RECOVERY OF SILVER FROM SILVER CHLORIDE RESIDUES

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Summary—A new chemical process for recovering silver metal from waste silver chloride residues is described. The silver chloride is digested in an oxidizing mixture before complexation with ammonia. High-purity free silver metal is precipitated from solution by the addition of ascorbic acid as the reducing agent.

Many analytical laboratories routinely discard considerable quantities of silver chloride, a practice that is wasteful and possibly environmentally hazardous. Numerous methods have been reported for the recovery of silver metal from waste,[1–6] but most suffer from a number of disadvantages. The primary variation in this process is in the type of reductant used. This note reports the use of ascorbic acid as the reducing agent.

EXPERIMENTAL

Silver chloride waste (from Mohr titrations and contaminated with meat by-products) was obtained from a local meat-processing plant.

The silver chloride suspension (0.5 litre) was acidified with 1–2 ml of concentrated hydrochloric acid and 50 ml of concentrated nitric acid, and digested at 100° with gentle stirring until the residue appeared white and the supernatant liquid was light green. Saturated potassium permanganate solution was added to the boiling mixture until a brown colour persisted for about one minute. Heating was continued until the brown colour dissipated. After cooling, the supernatant liquid was decanted and the silver chloride was filtered off on Whatman No. 541 paper on a Büchner funnel.

The silver chloride was transferred to a beaker and stirred while 28–30% ammonia solution was added until dissolution was complete. Then 0.94*M* ascorbic acid was added until no more silver was formed.

The silver was allowed to settle and the ammoniacal solution was decanted and saved for reuse. The silver was filtered off on Whatman No. 41 paper in a 30-cm Büchner funnel and washed with three 0.5-litre portions of demineralized water.

The silver was allowed to dry in air for 48 hr on the filter paper before being transferred to an alundum crucible coated with a borax flux. The crucible was placed in a muffle at 1200°. When melting was complete (within 30 min), the metal was poured into a 2-litre beaker of ice-water. The yield was 50.5 g of silver metal in the form of small beads.

The efficiency of this method was determined by processing a known quantity of silver chloride: 18.39 g required 190 ml of 28–30% ammonia solution for dissolution, and 54 ml of 0.94*M* ascorbic acid for complete precipitation. The amount of silver recovered after refining was 13.7 g (99.3%).

DISCUSSION

The redox potential of ascorbic acid is pH-dependent and ranges from +0.127 V at pH 4 to +0.34 V at a pH of 7, and may be greater at higher pH. Ascorbic acid is capable of reducing silver ions at any pH from 4 to 7 or higher since the standard reduction potential for the silver ion is +0.8 V. The reaction is found to be fast and quantitative.

Other chemicals often used[1,3,7] in the recovery of silver were found to have numerous disadvantages. Sodium sulphide, used for the initial separation of silver, forms insoluble silver sulphide. This process can be dangerous in acidic medium and additional steps in the recovery procedure are required.

Reduction with zinc, steel wool, or sodium borohydride is found difficult to control, and the silver produced is often contaminated. Hydroquinone produces silver particles less than about 8 μm in size, which causes problems in filtration because of clogging. Hydrolyzed sugar solutions[8] do not seem very effective.

With pure silver solutions, ascorbic acid gives silver particles larger than 8 μm, but typical silver chloride wastes are frequently contaminated with chromate indicator, fats, proteins, or other organic materials. These impurities lead to the formation of a much smaller particle size and must be removed. The silver chromate can be converted into the chloride by the addition of hydrochloric acid and the organic materials wet-oxidized with nitric acid and potassium permanganate.

CONCLUSION

The advantages offered by this method are simplicity and its use of inexpensive reagents and equipment. The product is pure and recovery is quantitative with all effluents being biodegradable. The process is applicable to any system yielding silver chloride or bromide, or to silver cyanide electroplating solutions. The usual procedure for plating solutions involves the precipitation of silver chloride by the addition of sodium hypochlorite[5] followed by as many as six additional steps. With the ascorbic acid procedure, only three steps may be needed.

Silver may also be reclaimed from out-of-date films and photographic papers after complexing with ammonia, thereby avoiding a pyrolysis step. Silver can also be recovered from photographic bleaches and fixers, but the amount of ammonia required makes this uneconomical since the silver concentration in these solutions is very low.

The process, which has been granted a United States Patent,[9] can also be used for gold, palladium and mercury. Platinum should also be recoverable, but a successful procedure has yet to be worked out.

Care must be exercised when working with solutions of silver and ammonia because of potential formation of the highly explosive "fulminating silver", (Ag_3N or AgH_2N)[10] if they are allowed to dry out or remain standing for long periods of time. However, with reasonable care and immediate precipitation with ascorbic acid, no hazard should exist.

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