

RECOVERY OF SILVER METAL USED IN CHEMICAL REACTIONS

A.M. Abdallah

*Department of Chemistry,
Faculty of Science,
University of Mansoura, P.O. Box 30, Mansoura*
and

M. M. El-Kersh, A.A. El-Toukhy and N. Th. Girgus

*Department of Chemistry,
Faculty of Science,
University of Tanta, Tanta
Egypt*

(Received July 24, 1985; revised January 13, 1986)

Two simple processes for silver recovery from the laboratory wastes are reported. One process depends on the dissolution of the wastes in sodium thiosulphate, detaching its sulphide sulphur by adding citric acid and coagulating the dispersed lyophobic sols of silver sulphide by lithium (carbonate). The other process depends essentially on the instantaneous reduction of manganate to a manganous ion in a strongly alkaline solution. This reaction is catalysed by $[\text{Ag}(\text{NH}_3)_2]^+$. The $\text{K}_2[\text{Mn}(\text{OH})_4]$ formed is rapidly oxidised to the brown MnOOH which is further oxidised to the black $\text{MnO}_2 \cdot \text{H}_2\text{O}$ with separation of metallic silver particles.

INTRODUCTION

Methods for the recovery of silver from many sources of wastes have been described in many articles [1-5]. However, most of these methods are confined to particular types of wastes and suffer from some disadvantages. Unsatisfactory results were obtained from the method suggested by Salazar *et al.* [6] for recovering silver from argentiferous wastes from photographic process and other industrial liquids. Silver was recovered from waste water [7] as silver sulphate crystals with purity > 99% and recovery rate of silver was 90%. Many methods were elaborated to separate silver from solutions, utilizing the difference in the electrode potentials between silver and aluminum [8-11] or copper [12]. Piret *et al.* [13,14] presented two sophisticated procedures for the recovery of silver from heavy metals of leach residues or chloride solutions. Perman [15] described a method for recovering silver from waste silver chloride residues, using hydrochloric and nitric acids for digestion before complexation with ammonia. A 99.3% purity silver metal was precipitated from solution using ascorbic acid as a reducing agent. Many hydrometallurgical methods have been described to recover silver from a variety of ores [16-18], intermediates [19, 20], laboratory [21] and dental amalgam [22]; wastes of silver were dissolved and converted to silver complexes before chemical reduction.

The present investigation is concerned with the development of two processes for the recovery of silver from laboratory wastes in good yield not less than 90%.

EXPERIMENTAL

Samples. The silver chloride waste used in the study was obtained from two sources, viz the Analytical Chemistry Section of the Health Laboratories of El-Gharbia Governorate (Tanta), where the determination of chlorides in milk, dairy products, canned food, meat and fishes, is routinely done using the methods of standard specifications; and the student laboratories of the Faculty of Science, where precipitation reactions involving argentometric titrations are carried out. Other insoluble salts of silver, viz, Ag_2SO_4 , Ag_2CO_3 , AgI , AgBr and $\text{Ag}_2(\text{COO})_2$ were prepared in the laboratory by the conventional methods from commercial salts.

A mixture of the dried salts was prepared to contain a calculated percentage of silver. The mixture was thoroughly ground to pass completely from the 90 mesh sieve and kept in a dark glass bottle.

Procedures: Two processes were followed to separate silver sulphide or metallic silver from the mixture.

Silver sulphide precipitation: About 12 g of the mixture were transferred to a 1000 - cm^3 low form lipped

beaker and stirred while 250 cm³ of 20% Na₂S₂O₃ solution were added and the mixture was digested on a steam-bath with gentle stirring until the residue disappeared. A 0.5M Solution of citric acid was poured to adjust the pH at 2.6 [≅ 100 cm³ of 10% (w/v) citric acid was found enough to effect the required pH range 2.5 – 2.7]. The solution then turned black as colloidal silver sulphide become dispersed in the medium. A 0.4 g of Li₂CO₃ was added to the hot solution to cause coagulation of the precipitate completely in a relatively short time (≅ 30 min). The solution pH thereafter was found to be ≅ 3.7. The silver sulphide precipitate was then filtered using Whatman No. 41 filter paper in a Buchner funnel.

Silver metal separation: A sample mixture of about 6 g was placed in a 400 cm³ beaker and stirred while 50 cm³ 28-30% ammonia solution plus 25 cm³ of 5% KOH solution were added and digested on a steam-bath until the residue disappeared^a. A 0.06M solution of KMnO₄ was added in a dropwise flow until the solution was light green. At the moment when the green colour was dissipated, an instantaneous colloidal brown precipitate of metallic silver was formed which changed to black. It was observed that the highly explosive "fulminating silver" (Ag₃N or AgH₂N) [23] may be formed if the upper surface of the precipitate was allowed to dry out. Addition of few drops of 0.2% gelatin solution, directly after the last addition of the permanganate solution, prevented the formation of such hazardous compounds. Moreover, this treatment was found effective in coagulating the silver particles to form small lumps. These were easily separated from the solution applying Whatman No. 541 filter paper in a Buchner funnel.

Ignition of the precipitate: Silver precipitates (whether in form of sulphide or metal) were allowed to dry in air or better, by leaving them in a drying oven for a period of time. The dried precipitate on the filter paper was transferred to a pre-treated^b thick walled pottery crucible lined with a paste of 1:1:2 potassium, sodium carbonate and borax respectively. The crucible was then ignited to 1200° using the usual technique of ignition. When melting

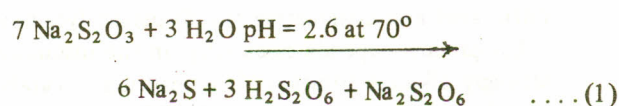
(a) Nearly all silver mixtures residues responded to that treatment of dissolution. However, mixtures containing perceptible residues of silver bromide and/or iodide (>5% of the mixture) did not dissolve completely in ammonia and KOH solutions. A preliminary sintering process for the residue with pyrolusite was carried out and treating the sintered mixture with conc. sulphuric acid and water, separating silver sulphate which was readily dissolved in ammonia and potassium hydroxide solution.

(b) It was found necessary to bring the pottery crucible to constant texture at 1200°. It was placed in an empty state in a muffle furnace which was then switched on and gradually raised the temperature to 1200° the heating was continued for 5–10 mins. The muffle was switched off while leaving the crucible inside to cool.

was complete (within 30 min), a few mg of zinc scrap were added to collect the slag and refine the silver melt. The crucible was left for 5 min more in the muffle furnace and the melt was poured into 2-dm³ container filled with ice-water, whereby small lustrous blocks of silver metal were obtained.

RESULTS AND DISCUSSION

(i) *The Silver Sulphide Precipitation Process.* The insoluble silver residues dissolve in an excess of Na₂S₂O₃ solution to form anionic complexes as [Ag(S₂O₃)]⁻ and [Ag(S₂O₃)₂]²⁻. In such neutral solution, it is well known that side reactions can take place and the solution attains equilibrium over a long period of time (>3 hr.) where SO₄²⁻, SO₃²⁻, and S²⁻ are the dominant species. The presence of citric acid in the solution represses the formation of SO₄²⁻ and SO₃²⁻, and induces the excess thiosulphate to undergo the following reaction:



The easily detectable S²⁻, produced essentially from detaching of the -2 valence sulphur of the excess S₂O₃²⁻, in the presence of citric acid, has the ability to convert the anionic complexes of silver to forming the very stable Ag₂S in a colloidal state. When Li (carbonate) is added, it enhances the coagulation of the precipitate and enables the whole process to reach completion in few min.

(ii) *The Silver Metal Separation Process:* The redox potential of KMnO₄ is pH dependent and ranges from + 1.70 v in neutral solution to + 1.51 v in acidic solution and most probably lower at higher pH. The standard oxidation potential of Mn²⁺ in MnO₂/Mn²⁺ system is 1.23 v, therefore it is capable of reducing Ag⁺ ion at higher pH since the standard reduction potential for the Ag⁺ ion is + 0.799 v. The reaction is found to be fast and quantitative. However, the following redox reactions are arranged in sequential steps as observed experimentally^c.

(1). Potassium permanganate in the strong alkaline solution undergoes the reaction:



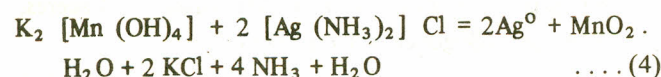
(2) The MnO₄²⁻ ion contains one unpaired electron and turns the solution green. Immediately, the argentous

(c) A blank was carried out and the reagents were added essentially with the same sequence as in the case of treating the sample mixture.

complex cation $[\text{Ag}(\text{NH}_3)_2]^+$ catalyses the reduction of MnO_4^{2-} ion to Mn^{2+} ion. The reaction thus proceeds as follows:



(3) The complex $\text{K}_2[\text{Mn}(\text{OH})_4]$ is rapidly oxidised to the brown MnOOH , which is further oxidised to the black $\text{MnO}_2 \cdot \text{H}_2\text{O}$ with instantaneous separation of silver particles.



With impure silver solutions, hydrated manganese dioxide gathers silver particles which makes the precipitate easily filtered without complications.

(iii) *Analysis of the products:* The yield of five replicates of each process was collected and two representative samples were taken (one sample for each process) using the usual abrasion technique for sampling metallic substances. Two different methods of analysis were followed for each sample.

(1) *The spectrographic method:* The silver sample was dissolved in HNO_3 and the dry salt was intimately mixed with graphite powder packed into a sample electrode. An ac arc device was used for excitation. A Hilger and Watts, Barfit fully automatic large-quartz spectrograph, wavelength range 280 – 500 nm, was used for the detection of the emitted radiation photographically. A silver reference sample of spec pure grade was obtained from SIGAL Co. for noble metals and jewels. Table 1 shows a comparison

Table 1. Comparison of the impurities concentration in the recovered and reference standard samples

Element	Concentration (ppm)		
	Recovered (i)	sample by process (ii)	SIGAL sample
Cu	100	20	—
Mn	<10	<10	<10
Sb	<100	<100	<100
Bi	<100	<100	<100
Be	<10	<10	<10
Ni	5	5	5
Cr	1	1	2
Ti	10	1	3
Co	30	15	30
Zn	<100	<100	<100

for concentration of some of the most common impurities in silver metal. It is obvious that the comparison is in great favour of the recovered samples.

(2) *The fire-assay method:* Analysis by this method was carried out in the Department of Impression of Noble Metals, Ministry of Interior Commerce, Egypt. The average purities of the recovered samples are 99.8 and 99.99% respectively.

The efficiency of the two processes were determined by processing a known quantity of silver wastes (12 g of silver residues containing 8.85 g of silver metal). The amount of recovered and refined silver were $\cong 94$ and $\cong 92\%$ for processes (i) and (ii) respectively. The recovery is practically quantitative and the two processes are applicable to any system yielding insoluble silver salts.

The present processes have the advantage that they need only four steps while other processes may require the application as many as seven steps [4]. The recovered silver pellets by the two processes were so large that the weight of one pellet reached 4 g. The use of very cheap pottery crucibles for ignition is an additional benefit for the two processes where other types of crucibles are expensive and almost subject to breakdown during pouring the melt into the ice-water.

CONCLUSION

The benefits offered by this work are primarily of economical interest. The procedures presented here not only use inexpensive chemicals and equipment but also increase the national income by recovering more than 90% of high purity silver metal from laboratory wastes.

It must be stressed here that the authorities need to revise their regulations to clarify and to lay stress on recovering silver from wastes in all laboratories. Such action, along with the wider use of the ecological defense programme, would conserve a valuable resource to prevent possible environmental harm, and save a part of the state budget.

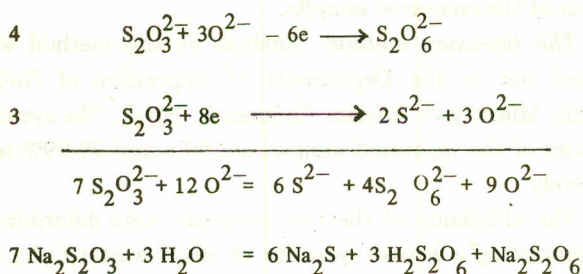
Experience gained during the present study permits us to state that the procedures given can be applied satisfactorily to recover silver from photographic wastes.

Acknowledgement: The authors wish to express their deep thanks to Prof. Dr. R. M. Issa, President, Tanta University and Prof. Dr. T. M. El-Shamy, Vice Dean, for their valuable help and interest during the course of the work.

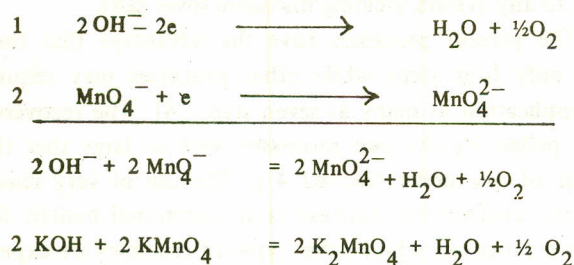
APPENDIX

Verification of equations 1 – 4:

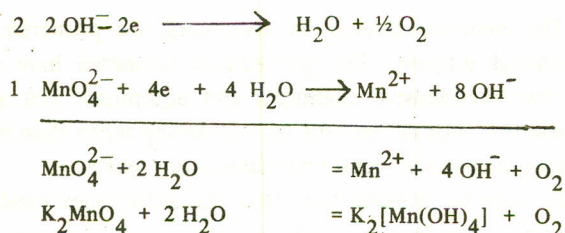
Equation (1)



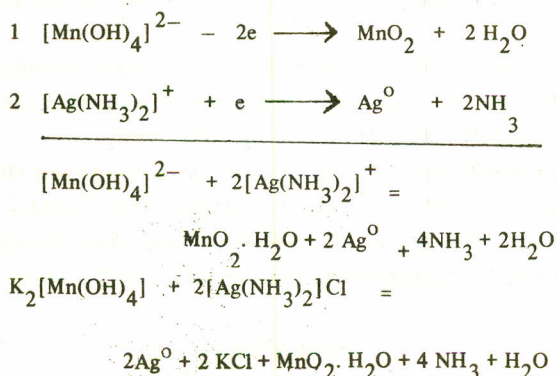
Equation (2)



Equation (3)



Equation (4)



REFERENCES

1. R. Roberts, J. D., Lewis and J. H., LaRochelle, *Ecolibriem* 10, 11. (1981).
2. G., Clarke, *Bur. Mines Bull.*, 4 (1975).
3. *Business Week*, November 2, 1974 p. 80 f.
4. C.H. Schack, and B.H. Clemmons, *U.S. Bur. Mines. Circ.* 8266, 36 (1965).
5. M.L., Schreiber, *J. Soc. Mot. Pict. Telev. Eng.*, 74, 505 (1965).
6. M.I. Salazar, A. Fonseca, L.A., Maldonado A. Caceres, *Quim. Ind. (Bogota)*, 8, 19 (1973).
7. S. Fukumoto, F. Masayuki, K. Tanaka, *Japan Kokai*, 7493, 213 (Cl. 10L 224), 5 Sept 1974; appl., 735934, 12 Jan. 1973.
8. T., Ohhachi, *Japan Kokai*, 7467, 819 (CL. 10L 22, 10 A2), 1 Jul. 1974, Appl. 71 110,357, 6 Nov. 1972.
9. R.A. Wallace, *U.S. Pat.* 4,008,077 (cl. 75 - 118 p; C 22B 11/04), 15 Feb. 1977; appl. 407,740, 18 Oct. 1973.
10. B. Balcar, *Povrchone Upravu*, 16, 33, (1976).
11. S.S., Montagne, *Japan Kokai*, 78 51, 127 (cl. C 22B 11/04), 10 May 1978, Belg. Appl., 76/45, 724, 19 Oct. 1976.
12. H. Nechamkin and P.E. Dumas, *J. Chem. Educ.*, 53, 370 (1976).
13. N. Piret, and W. Røever, *Ger offen.*, 2,528,989 (cl. C 22B 7/02), 27 Jan. 1977, Appl., 28 June 1975.
14. N. L., Piret, M. Hoeppe, and H. Hudelka, *Ger.* 2,656, 233 (Cl. C 22B 11/04), 29 Dec. 1977, Appl. 11 Dec 1976.
15. C.A., Perman, *Talanta*, 26, 603 (1979).
16. M. Toyota, A. Ota, T. Shinizu and S. Kitamura, *Japan Kokai*, Tokyo Koho 7993, 604 (Cl. C 22B 7/00), 24 Jul. 1979, Appl. 77/160,061, 30 Dec. 1977.
17. W.H., Lee, J. H., Min, J. C., Lee and S. J. Lee, *Taehan Kwangsan Hakhoe Chi* 16, 152 (1979).
18. S. Richter and A. Maksi, *Rudy* 29, 313 (1981).
19. G. Sokalska And F., Letowski, *Pol.* 80092 (cl. C 22B 15/10), 10 Sep. 1975, Appl. 166,089, 25 Oct. 1973.
20. L.T. Edwards and L.N. Trowbridge, *U.S. Pat.*, 4, 131, 455 (Cl. 75-118R; C 22B 11/04), 26 Dec. 1978, Appl. 859, 154, 9 Dec. 1977.
21. S.I. Kandrina and N. I. Grigorov, *Molochn. Prom-st.*, 6, 39 (1980).
22. C.W. Lee, and K.W. Fung, *Resour. Recovery Conserv.*, 5, 363. (1981).
23. R.K. McAlpine and B.A. Soule, *Quantitative chemical Analysis*, Van Nostrand, New York, p. 176 (1933).