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Determination of Silver, Cadmium, Indium, and Tin in Silver-Base Alloys

D. P. Stricos

J. T. Porter II

July 17, 1958

Operated for the
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UC-4, Chemistry - General
(TID-4500, 14th Edition)

DETERMINATION OF SILVER, CADMIUM, INDIUM, AND TIN
IN SILVER-BASE ALLOYS

D. P. Stricos and J. T. Porter II

July 17, 1958*

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ABSTRACT

A procedure has been developed for the determination of silver, cadmium, indium, and tin in an alloy composed of these metals. The sample is dissolved in a mixture of nitric and fluoboric acids, after which the silver is determined gravimetrically as the chloride. The cadmium and indium are then determined polarographically in a potassium iodide solution, and the tin is determined polarographically in an ammonium chloride - hydrochloric acid supporting medium.

DETERMINATION OF SILVER, CADMIUM, INDIUM, AND TIN IN SILVER-BASE ALLOYS

D.P. Stricos and J. T. Porter II*

INTRODUCTION

A program has been designed to study the effects of dynamic irradiation on the silver-cadmium-indium alloy prior to its anticipated use as a nuclear reactor control rod material. This program has necessitated the development of an analytical procedure to determine these three constituents, along with tin, which is produced as a transmutation product during irradiation.

Alloys containing only silver, cadmium, and indium were analyzed first. Once the silver had been removed from solutions of these alloys, the cadmium was determined polarographically in M ammonium hydroxide - M ammonium chloride. In this medium the indium wave was completely suppressed, and satisfactory results were obtained. A polarogram of a separate aliquot in 0.1M hydrochloric acid then gave a combined indium-cadmium wave. The contribution of the cadmium was subtracted, and a value was obtained for the indium.^{1,5}

It was discovered that if tin is present the procedure is inoperable because the cadmium wave in M ammonium hydroxide - M ammonium chloride is significantly reduced. This difficulty was eliminated, however, by using a potassium iodide base electrolyte recommended by L. Treindl.² In this medium the half-waves of indium and cadmium are separated sufficiently to permit a simultaneous determination of the two elements.

The determination of tin (0.5 to 5%) in this alloy presented the greatest difficulty. Attempts to separate and redissolve the metastannic acid formed by reacting the sample with nitric acid were unsuccessful. However, it was

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found that a mixture of fluoboric and nitric acids effected complete solution of the sample, including the tin. Furthermore, the presence of fluoboric acid had no adverse effect upon the subsequent gravimetric silver determination. Once the tin was dissolved, the method of Lingane³ was adopted for the polarographic tin analysis.

APPARATUS AND PROCEDURE

Polarograms were obtained from a Leeds & Northrup Electrochemograph Type E. The cell used was an H type with a saturated calomel reference electrode isolated by a sintered-disc agar bridge. The cell was thermostatically controlled at $25 \pm 0.2^{\circ}\text{C}$.

Analytical grade reagents were used throughout. The polarographic standards were prepared from the pure metals. The procedure is as follows:

To determine the silver, weigh out 0.25 gm of the sample and place in a 20-ml beaker. Add 2 ml of water, 1 ml of fluoboric acid (48 to 50%), and enough nitric acid (added dropwise) to initiate the reaction. The sample may be heated gently to hasten solution.

Transfer this solution to a 400-ml beaker and dilute to 200 ml with water. Heat on a hot plate or steam bath to 70°C . Precipitate the silver by adding slowly, and with constant stirring, 10 ml of 0.2M hydrochloric acid. Wash the precipitate with 0.01M hydrochloric acid. Let the solution with the silver chloride precipitate stand in a dark place for several hours or, preferably, overnight. Then filter off the silver chloride through a medium-porosity sintered glass filter, dry at 100°C for 15 min, and complete drying at 130°C for 2 hr. Weigh the precipitate and compute the per cent silver.

For the determination of cadmium and indium, evaporate the filtrate down to 10 to 15 ml, transfer to a 25-ml volumetric flask, and dilute to the mark. Take a 2-ml aliquot. Add 4.15 gm of potassium iodide and 1 ml of 0.125% bacto-peptone. Dilute to 25 ml and immediately record the polaro-

gram from -0.4 to -0.9 v. The potassium iodide solution is sensitive to oxidation on standing; hence there should be no delay between the preparation of a solution and the recording of its polarograms.

For the tin, take a 10-ml aliquot. Add 5 ml of 5M hydrochloric acid, 5.35 gm of ammonium chloride, and 1 ml of 0.125% bacto-peptone. Dilute to 25 ml, warm the solution to room temperature, and record the polarogram from -0.3 to -0.7 v.

RESULTS AND DISCUSSION

For cadmium and indium in M potassium iodide, half-waves at -0.57 v were found for indium and -0.75 v for cadmium (see Fig. 1). The precision of the method for cadmium and indium may be demonstrated by data obtained from eight typical samples. See Tables 1 and 2. In addition, the values in Table 3 were obtained for silver and tin on these samples. The results of Tables 1, 2, and 3 are summarized in Table 4.

Tin in 4M ammonium chloride - M hydrochloric acid gave a half-wave at -0.55 v. The diffusion current plateau is partly concealed by the indium wave which follows. However, if i_d is read 0.055 v to the right of the half-wave, reproducible results are obtained (see Fig. 2).

The data in Table 5 illustrate the precision to be expected from the tin determination.

TABLE 1. Precision of Indium Analysis

<u>Sample</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>	<u>Average</u>
A	15.19%	15.30%	15.68%	15.44%	15.40%
B	15.35	15.08	15.53	15.44	15.35
C	15.31	15.29	15.65	15.55	15.45
D	14.81	15.28	14.96	15.46	15.13
E	14.98	15.10	15.08	15.16	15.08
F	15.09	15.11	15.12	15.22	15.14
G	15.54	15.31	15.43	15.43	15.43
H	15.21	15.29	15.40	15.43	15.33

Statistical Analysis of Data in Table 1

<u>Sample</u>	<u>(Run 1 - Avg)²</u>	<u>(Run 2 - Avg)²</u>	<u>(Run 3 - Avg)²</u>	<u>(Run 4 - Avg)²</u>	<u>D.F.</u>
A	0.0441	0.0100	0.0784	0.0016	3
B	0.0000	0.0729	0.0324	0.0081	3
C	0.0196	0.0256	0.0400	0.0100	3
D	0.1024	0.0225	0.0289	0.1089	3
E	0.0100	0.0004	0.0000	0.0064	3
F	0.0025	0.0009	0.0004	0.0064	3
G	0.0121	0.0144	0.0000	0.0000	3
H	0.0121	0.0016	0.0049	0.0100	3

Sum of squares = 0.6875

Standard deviation based on 24 degrees of
freedom = 0.169 (1.1% relative)

95% confidence limits for a single measure-
ment = ± 2.064 S.D. = ± 0.35 (2.5% relative)

TABLE 2. Precision of Cadmium Analysis

<u>Sample</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>	<u>Average</u>
A	4.71%	4.78%	4.92%	4.82%	4.81%
B	4.67	4.73	4.72	4.85	4.74
C	3.97	3.79	3.59	3.73	3.77
D	3.96	3.76	3.48	3.81	3.75
E	4.53	4.63	4.84	4.80	4.70
F	4.83	4.64	4.93	4.85	4.81
G	4.74	4.94	5.07	5.04	4.95
H	4.69	4.79	4.92	4.85	4.81

Standard deviation based on 24 degrees
of freedom = 0.135 (2.7% relative)

95% confidence limits for a single measure-
ment = 2.064 S.D. = 0.28 (5.8% relative)

TABLE 3. Analysis of Silver and Tin

<u>Sample</u>	<u>% Ag</u>	<u>% Sn</u>
A	79.9	----
B	80.0	----
C	79.7	1.42
D	79.7	1.42
E	80.1	----
F	79.9	----
G	79.7	----
H	80.0	----

TABLE 4. Summary of Silver, Indium, Cadmium,
and Tin Analyses

	<u>Sample</u>							
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
% Ag	79.9	80.0	79.7	79.7	80.1	79.9	79.7	80.0
% In	15.4	15.4	15.4	15.1	15.1	15.1	15.4	15.3
% Cd	4.8	4.7	3.8	3.8	4.7	4.8	5.0	4.8
% Sn	--	--	1.42	1.42	--	--	--	--
% Total	100.1	100.1	100.3	100.0	99.9	99.8	100.1	100.1

TABLE 5. Precision of Tin Analysis

<u>Sample</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Average</u>
I	0.527%	0.596%	0.562%
J	0.532	0.547	0.540
K	0.528	0.525	0.526
L	0.542	0.505	0.524
M	0.530	0.508	0.519
N	0.535	0.526	0.530
O	0.533	0.515	0.524
P	0.522	0.479	0.500
Q	0.522	0.503	0.512
R	0.545	0.523	0.534
S	0.513	0.513	0.513

Standard deviation based on 11 degrees of freedom =
0.021 (4.0% relative)

95% confidence limits for a single measurement =
± 0.046 (8.7% relative)

CALIBRATION

The external standard method of calibration⁴ was found most convenient. Hence, polarograms of a cadmium standard in 0.1M hydrochloric acid were recorded concurrent with the samples. The constants relating the cadmium standard with the elements in question were:

$$I_d (\text{indium in } \underline{M} \text{ potassium iodide}) / I_d (\text{cadmium in } 0.1\underline{M} \text{ hydrochloric acid}) = 1.301$$

$$I_d (\text{cadmium in } \underline{M} \text{ potassium iodide}) / I_d (\text{cadmium in } 0.1\underline{M} \text{ hydrochloric acid}) = 1.066$$

$$I_d (\text{tin in } 4\underline{M} \text{ ammonium chloride} - \underline{M} \text{ hydrochloric acid}) / I_d (\text{cadmium in } 0.1\underline{M} \text{ hydrochloric acid}) = 0.8771$$

$$I_d (\text{cadmium in } \underline{M} \text{ ammonium hydroxide} - \underline{M} \text{ ammonium chloride}) / I_d (\text{cadmium in } 0.1\underline{M} \text{ hydrochloric acid}) = 1.088$$

where I_d is expressed in $\mu\text{a}/\text{mg}/\text{ml}$ for each element.

CONCLUSION

The procedure described permits the determination of silver, cadmium, indium, and tin. The indium-to-cadmium ratio for samples here analyzed varied from 1 to 5. In this range there was no difficulty in determining cadmium. For ratios much larger, however, the sensitivity of the cadmium analyses would be a factor to contend with. Of course, if no tin were present, the cadmium could be determined in M ammonium hydroxide - M ammonium chloride.

Indium-to-tin ratios of up to 35 were handled routinely. While this is not a limiting ratio, extension of the method to ratios an order of magnitude larger would probably require a correction factor for the toe of the indium wave.

The fact that tin can be dissolved in a mixture of nitric and fluoboric acids will doubtless be of some value for other applications in which the introduction of hydrochloric acid is undesirable.

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