

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE

Phenylarsonic Acid as a Reagent for the Determination of Tin

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Attention has been called to the possibilities of phenylarsonic acid as an analytical reagent in methods described by Rice, Fogg and James¹ for the determination of zirconium and thorium. The present investigation extends this study to include conditions for the separation and determination of tin.

Phenylarsonic Acid.—Eastman phenylarsonic acid was used without purification. Some samples left no non-volatile residue on ignition; others contained a small amount of sodium salts which did not interfere. A saturated aqueous solution was used as the reagent.

Tin Standards.—For the determination of tin in the absence of other metals Bureau of Standards Sample No. 42B, 99.99% tin, was used. For the determination of tin in the presence of other metallic ions Bureau of Standards Samples No. 37B, sheet brass and No. 52, cast bronze, were used. Other samples were prepared from the pure tin and purified salts of the metals.

Determination of Tin.—Samples of approximately one-tenth of a gram of the pure tin were treated with 10 cc. of 1:1 nitric acid and the mixture heated gently until the metal was completely oxidized. The heating was continued until any excess nitric acid was driven off, care being taken not to dehydrate the metastannic acid. Concentrated hydrochloric acid was then added, dropwise, until the tin was in solution. It was found that phenylarsonic acid would form a precipitate with tin in solutions which contained as much as 50% by volume of hydrochloric or sulfuric acid. However, precipitation was not quantitative when the acid concentration was greater than 5% by volume of hydrochloric acid or 7.5% by volume of sulfuric acid and reasonable amounts of reagent were used. Sufficient acid was added so that the final concentration was within these values upon dilution with water to a volume of 150–200 cc.

The tin was precipitated in hot solution by the addition of 35 cc. of the saturated aqueous solution of phenylarsonic acid. When only enough hydrochloric acid to dissolve the metastannic acid was added, about 1 cc. for this weight of tin, the solution could be filtered immediately. When acid in amounts approaching the limits indicated was added, it was necessary to allow the solution to stand for several hours before filtering. A small amount of paper pulp aided in the filtration. The precipitate was washed with a 4% solution of ammonium nitrate until free of chlorides or sulfates.

All precipitates were ignited to the oxide, no attempt being made to determine composition. The precipitate was ignited gently over a flame until all of the carbon was burned off. It was then heated in an electric furnace at a temperature of 1075–1100° to constant weight. Samples of pure stannic oxide heated under the same conditions showed no loss in weight.

Taking amounts of stannic oxide between one and three tenths of a gram and concentrations of hydrochloric acid or sulfuric acid of 2.5–5.0 and 7.5%, respectively, twelve determinations gave results with an average deviation of 1.1 parts per thousand. The somewhat higher acid concentration permissible in solutions acid with sulfuric acid may possibly be explained on the basis of a complex formed by stannic chloride with hydrochloric acid.²

(1) Rice, Fogg and James, *THIS JOURNAL*, **48**, 895 (1926).

(2) Dickinson, *ibid.*, **44**: 276 (1922).

In general, completeness of precipitation depended upon the relative amounts of acid and reagent present. With acid concentrations above those given, impractical quantities of reagent were required.

Separation from Other Elements.—In aqueous solutions of the chlorides or sulfates most of the elements commonly found in alloys of tin formed precipitates with phenylarsonic acid. With aluminum salts, hydrolysis made the solution sufficiently acid to prevent precipitation. These precipitates were readily soluble in acid and quantitative separations of tin were made in solutions of brass and bronze samples in which as small an amount as one cc. of concentrated hydrochloric acid was added to the 200 cc. volume. None of the elements showed any tendency to be carried down with the tin salt except iron. The difficulty was overcome by one reprecipitation. The precipitate, after washing, was returned to the original beaker, 5 cc. of concentrated hydrochloric acid added and the mixture heated until the precipitate was disintegrated. Water was added to bring the volume to 150–200 cc. and the tin was reprecipitated with 15 cc. of the phenylarsonic acid solution. The determination was then completed in the manner described.

The results obtained for the separation of tin from varying amounts of other elements are given in Table I.

TABLE I
DETERMINATION OF TIN IN PRESENCE OF OTHER ELEMENTS

(a) B. of S. Sample No. 52. Cast Bronze							
Sample, g.	Tin, g. (calcd.)	Tin, in sample, %	Other elements present, %	Tin found, g.	% of tin found	Diff., g.	
0.5018	0.0396	7.90	Cu 88.33	0.0399	7.95	+0.0003	
.5044	.0398		Zn 1.89	.0397	7.87	— .0001	
.5011	.0396		Pb 1.52	.0399	7.96	+ .0003	
.5081	.0401		Sb 0.16	.0404	7.95	+ .0003	
.5001	.0395		Ni 0.13	.0398	7.96	+ .0003	
.5073	.0401		Fe 0.12	.0400	7.89	— .0001	
				Av.	7.93		
(b) B. of S. Sample No. 37b. Sheet Brass							
1.0066	0.0099	0.99	Cu 70.36	0.0096	0.95	—0.0003	
1.0029	.0099		Zn 27.09	.0099	0.99	.0000	
1.0010	.0099		Pb 0.90	.0101	1.01	+ .0002	
1.0008	.0099		Ni 0.45	.0099	0.99	.0000	
1.0024	.0099		Fe 0.21	.0097	0.97	— .0002	
				Av.	0.98		
(c) Sample Prepared from Pure Salts							
0.8350	0.1002	12.00	Cu 40.00	0.0998	11.95	—0.0004	
.8733	.1048		Zn 20.00	.1047	11.99	— .0001	
.8733	.1048		Pb 10.00	.1045	11.97	— .0003	
				Av.	11.97		
				Fe 5.00			
				Sb 5.00			
				Cd 2.00			
				Al 2.00			

Zirconium.—Conditions satisfactory for a quantitative separation of zirconium and tin by means of phenylarsonic acid could not be obtained. While the acid concentration permissible for complete precipitation of tin is fixed at 5% hydrochloric acid or

7.5% sulfuric acid, the element will precipitate to some extent when as much as 0.2 g. is present, even in solutions containing 50% by volume of either acid.

Thorium.—The determination of thorium with phenylarsonic acid was accomplished by Rice, Fogg and James¹ only in solutions containing acetic acid and ammonium acetate. However, in the present work it was found that part of the thorium was precipitated, when 35 cc. of reagent was used, in a 5% solution of hydrochloric acid. This is the upper limit of acidity permissible for the determination of tin. A satisfactory separation of tin and thorium with this reagent does not seem possible.

Bismuth.—Due to the tendency of bismuth salts to hydrolyze it was necessary to precipitate in solution containing 5% by volume of hydrochloric acid. Results were not satisfactory in sulfuric acid solution. The volume of the solution was kept at approximately 200 cc. Precipitation was done in hot solution by the addition of 40–50 cc. of the reagent and the mixture was allowed to stand several hours before filtering. Reprecipitation was not necessary. The determination was completed in the manner already described. Taking amounts of stannic oxide between one and two tenths of a gram, in the presence of approximately equal amounts of Bi_2O_3 , four determinations gave results with an average deviation of two parts per thousand.

Summary

A new gravimetric method for the determination of tin has been described, in which the tin is precipitated with phenylarsonic acid. This method separates tin quantitatively from a number of elements commonly occurring with it in alloys, but not from zirconium or thorium.

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The Action of Hydriodic Acid on the Difficultly Soluble Sulfates¹

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While a number of facts indicate that hydriodic acid is generally more reactive chemically than either hydrochloric acid or hydrobromic acid under like conditions, it has not been recognized that this difference is so great that a number of slightly soluble compounds, quite inert toward the latter acids, react easily with hydriodic acid, a striking example being stannic oxide.² In a preliminary note³ it was stated that a number of other compounds highly resistant to hydrochloric acid, and even such active solvents as nitric acid and aqua regia, are more or less readily decomposed by hydriodic acid. This present paper contains a more detailed account of the action of the latter acid on certain of these compounds.

Materials and General Procedure.—The hydriodic acid used in the experiments was principally the constant boiling acid of specific gravity

(1) Abstracted from a paper presented at the 85th meeting of the American Chemical Society, Washington, D. C., March, 1933.

(2) Caley, *THIS JOURNAL*, **54**, 3240 (1932).

(3) Caley, *ibid.*, **54**, 4112 (1932).