study show that traces and milligram amount of silver could be separated from lead by fixing the two metal ions in a column with a cation exchange resin (Dowex 50, H^+ form), followed by their selective elution. The best results were obtained by using 5% Na_2SO_3 for silver elution, followed by lead elution with 2M HNO_3.

REFERENCES

1. *** Lorenzo, A., Curtis Rhodes, O. and Susan Grube, M., *US Patent* **221.502**, 1990, *112*, 206750j.

2. *** Iske, U. and Huebner, K., *Ger. Patent.* **314.696**, 1990, *112*, 202501f.

3. *** Peter Hess, L., *US Patent.* **152.321**, 1990, *112*, P 238644u.

4. *** Mamoru, H. and Nobuyasu, E., *Jpn. Patent* **88/4, 090**, 1990, *112*, R183374y.

5. Yanli, H. E. (1989) *Huanjing Baoku* **5**, 20.

6. Zhou, Z., Li, H. and Xu, J. (1993) *Yejin-Fenxi* **13**, 20.

7. Wang, J. and Liang, J. (1988) *Yankuang-Ceshi* **7**, 39.

8. Zhang, H. Y. and Liu, F. Y. (1992) *Lihua-Jianyan*, *Huaxue-Fence*, **28**, 280.

9. Alimarin, P., Zhukova, L. N., Runov, V. K., Simonov, E. F., Talut, T. E. and Trofimchuke (1991) A. K. *Zh. Anal. Khim*., **46**, 695.

10. Burmaa, G., Pestunovich, A. E., Vlasova, N. N. and Voronkov, M. G. (1990) *Izv. Sib. Otd. Akad. Nauk. SSSR*, *Ser. Khim. Nauk*, **5**, 66.

11. Roy, S. K. and Kundu, D. (1991) *Anal. Lett.*, **24**, 139.

12. Yang, L., Jin, L., Xu, T. and Fang, Y. (1989) *Lihua-Jianyan*, *Huaxue-Fence*, **25**, 18.

13. Lalit Eusebius, C. T., Animesh Ghose, K. and Dey, A. (1981) *Analyst*, **106**, 529.

14. Weinert, C. H. S. and Strelow, F. W. E. (1983) *Talanta*, **30**, 755.

15. Zhang, J., Guo, X. and Su, Z. (1990) *Yejin Fenxi*, **10**, 4.

16. Raj Singh, P. and Erneste Pambid, R. (1990) *Analyst*, **115**, 301.

17. Li, Y. Z., Rao, Z. and Zhu, Y. L. (1992) *Fenxi Huaxue*, **20**, 1333.

18. Shevchuk, I. A. and Trekhos, E. E. (1988) *Zh. Anal. Khim*., **43**, 441.

19. Oue, M., Kimura, K. and Shono, T. (1988) *Analyst*, **113**, 551.

20. Kucharev, E. A., El-Yas, B. and Petrukhin, O. M. (1989) *Zavod. Lab.*, **55**, 32.

21. Hasany, S. M. and Ali, A. (1990) *J. Radioanal. Nucl. Chem.*, **139**, 99.

22. Gu, Z. K., Lu, Z. E., Lu, Y. H., Tong, J. Y. and Hong, L. (1993) *Lihua-Jianyan, Huaxue Fence*, **29**, 291.

23. Zelentsova, A. M. and Mazunyak, N. V. (1989) *Zavod Lab.*, **55**, 30.

24. Dolaberidze, L. D., Todradze, G. A., Shanidze, M. K. and Chikvaidze, (1993) G. G. *Zavod. Lab.*, **59**, 27.

25. Lurie, Iu. Iu. (1967), *Spravocinik po analiticeskoi himi*, Moskva, p. 244.

26. Khapkar, S. M. and De, A. K. (1960) *Talanta*, **7**, 7.