We have tried various procedures for the recovery of silver from the wastes from experiments in the courses in quantitative analysis and have settled on cathodic deposition of silver from a cyanide solution in a non-partition cell with stainless steel electrodes. All of the equipment needed can be found in most laboratories or can be purchased at little expense. The procedure is unusually good for instruction and projects at the upper class level.

Of the older procedures we have used that of Willbanks (1) many times with success. It is based on converting the various insoluble silver salts collected to silver hydroxide by digesting with sodium hydroxide, decomposing the oxide to silver metal at 500°C, and finally melting the silver into a bar. The chemistry is simple and the procedure an enormous improvement over an earlier scheme in which the solid silver residues (chloride, etc.) are mixed with sodium carbonate and heated to 1000° to 1100°C. Our troubles with these procedures curiously came on two occasions, from breakage of crucibles and consequent damage to the lining and heating elements of the electric muffle. Steed and Hayes (2) improved the older fusion procedure by using potassium carbonate and provided some useful hints on how to improve the yield and protect the furnace. Our feeling is that securing the large clay crucibles, ball-milling the silver residues with the carbonate (as in the Steed and Hayes procedure), and risking the furnace is too much trouble, even with silver at $0.18 per gram (1977). Of course, if the residues are silver and silver oxide only (from organic preparations), dissolution and digestion with nitric acid, evaporation, and crystallization of silver nitrate, as recommended by Garin and Henderson (3), is more straightforward. An older procedure for converting silver chloride to silver nitrate, Meyer (4), by digesting a suspension of the silver chloride in dilute hydrochloric acid with metallic zinc (powder or fine wire) and working up the metallic silver so formed we found simply too cumbersome and expensive; the digestion is time-consuming, and a second digestion of the metallic silver with hydrochloric acid is necessary to remove the excess zinc. Meyer was interested in the recovery of silver from alloys (silver solder, coinage) and recommended precipitation of the chloride to separate the silver from copper, cadmium, and other metals.

We chose electrodeposition of the silver from a cyanide solution rather than from an ammonia solution primarily because we feared that silver-ammonia solutions by careless handling might be slopped about, allowed to dry and produce a shock-sensitive explosive residue. Silver can, of course, be deposited very nicely from an ammonia solution (5, 6, 7), but silver iodide will not dissolve in a solution of ammonia. On the other hand, all silver salts, except for the sulfide, dissolve in solutions of the alkali cyanides, the electrodeposition can be made from a non-partition cell of simple construction, and excellent deposits of large amounts of silver can be obtained (as for example in the fabrication of silver crucibles for analytical work (8, 9)).

The chemistry involved is

**Dissolutions of the silver precipitate:**

\[ \text{AgCl} (\text{Br}^-, 1-, \text{oxide}) + 2\text{KCN} = \text{KAg(CN)}_2 + \text{KCl} \]

**Cathode:**

\[ \text{Ag(CN)}_2^- + e^- = \text{Ag}^0 + 2\text{CN}^- \]

**Anode:**

\[ 2\text{CN}^- = (\text{CN})_2^2 + 2e^- \]

**Overall:**

\[ 2\text{Ag(CN)}_2^- + 2e^- = 2\text{Ag}^0 + 2\text{CN}^- + (\text{CN})_2^2 \]

**Procedure for the Recovery of Silver**

**Accumulation of Wastes.** Pour the liquids containing the silver in a large container to which handfuls of the cheapest grade of solid chloride are added occasionally. Stir the mixture occasionally to keep the solution slightly acid by the additional of hydrochloric when necessary. If the waste solutions contain cyanide, keep container in a ventilated hood. Discard the supernatant liquid at intervals after the silver chloride has settled. After a sufficient slurry of silver chloride has accumulated, filter through a large Buchner funnel and wash several times by stirring with water and filter. Place the cake of silver chloride (plus silver bromide and silver iodide if present) in evaporating dishes and allow to dry by exposure to air.

**Electrolysis Cell.** Arrange a 1-l beaker so that a solution in it be stirred magnetically. Place two stainless steel sheets, each 5 × 5 cm in size and prepared and pretreated as described in the next paragraphs. The sheets may be suspended from the electrical leads (No. 10 or 12 insulated copper wire) and electrical contact made with alligator clips.

Place a bead of epoxy resin around the rim of each stainless steel strip.

**Note on the Care Required in Handling Cyanides**

This process for recovering silver must be conducted in a reasonably well ventilated hood, acids must not be added to the potassium cyanide electrolyte at any time, and potassium cyanide on the skin should be washed away with water promptly. The alkali cyanides are, of course, poisons when taken internally. Short contact with the skin is harmless and the salts on the skin or table tops are removed simply by washing well with water. Taken orally, alkali cyanides lead to death in a very few minutes; they affect the nervous system and combine with the hemoglobin of the blood; after ingestion, quick treatment is necessary; induce vomiting, oxidize the cyanide with dilute hydrogen peroxide, inject (hospital) methylene blue into the blood stream.

Hydrogen cyanide, formed by acids and water, is a liquid boiling at 26°C. It is miscible in all proportions with water, but the high volatility means that a considerable quantity will find its way into air from a water solution. It has a sweet odor and can actually be detected by most people in a room in which a solution of an alkali cyanide in water is exposed, the hydrogen cyanide being formed in small amount by hydrolysis. The toxicity of hydrogen cyanide and of cyanogen (formed at the anode during the electrodeposition of silver) is about the same as that of carbon monoxide and hydrogen sulfide. The electrodeposition of silver in this recovery process, as in the large scale commercial electroplating of silver, is made from a highly alkaline solution and there is no chance that the solution will go acidic during the electrolysis. Electrolysis is a relatively slow operation; 53.8 A·h are required for the formation of one mole of cyanogen (22.41 of gas). Sufficient protection is provided for the electrodeposition cell by a good hood with a modest draft vented through a roof.
Precondition the stainless steel electrode to be used as the cathode by making it an anode for 1 minute; this is most conveniently done at the time the electro-deposition of silver is just begun. This procedure places a layer of chromic oxide on the stainless steel making it possible to remove the deposit of silver later by merely peeling the deposit from the electrode.

Connect the electrodes to a source of direct current. A convenient source is a battery charger, available at the automotive accessory stores for $20 to $30. By operating the battery charger from an auto-transformer (Varicore) the potential applied to the electrolysis cell may be easily adjusted to any desired value.

Electroposition of Silver. Cover the precipitate of silver chloride (plus bromide, iodide, oxide, and other silver salt present) with a 40% solution of KCN. Stir occasionally and after a few hours filter through a Buchner funnel. Reserve the remaining silver chloride for a later batch. To the filtrate add a volume of 40% solution of KCN equal to 1.5 times the volume of the silver cyanide solution. Adjust the pH to 12.5 by adding 1.0 M KOH. Transfer the solution to the electrolysis cell. Place the cell in a ventilated hood. Start the magnetic stirrer and electrolyze with a current of 2 A for 1 minute. Then reverse the polarity and adjust the current to 2 A/dm² (ampere per square decimeter). Continue the electrolysis until silver is no longer deposited. Remove the cathode and wash it with distilled water. Peel the deposits of silver from the front and back of the cathode.

Dissolve the silver in 30% HNO₃. Filter the solution through a Buchner funnel to remove the solid particles present. Evaporate the solution to dryness on a hot plate. Toward the end of the evaporation, nitrogen oxides are trapped in the forming crystals of silver nitrate and discolor them. Recrystallize the nitrate from water. The resulting silver nitrate will be in the form of large, colorless crystals.

Notes on the Procedure

Sheets of platinum were used as electrodes successfully in our early work; stainless steel electrodes are preferable because of the much lower cost and the ease of removing the silver deposit. Compressed carbon (from crucibles, or the center pole of the common dry-cell, and from other sources) did not withstand the highly corrosive alkaline cyanide solutions; particles of carbon were released to the solution and with the applied potential being held constant, the current should drop. In practice the current does not drop, probably as the result of the offsetting effect of the concomitant increase in the concentration of the free cyanide. When the concentration of silver in the electrolyte drops to about 0.1 M, hydrogen evolution begins. This point is determined primarily by the pH of the solution, the higher pH permitting further removal of silver before the beginning of evolution of hydrogen. The evolution of hydrogen causes the deposit of silver to develop bumps and blisters but does not affect the purity of the silver deposited.

The purity of the silver nitrate obtained by this procedure was determined by titration with standard potassium chloride using di- chloroarsenic acid indicator and was found to be 100% within the error inherent to the titration.

In the course of the tests made to develop this procedure, analyses of the electroplating bath for the dicynoargentate ion and the "free cyanide" ion were made. The methods of analysis used are described in the M. S. thesis of K. J. Bush (10).

Considerable information about the practical aspects of operating cyanide baths for the commercial electroplating of silver will be found in the book by The Electrochemical Society (11).

A Simple Compensating-Type Gouy Tube

I would like to draw attention to a design of a compensating Gouy tube which is a great deal simpler and cheaper to construct than the modification described by Zimmerman and Duffy2 or of the original tube3 designed to overcome the difficulty of eliminating gas bubbles from the lower compartment. The trick is to etch a shallow longitudinal groove in the ground surfaces of both the cone and socket of the lower compartment as shown in the diagram. After filling with an excess amount of the solvent the stopper is inserted with the grooves in a straight line. This allows the excess to be expelled through the capillary formed by the overlapping grooves. The stopper is then turned to close the tube. Any solvent in the uppermost 'half groove' is then removed with a sprig of filter paper. The etching can easily be carried out on the top inside of the socket and the bottom outside of the cone by coating with wax (paraffin, or preferably beeswax), scraping away the excess to expose the necessary length and dipping the glass into 40% HF solution contained in a polyethylene beaker.

Potassium cyanide is preferable to sodium cyanide as the electrolyte because potassium carbonate is much more soluble than is sodium carbonate. Being strongly alkaline, the plating bath absorbs carbon dioxide from the atmosphere and after a time sodium carbonate precipitates and causes the growing deposit of silver to become rough, to darken, and to become contaminated. Also, for some reason, the permissible current density appears to be greater.

A large excess of cyanide in the plating bath is necessary. If too little is present a coating of silver cyanide or of silver oxide forms on the anode and the nature of the anode process changes; colored material is formed, probably as oxidation and polymerization products of cyanide and cyanogen. The quality of the silver formed from such solutions is poor. The formation of these colored materials is less at a higher pH, a starting pH of 12.5 was found to be the optimum.

As silver is removed from the solution, the single electrode potential of the cathode would be expected to shift in the negative direction, and with the applied potential being held constant, the current should drop. In practice the current does not drop, probably as the result of the offsetting effect of the concomitant increase in the concentration of the free cyanide. When the concentration of silver in the electrolyte drops to about 0.1 M, hydrogen evolution begins. This point is determined primarily by the pH of the solution, the higher pH permitting further removal of silver before the beginning of evolution of hydrogen. The evolution of hydrogen causes the deposit of silver to develop bumps and blisters but does not affect the purity of the silver deposited.

The purity of the silver nitrate obtained by this procedure was determined by titration with standard potassium chloride using di-chloroarsenic acid indicator and was found to be 100% within the error inherent to the titration.

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William J. Davis

University of Dublin
Trinity College,
Dublin 2, Ireland

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