

WET ANALYSIS OF GOLD-SILVER ALLOYS OF HIGH GOLD CONTENT¹

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ABSTRACT

Gold-silver alloys dissolve completely in mixtures of hydrochloric and nitric acids containing potassium chloride in high concentration. In an analytical procedure based on this observation, silver is separated and determined as the chloride, and gold as the metal after reduction with sulfite. Analyses of test alloys, synthetic mixtures, and ancient objects showed that this new procedure is practicable and that results of satisfactory accuracy can be obtained.

INTRODUCTION

Because neither hydrochloric acid nor nitric acid attacks gold-silver alloys of high gold content, and because mixtures of the two acids do not dissolve all such alloys completely or rapidly, the assay method used for centuries has been first to fuse samples of these alloys with sufficient pure silver to bring the gold content down to about 25 percent, and then to treat this with nitric acid to separate the gold from the silver and base metals. This standard method requires special apparatus for the fusion step that may not be available in laboratories in which gold alloys are infrequently analyzed. In an alternate method here described, the fusion step is eliminated.

A hot mixture of hydrochloric acid and nitric acid attacks an alloy of high gold content, but the silver chloride that is formed coats the unattacked alloy so that decomposition is incomplete unless the proportion of silver is unusually low or unless the treatment is continued for a long time with successive fresh portions of the acid mixture. However, if potassium chloride is present in sufficient concentration in the acid mixture, no separation of silver chloride occurs and the alloy dissolves completely in a conveniently short time.

SOLUBILITY EXPERIMENTS

The solubility of silver chloride in aqueous solutions is increased by high temperature, high chloride concentration, high hydrogen-ion concentration, and by combinations of these conditions. This increase is largely due to the formation of soluble complex ions such as AgCl_2^- , so the maximum effect occurs when the active concentration of chloride ions is as high as possible. Results from experiments on the simultaneous effect of high temperature and high alkali-chloride concentration are shown in table 1. In these experiments a boiling salt solution containing an excess of solid silver chloride was refluxed until no more dissolved. An aliquot of clear solution was withdrawn with a heated pipet and allowed to cool to room temperature, which caused much of the silver chloride to precipitate. The mixture was then diluted with sufficient water to precipitate the remainder quantitatively. After coagulation by stirring and standing, the silver chloride was filtered off, washed, dried, and weighed in the usual way. It will be seen that the solubility in molar solutions of the different salts is about the same, that it increases greatly with increase in concentration, and that the degree of increase is markedly different for the individual salts, probably because of the differences in their ionic character in concentrated solutions. Potassium chloride is clearly the most effective for dissolving silver chloride. Although ammonium chloride is somewhat less effective, its use might be considered more desirable in analytical procedures because of the ease with which it can be removed. However, it is not

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effective for preventing the separation of silver chloride from hot mixtures of hydrochloric and nitric acids because of the rapidity with which the ammonium ion is oxidized.

Results from similar experiments on the solubility of silver chloride in boiling hydrochloric acid and in boiling hydrochloric acid containing potassium chloride

TABLE 1
*Solubility of silver chloride in solution of alkali chlorides
at the boiling point*

Salt	Mg of AgCl dissolved in 50 ml of solutions of stated molarity		
	1.0 M	3.0 M	5.0 M
KCl	11	123	614
NH ₄ Cl	12	111	472
NaCl	10	82	292
LiCl	9	38	100

are shown in table 2. It will be seen that its solubility in the molar acid is about the same as in molar solutions of alkali chlorides, and that its solubility increases regularly with increase in concentration. However, as is apparent from a comparison of the data in tables 1 and 2, the solubility of silver chloride in 3.0 and 5.0 molar solutions of the acid is less than in 3.0 and 5.0 molar solutions of any salt except lithium chloride. The solubility of silver chloride in hot hydrochloric acid solutions containing potassium chloride is greater than in hot potassium chloride

TABLE 2
*Solubility of silver chloride at the boiling point in
hydrochloric acid and in hydrochloric acid 3.0 M
in potassium chloride*

Concentration of acid M	Solubility in acid alone mg/50 ml	Solubility in acid plus KCl mg/50 ml
1.0	11	222
2.0	33	433
3.0	66	698
4.0	112	---
5.0	175	---

solutions of the same concentration. This effect is limited by the decrease in the solubility of potassium chloride as the concentration of the acid increases. As is indicated in table 2, it is no longer possible to maintain the concentration of the salt at 3.0 molar in acid solutions more concentrated than about 3.0 molar. In spite of this limitation, the solubility of silver chloride in hot acid of higher concentration nearly saturated with potassium chloride is such that a sample of gold-silver alloy containing 50 percent silver and weighing as much as 0.5 gram will be completely dissolved by a conveniently small volume of this solvent.

ANALYTICAL PROCEDURE

Take a sample of fine chips or drillings that weighs no more than 0.5 gram, place it in a 250-ml Erlenmeyer flask, add 10 grams of potassium chloride, 40 ml

of concentrated hydrochloric acid, and 10 ml of concentrated nitric acid. Heat just below boiling until the sample dissolves completely. If potassium chloride crystallizes out before the sample dissolves, add just enough water to redissolve the salt. Add 10 ml of concentrated nitric acid and evaporate to a thick slurry. Add 5 ml of concentrated hydrochloric acid, again evaporate to a thick slurry, and repeat this addition and evaporation. Add 25 ml of cold water slowly with agitation to precipitate and coagulate most of the silver chloride. Add 125 ml more water to complete the precipitation and set aside with occasional stirring until all the silver chloride coagulates. Collect the precipitate in a weighed filter crucible, and filtrate and washings in a 400-ml beaker. Wash with cold 0.01 M nitric acid, dry to constant weight at 150° C, and weigh.

Evaporate the filtrate and washings to a volume of about 75 ml, cool to about 50° C, and add 5 ml of concentrated hydrochloric acid, followed by 25 ml of saturated sodium sulfite solution. Boil and stir the mixture for about two minutes and allow it to stand below the boiling point for about 45 minutes. If any pink color is still visible in the solution, heat to boiling, add 1 ml of concentrated hydrochloric acid followed by 5 ml of saturated sodium sulfite solution, and allow to stand below the boiling point for 15 more minutes. After cooling, collect the gold in a weighed filter crucible, wash with hot 0.1 M hydrochloric acid, dry briefly at 120° C, ignite to constant weight at full red heat, and weigh.

Notes on Procedure

The purpose of the repeated evaporations and additions of acids after the sample dissolves is to remove most of the hydrochloric acid, and all of the nitrosyl chloride and oxides of nitrogen. If the silver chloride is not completely coagulated, some may appear in the filtrate when this is evaporated, and another filtration may be needed to recover this additional precipitate. The filtrate from the separation of the gold may be used for the determination of copper and other base metals by various procedures. If copper is to be determined electrolytically, all the chloride must be removed. This may be done by adding 10 ml of concentrated sulfuric acid and evaporating until dense fumes of sulfur trioxide evolve for a few minutes.

TEST ANALYSES

Results of analyses of two gold-silver alloys are shown in table 3. These alloys were made in the Department of Metallurgy, The Ohio State University,

TABLE 3
Test analyses of alloys

Alloy No.	Sample Weight Gram	Solution Time Min.	Gold Found %	Silver Found %
1	0.1293	120	49.88	50.00
1	0.1094	55	50.00	50.08
2	0.2495	55	63.37	36.11
2	0.2010	55	63.38	36.13

for an earlier investigation, by melting together weighed amounts of the pure metals in an induction furnace. Because of the possibility of differential loss of metal by volatilization, these alloys could not be taken as reliable standards for testing the accuracy of the procedure. Instead, they were used primarily to test its practicality, especially with respect to the time needed to dissolve samples.

It will be seen that the first sample, which was in the form of a few coarse pieces, took two hours to dissolve, whereas the others, in the form of small chips, took less than an hour. Samples in the form of fine drillings or filings require still less time.

These test analyses also indicate that the procedure is capable of yielding precise results. In spite of the uncertainty about the exact composition of these alloys, the results obtained on No. 1 agree well with its stated gold content of 50 percent. The results for the other are over 1 percent off from its stated gold content, and the summation is low, apparently in part because of the presence of nonmetallic inclusions.

As a more reliable test of the accuracy of the procedure, test analyses were made of synthetic samples prepared by mixing weighed amounts of pure granular gold and silver obtained by the electrolytic reduction of solutions of gold chloride and silver nitrate. The results are shown in table 4. It will be seen that the

TABLE 4
Test analyses of synthetic samples

Sample No.	Sample Weight Gram	Gold Taken Gram	Gold Found Gram	Silver Taken Gram	Silver Found Gram
1	0.3998	0.3243	0.3247	0.0755	0.0754
2	0.4004	0.3194	0.3189	0.0810	0.0811
3	0.4588	0.3409	0.3403	0.1179	0.1181
4	0.4602	0.3433	0.3425	0.1169	0.1169

absolute errors for silver are small, the average being only 0.0001 gram when the direction of the individual errors is neglected. The absolute errors for gold are larger, the average being 0.0006 gram when the direction of the errors is neglected. However, the relative errors on this same basis are not very different, the average being 1.1 parts per thousand for the silver and 1.8 parts per thousand for the gold. The generally negative error for the proportion of gold, as determined by this procedure, appears to be caused in part by the difficulty of reducing the gold completely and in part by the manipulative difficulty of collecting all the particles of finely divided gold.

Results of analyses of two gold objects, in the form of damaged ornaments from excavations in Mexico, are shown in table 5. The copper was determined electrolytically in the filtrate from the gold separation. It will be seen that the results on the two samples of the first object agree well and that the summations

TABLE 5
Analyses of ancient objects

Object No.	Sample Weight Gram	Gold Found %	Silver Found %	Copper Found %	Total Found %
1	0.2883	71.59	27.74	0.59	99.92
1	0.1484	71.52	27.81	0.61	99.93
2	0.2671	61.91	37.19	0.94	100.04

of all three analyses are very satisfactory. The data indicate that the objects were made from native gold.

In general, these test analyses show that this new procedure yields satisfactory results for the determination of the main components of alloys of gold and silver, or gold, silver, and copper. It has the advantage of requiring no special apparatus or chemicals. Hence it should be very suitable for the analysis of gold artifacts in museum or field laboratories. In fact the procedure was devised for this purpose.
