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Recovery of Silver as Silver Nitrate from Waste Silver Chloride in Quantitative Analysis Laboratory

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ABSTRACT

Various methods for recovery of silver as silver nitrate from waste silver chloride in the quantitative analysis laboratory of the Department of Chemistry, Kasetsart University were investigated. Most of the methods based on the reduction of silver chloride to metallic silver and followed by the oxidation of metallic silver to silver nitrate by nitric acid. The electrolysis of silver (I) solution to give metallic silver also was investigated. The percent recovery and percent purity of the recovered-silver nitrate were in the range of 89.49-97.33 and 99.29-99.66, respectively. The reduction of silver chloride at 1,000 °C in electric furnace gave the highest percent recovery with high purity silver nitrate. The operation cost of each method was compared, and the reduction of silver chloride by formaldehyde, which gave 95.14% recovery and 99.29% purity, is recommended as a suitable method for recovery of silver as silver nitrate.

Key words: recovery of silver, silver chloride, silver nitrate

INTRODUCTION

In general quantitative analysis laboratories, silver is commonly used as silver nitrate for qualitative and quantitative analysis of chloride, bromide and iodide ions, and generated silver halides as chemical waste. Because of the high cost of silver, a number of articles have appeared in the literature concerning reclamation of silver from its various compounds. Many of these methods use high temperature reactions (500-1,000°C), or hazardous materials such as cyanides, silver-ammonia solutions, concentrated base or aqua regia (Hayes and Steed, 1972; Foust, 1984; Hill and Bellows, 1986; Rawat and Kamoonpuri, 1986; Murphy *et al*., 1991).

As the price of silver nitrate increases and chemistry department budgets tighten, the recovery of silver from silver residues of analytical laboratory becomes necessary. Reverting wastes obtained in the experiment into useful materials can offset a portion of the cost. There are various procedures for recovering silver as silver nitrate from silver halide residue. Nevertheless, the search for the procedure using common and inexpensive laboratory reagents is also necessary.

This work focused on three general objectives: recovery of metallic silver from silver chloride waste from quantitative analysis laboratory of the Department of Chemistry (Kasetsart University) by various methods, conversion of the metallic silver back to silver nitrate, and comparison of percent purity and percent recovery of the products from each method. The cost for the recovery of silver from each procedure had also been investigated.

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MATERIALS AND METHODS

Recovery of metallic silver from silver chloride waste

The silver chloride residue obtained from quantitative analysis laboratory as waste was acidified with hydrochloric acid to ensure complete precipitation of silver as silver chloride. It was heated at 100°C until the residue appeared white. After cooling, the supernatant liquid was decanted, and silver chloride was filtered off on Whatman No. 42 paper on a Buchner funnel.

Reduction of formaldehyde

$2AgCl + 3NaOH + CH_2O \rightarrow 2Ag + HCO_2Na + 2NaCl + 2H_2O$

A 4.10 g of NaOH (Merck, AR. grade) was dissolved in 100 ml of water in a beaker and 5 g of finely ground silver chloride was added with rapid stirring, followed by 3 ml of 37% formaldehyde (BDH, Lab grade). The beaker was covered with a watch glass and stirring continued. After 10 minutes the mixture was heated to 60-70°C, and stirring was continued for a total time of about 1 hour. By the end of this time the metallic silver will have agglomerated into small shiny pellets. The pellets were collected on a sintered glass filter, washed several times with water, then acetone and air dried.

Reduction with glucose and fructose

$2AgCl + 3NaOH + C_6H_{12}O_6 \rightarrow 2Ag + C_6H_{11}O_7Na + 2NaCl + 2H_2O$

A 2.7 g of NaOH (Merck, AR. grade) was dissolved in 100 ml of water, and 5 g of silver chloride was suspended in the resulting solution. A 3.675 g portion of glucose (Ajax, Lab grade) or fructose (Fluka, Lab. grade) was added. The reaction mixture immediately turned black. It was covered with a watch glass and heated to 70-80°C with stirring for about 1 hour. The resulting silver pellets were collected on a sintered glass filter, washed several times with water, then acetone and air dried.

Reduction with sodium borohydride

$8Ag^+ + BH_4^- + 8OH^- \rightarrow 8Ag + B(OH)_4^- + 4H_2O$

A 0.75 g of $NaBH_4$ (Fluka, AR. grade) was dissolved in 50 ml of ammonia solution (5 g AgCl / 50 ml concentrated ammonia solution) in a beaker. A vigorous reaction took place, a powdery precipitate of silver was observed in about 1 minute. The beaker was covered with a watch glass and heated to 70-80°C with stirring for about 1 hour. The silver pellets were collected on a sintered filter, washed several times with water, then acetone and air dried.

Reduction with zinc, copper and magnesium powder

$2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+}$

$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$

$2Ag^+ + Mg \rightarrow 2Ag + Mg^{2+}$

For 5 g of silver chloride which dissolved in 50 ml of concentrated ammonia solution, 1.5 g of zinc (Mallinckrodt, Lab grade) or 1.15 g of copper (Merck, Lab grade) or 0.43 g of magnesium (Riedel-de Haen, Lab. grade) powder was used. A portion of metal powder was added in the silver-ammonia solution. The mixture was stirred at 40°C for 1 hour, and the resulting precipitated was collected on a sintered glass filter and washed with water several times. The resulting precipitated was washed with 6M H_2SO_4 to wash out the excess metal powder.

Silver electrodeposition method

A 2.5 g of AgCl was dissolved in 100 ml of 5% KCN (Carlo Erba, Lab grade) solution. A 2.4 g of potassium carbonate (Unilab, Lab grade) was added into the silver chloride solution. A carbon rod electrode was used as the cathode and a stainless steel rod electrode as the anode. The electric current was adjusted to 1-3 A, and the solution was stirred gently and electrolyzed for 15-45 minutes. The silver will have deposited as a coarse adherent coating on the carbon rod electrode. The concentration of cyanide ion left in the solution after the electrolysis was determined by Volhard's method (Bassett *et al*., 1978).

Silver recovery with high temperature method

A dried residue of silver chloride was

thoroughly mixed with an equivalent of potassium carbonate. The mixture was placed in a graphite crucible and baked in a furnace at 1,000°C. At this temperature the reduced silver melts, forming a puddle at the bottom of the crucible. The crucible was filled with the mixture no more than three-fourth full as foaming occurs. After 1 hour, the crucible was removed and silver ingot was obtained.

Preparation of silver nitrate from recovered silver

Approximately 15 ml of water was added into 3.7 g of recovered silver and heated to 50°C, then concentrated HNO_3 (Carlo Erba, Lab grade) was added dropwise with occasional swirling until all the silver has dissolved. The solution was filtered through the Whatman No. 42 paper to remove undissolved material. The filtrate was concentrated on a hot plate until precipitation occurred. The excess HNO_3 was neutralized in a desicator filled with NaOH. The recovered silver nitrate was characterized by X-ray powder diffractometer. The purity of the recovered silver nitrate was determined by atomic adsorption spectrophotometer using PERKIN ELMER, AAnalyst 800.

RESULTS AND DISCUSSION

The X-ray powder diffraction (XPD) spectrum of the recovered silver nitrate is shown in Figure 1. The spectrum shows a strong peak at 35.80 degrees with two weak peaks at 54.96 and 75.37 degrees, indicated that only silver nitrate in the product. The percent purity and recovery of silver nitrate from waste silver chloride from each method is shown in Figure 2 and 3, respectively.

Silver in the form of $[Ag(NH_3)_2]^+$ ion or $AgOH_{(aq)}$ was easily reduced by aqueous borohydride, formaldehyde, reducing sugar (glucose and fructose), as well as active metals such as zinc, magnesium and copper. The electrolysis of $[Ag(CN)_2]^-$ ion gave quite a promising yield of recovered-silver nitrate. High temperature method using potassium carbonate (K_2CO_3) as reducing agent also gave a good yield of recovered-silver nitrate when the experiment was performed on a high temperature furnace.

Among all the reducing agents used in the experiments, sodium borohydride and formaldehyde seem to be more powerful than other reducing agents. As seen in Figure 3, the aqueous sodium borohydride and the aqueous formaldehyde procedures gave 95.59% and 95.14% recovery of

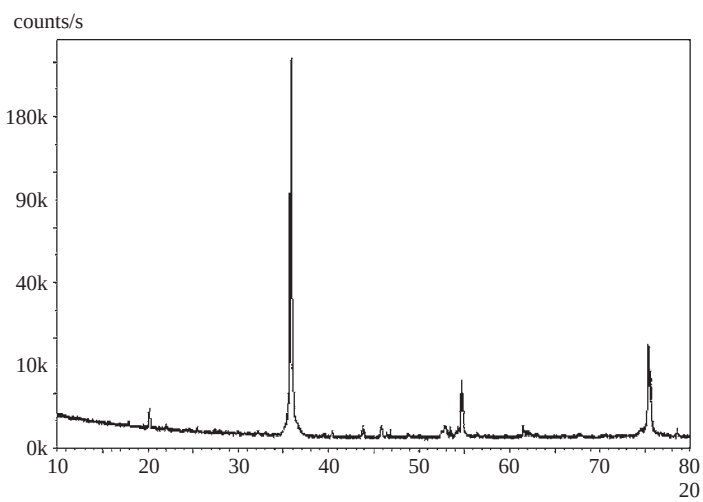

Figure 1 X-ray powder diffraction (XPD) spectrum of the recovered silver nitrate.

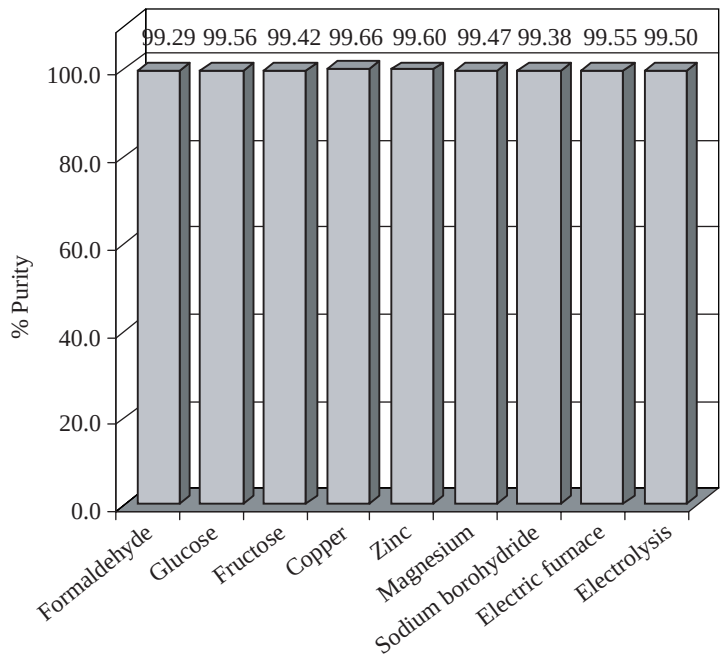

Figure 2 Percent purity of recovered-silver nitrate prepared by various methods.

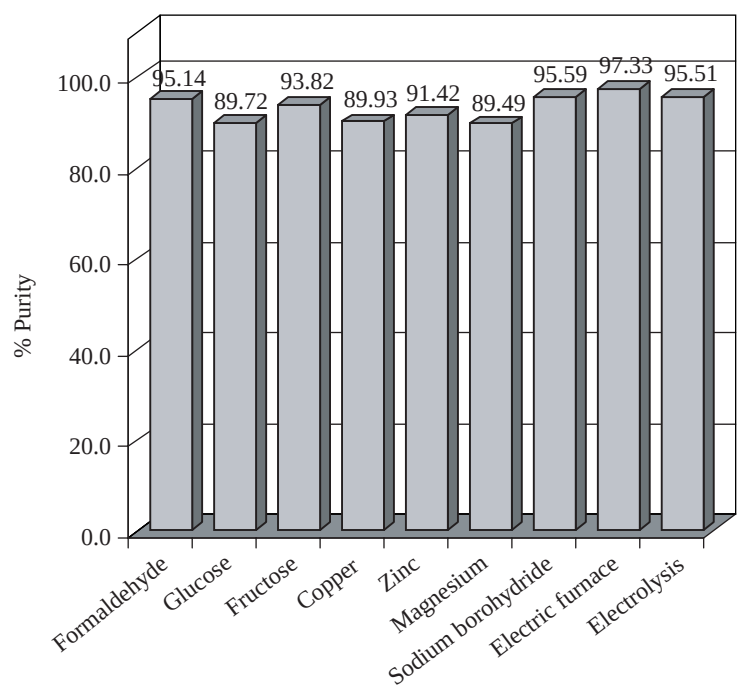

Figure 3 Percent recovery of silver nitrate prepared by various methods.

silver nitrate, respectively, which were higher than when other reducing agents were used. This may be because both of them were used in aqueous form while the others in solid form, and the reduction potential of sodium borohydride and formaldehyde were very low compared to other reducing agents used (Table 1). Another reason is the feature of recovered-metallic silver (Table 2). When both formaldehyde and sodium borohydride were used as the reducing agent, the size of recovered-metallic silver were small and shiny which was easier to react and change to silver nitrate. Although the reduction of silver ion by reducing metals also gave small size silver pellet, the color of the pellet was not shiny which may indicate the presence of Ag_2O at the surface of silver metal which made them difficult to react with nitric acid in the final step.

The electrolysis of $[Ag(CN)_2]^-$ when stainless steel were used as both anode and cathode gave quite a promising result (95.51% recovery). However, this method is not recommended due to a quantitative amount of cyanide ion left in the post-electrolysis solution. Using this method, the initial concentration of cyanide ion was 0.75 molar, and it was found that the concentration of cyanide ion after the electrolysis was 0.18 molar which was still too high and could cause some problems to the environment.

The reduction of silver chloride by formaldehyde and fructose seems to be a suitable method (Table 3), both in the quality of recovered-silver nitrate and the operation cost. Although the operating cost of the reduction of silver chloride at 1,000°C in electric furnace was double to the reduction by formaldehyde, this method may be recommended if the high purity of recovered-silver nitrate is required.

CONCLUSION

The methods for recovery of silver as silver nitrate from silver chloride waste have been compared. The reduction of silver chloride by formaldehyde and fructose has proved to be a suitable method both in percent yield and operation cost. The reduction of silver chloride at 1,000°C is suitable if the high purity of recovered-silver nitrate is required. These methods can be applied for the recovery of silver from the general quantitative analysis laboratories.

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Table 1 Standard reduction potential of some metals and compounds.

Reaction	E^o/V
$Ag^+ + e^- \rightarrow Ag$	0.800
$Cu^{2+} + 2e^- \rightarrow Cu$	0.342
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.356
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.762
$H_2BO_3^- + 5H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$	-1.240
$HCO_2^- + 2H_2O + 2e^- \rightarrow CH_2O + 3OH^-$	-1.160

Table 2 The appearance of recovered-metallic silver prepared by various methods.

Procedure	Appearance of recovered-metallic silver
1. Using sodium borohydride as reducing agent	Small size shiny pellets (~3 mm)
2. Using formaldehyde as reducing agent	Small size shiny pellets (~3 mm)
3. Using glucose as reducing agent	Medium size pellets (~5 mm)
4. Using fructose as reducing agent	Medium size pellets (~5 mm)
5. Using copper as reducing agent	Small size pellets (~3 mm)
6. Using zinc as reducing agent	Small size pellets (~3 mm)
7. Using magnesium as reducing agent	Fine brown-gray powder,
8. Electrolysis	Shiny film deposited on the electrode
9. High temperature (using electric furnace)	Large size shiny pellet (~8 mm)

Table 3 Cost of recovered-silver nitrate by various methods and commercial price.

Method	Cost of silver nitrate (Baht/gram)
1. Using formaldehyde as reducing agent	2.66
2. Using glucose as reducing agent	3.25
3. Using fructose as reducing agent	3.00
4. Using copper as reducing agent	5.42
5. Using zinc as reducing agent	4.71
6. Using magnesium as reducing agent	5.18
7. Using sodium borohydride as reducing agent	10.34
8. High temperature (using electric furnace)	7.28
9. Electrolysis	6.43
10. Commercial price	21.94*

* Average price for 100 g/package from 3 companies.

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