[Contribution from the Chemical Laboratories of the University of New Hampshire]

PHENYLARSONIC ACID AS A REAGENT FOR THE DETERMINATION OF ZIRCONIUM AND THORIUM

By A. C. Rice, H. C. Fogg and C. James

Received November 18, 1925 Published April 5, 1926

Part 1. Zirconium

During the last few years a number of methods for the determination of zirconium have been described. In general, these procedures are either complicated or involve costly reagents. The authors have noticed that many organic phosphorus acids give precipitates with zirconium solutions. These precipitates in most cases were very insoluble. However, this type of reagent was not all that could be desired since the precipitates were not well defined and the removal of phosphorus gave too much trouble. Attention was, therefore, directed to corresponding arsenical derivatives with the expectation that the precipitates could be readily changed to zirconium dioxide by simple ignition.

Among the first compounds employed, phenylarsonic acid, $C_6H_5AsO(OH)_2$, was selected since tests showed that the zirconium compound appeared to be the most insoluble of all phenylarsonates. In addition, this acid is very readily prepared from cheap reagents as described by Palmer and Adams.[1]

The zirconium employed in this work was derived from commercial Brazilian zirkite. The mineral, ground to 200 mesh, was stirred with twice its weight of flake sodium hydroxide in a large iron kettle heated by a powerful oil burner. The mixture, which was soft at first, gradually dried to a powder which was never heated to a sufficiently high temperature to bring about fusion resulting in the formation of a glass. The powdery product was thoroughly extracted with water to remove as much alkali as possible. The residue consisting of hydroxides and undecomposed mineral, etc., was dried, powdered, heated and stirred with sulfuric acid in Duriron pans until white fumes of sulfuric acid were evolved. This sulfated product was stirred with water, filtered and boiled with a slight excess of sodium hydroxide. The hydroxides were filtered off, well washed with boiling water and dissolved in commercial hydrochloric acid. The solution was evaporated until crystals commenced to form on the surface. After the mass had been allowed to cool, the crystals of zirconyl chloride were separated by filtration and the liquid was concentrated further. This gave a second crop which was added to the main bulk. The zirconyl chloride was further purified by several recrystallization from 1:1 hydro-

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[1] Palmer and Adams, This Journal, **44**, 1361 (1922).

chloric acid. The purified crystals were then dissolved in water, and the solution was filtered and diluted to the desired concentration.

The solution of zirconyl chloride gave no coloration with ammonium thiocyanate or hydrogen peroxide, indicating the absence of iron and titanium.

Standardization of Zirconyl Chloride

The zirconyl chloride solution was standardized by precipitating with selenious acid,[2] cupferron and ammonium hydroxide. It was found that while impure selenious acid gave results slightly higher than cupferron, the highly purified product gave results a trifle lower.

STANDARDIZATION

	Pure selenious acid, g. of ZrO_2	Cupferron, g. of ZrO_2	Ammonium hydroxide, g. of ZrO_2
	0.2440	0.2453	0.2449
	.2441	.2456	.2457
	.2439	.2453	.2455
	.2440	.2452	.....
	.2441	....	.....
Av.	.2440	.2453	.2454

Precipitation by Phenylarsonic Acid

The first problem investigated was the action of phenylarsonic acid upon zirconyl chloride in various concentrations of hydrochloric acid.

Procedure.—Twenty-five-cc. portions of zirconyl chloride solution with various amounts of hydrochloric acid were diluted to about 200 cc., 10 cc. of 10% phenylarsonic acid solution was added, and the whole heated to boiling. After boiling for about a minute, the mixture was filtered hot and the precipitate washed with 1% hydrochloric acid, dried and ignited.

It was found that direct ignition usually gave high results, owing to the fact that some arsenic remained, unless an exceptionally high temperature was obtained. However, the best procedure was found to be as follows. The dried precipitate was gently ignited until all of the carbon was burned off; after which it was heated in a stream of hydrogen and finally ignited over the blast, the following results being obtained.

	Concn. of HCl, 1% by vol.	10	25	50
G. of ZrO_2	0.2441	0.2440	0.2444	0.2444
	.2442	.2439	.2441	.2441
	.2442	...	...	...
	.2444	...	...	...

These figures indicate that zirconyl phenylarsonate is not soluble in hydrochloric acid, even of high concentrations.

These results were checked against another solution of zirconyl chloride, as indicated below.

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[2] THIS JOURNAL, **42,** 1764 (1920).

Twenty-five cc. of this new solution showed an average of 0.2926 g. of zirconium dioxide by analyses with selenious acid.

HCl, % by vol.	1	3	5	10
G. of ZrO$_2$	0.2922	0.2932	0.2917	0.2924
	.2926	.2928	.2925	.2926
	...	.2924	...	.2926

A concentration of 25% hydrochloric acid yielded a satisfactory result of 0.2925 g. of zirconium dioxide.

Determination of Zirconium in the Presence of Iron

The separation of fairly large quantities of ferric iron from zirconium was found to be incomplete, even when the phenylarsonate was formed from large volumes in the presence of 10% hydrochloric acid and washed with hot 5% hydrochloric acid. However, when the amount of iron was very small, good results were obtained. It became necessary, therefore, to find conditions under which all of the iron could be removed. When the iron did not greatly exceed the zirconium, it was completely removed by transferring the precipitate and paper back to the beaker and digesting with 1:1 hydrochloric acid until disintegrated. After dilution to 500 cc. and the addition of 15 cc. of phenylarsonic acid, the whole was boiled, filtered, washed, ignited and weighed.

Fe$_2$O$_3$ taken, g.	0.2467	0.2467	0.3701	0.3701	0.2960	0.2960
ZrO$_2$ taken, g.	.2442	.2442	.2442	.2442	.0980	.0980
ZrO$_2$ found, g.	.2441	.2445	.2439	.2442	.0978	.0983

When the ratio of iron to zirconium was very large, the method had to be modified still further. In this case the precipitate and filter paper were removed to the original beaker, treated with 15 cc. of 1:1 sulfuric acid, warmed until the zirconium had dissolved, after which 50 cc. of concd. hydrochloric acid was added, the whole diluted to 500 cc., boiled and treated with 30 cc. of phenylarsonic acid. In two experiments 0.9868 g. of ferric oxide and 0.0490 g. of zirconium dioxide were taken in each and 0.0488 g. and 0.0491 g., respectively, of the latter were found.

The separation of zirconium from iron in the ferrous condition was easily carried out in the presence of 10% hydrochloric acid. The total volume employed was 500 cc., similar to the previous case. In two experiments 0.4072 g. of iron as ferric oxide and 0.2442 g. of zirconium dioxide were taken and 0.2440 g. and 0.2440 g. were found, respectively, of the latter.

Determination of Zirconium in the Presence of Aluminum

In this separation a concentration of 10% hydrochloric acid and total volume of 500 cc. were employed as in the foregoing work. In this case no difficulty was encountered. In three experiments 0.2472 g. of alumina and 0.2442 g. of zirconia were taken, and 0.2448 g., 0.2445 g. and 0.2445 g. of the latter were found.

Determination of Zirconium in the Presence of Titanium

Very dilute and very acid titanium solutions are not very readily precipitated by phenylarsonic acid solution. As would be expected, hydrogen peroxide absolutely prevents the precipitation of titanium by the reagent. Moreover, it was found that hydrogen peroxide rapidly brings about the solution of any titanium that has been precipitated.

In order to test this separation 10 cc. of zirconyl chloride, 50 cc. of hydrochloric acid and 10 cc. of titanium chloride were diluted with 400 cc. of water; next, 35 cc. of 3% hydrogen peroxide was added and finally 30 cc. of phenylarsonic acid, and the whole thoroughly stirred, then heated to boiling, filtered and the precipitate washed.

The precipitate was dissolved in 20 cc. of 1:1 sulfuric acid; 20 cc. of hydrogen peroxide and 50 cc. of hydrochloric acid were next added, after which the whole was diluted to 500 cc., when the zirconium phenylarsonate was reprecipitated. Twenty cc. of phenylarsonic acid was added in order to make sure that all zirconium would be precipitated.

It was usually found that the solution of the first precipitate gave no coloration upon the addition of hydrogen peroxide, indicating that practically all of the titanium had been removed in the first precipitation. In three experiments, 0.0727 g. of titanium dioxide equivalent and 0.0980 g. of zirconia were taken, and 0.0983, 0.0979 and 0.0981 g., respectively, of the latter were found.

Determination of Zirconium in the Presence of Thorium

A solution of thorium chloride was made up and standardized.

It was found that zirconium could not be separated quantitatively from thorium with a single precipitation by the use of phenylarsonic acid even when the solution contained 10% hydrochloric acid. Therefore, double precipitation was employed as in the separation from large amounts of iron. In three experiments, 0.1033 g. of thorium dioxide equivalent and 0.0980 g. of zirconia were taken, and 0.0980, 0.0982 and 0.0978 g., respectively, of the latter were found.

Determination of Zirconium in the Presence of Cerium Group Elements

The separation of zirconium from a mixture of the cerium metals (cerium in the cerous state) was readily carried out in the presence of 10% hydrochloric acid by means of phenylarsonic acid. With equal amounts of each, it was found that the resulting zirconium oxide was pure white and good results were obtained. Thus, when 0.0980 g. of zirconia was taken, 0.0981 g. was recovered.

Determination of Zirconium by Phenylarsonic Acid in 10% Sulfuric Acid Solution

This work was carried out in order to determine whether zirconium was completely precipitated under these conditions. To 25 cc. of zirconyl chloride were added 400 cc. of water and 50 cc. of sulfuric acid. The resulting solution was precipitated by 40 cc. of phenylarsonic acid. In each of two experiments 0.2442 g. of zirconia was taken, and 0.2441 and 0.2437 g., respectively, were found.

It was found that 20% of sulfuric acid by volume prevented complete precipitation. Thus, in each of two experiments 0.2442 g. of zirconia was taken and 0.2382 and 0.2377 g., respectively, were found.

Determination of Zirconium in the Presence of Potassium

A mixture of 25 cc. of zirconyl chloride, 5 g. of potassium chloride and 50 cc. of hydrochloric acid was diluted to 500 cc., precipitated by means of 40 cc. of phenylarsonic acid, heated and filtered. In each of two experiments 0.2442 g. of zirconia was taken and 0.2441 and 0.2439 g., respectively, were found. This shows that the separation of zirconium from potassium leaves nothing to be desired.

Determination of Zirconium in the Presence of Phosphoric Acid

A solution of phosphoric acid was prepared which contained roughly 0.048 g. of H_3PO_4 in 5 cc.

The separation of small amounts of phosphoric acid from zirconium can be carried out as follows. A mixture of 25 cc. of zirconyl chloride, 5 cc. of this phosphoric acid solution and 50 cc. of sulfuric acid was diluted to 150 cc., treated with 35 cc. of phenylarsonic acid diluted to 500 cc., heated and filtered. The precipitate and paper were treated with 50 cc. of 1:1 sulfuric acid in the same beaker. After the precipitate had dissolved, the liquid was diluted to 150 cc., treated with 20 cc. of phenylarsonic acid, then diluted to 500 cc., heated, filtered, the precipitate washed, dried and ignited. In each of two experiments 0.2442 g. of zirconia was taken, and 0.2440 and 0.2438 g., respectively, were found.

Determination of Zirconium in the Presence of Manganese, Cobalt, Nickel, Zinc and Beryllium

A solution of the chlorides of manganese, cobalt, nickel, zinc and beryllium was made up to contain 0.05 g. of each element calculated as metal in 25 cc. or 0.25 g. of total metal equivalent in 25 cc.

These elements can be readily separated from zirconium in the presence of 10% hydrochloric acid. Twenty-five cc. of zirconyl chloride was taken, together with 25 cc. of the mixed chlorides. The mixture was treated with 50 cc. of hydrochloric acid diluted to 450 cc. and precipitated with 35 cc.

of phenylarsonic acid. In each of two experiments 0.2442 g. of zirconia was taken and 0.2442 and 0.2441 g., respectively, were found.

Determination of Zirconium in the Presence of Uranium, Bismuth and Copper

A solution of the chlorides of uranium, bismuth and copper was employed such that 25 cc. contained the equivalent of 0.1062 g. of each oxide or a total of 0.3186 g. of the total oxides.

It was found in this case that uranium tended to accompany the zirconium. This difficulty was overcome by precipitating from sulfuric acid solutions, redissolving and reprecipitating in a similar manner to that described under the determination of zirconium in the presence of iron. Twenty-five cc. of zirconyl chloride and 25 cc. of the mixed chlorides were employed. In each of two experiments 0.2442 g. of zirconia equivalent was taken and 0.2439 and 0.2441 g., respectively, were found.

Part 2. Thorium

The ordinary methods for the determination of thorium are, in general, long and tedious. Phenylarsonic acid gives a precipitate when added to solutions of thorium salts in the presence of ammonium acetate and acetic acid. Since this reagent does not give precipitates with the rare earths (cerium being in the cerous state) under these conditions, it seemed highly probable that phenylarsonic acid could be used with advantage for the quantitative determination of thorium.

Twenty-five cc. of thorium chloride solution was diluted to 500 cc. and heated to just below the boiling point. Thirty cc. of a 10% solution of phenylarsonic was added and this followed by 75 cc. of glacial acetic acid and 5 g. of ammonium acetate in concentrated solution. It was found that a considerable variation in the quantity of acetic acid did not change the results. The precipitate was filtered off, washed, returned to the original beaker, dissolved in 10 cc. of hydrochloric acid, the solution diluted to 400 cc., heated to boiling and precipitated with 5 g. of oxalic acid. After standing overnight the oxalate was removed by filtration, washed, ignited and weighed. The precipitation as oxalate proved necessary because simple ignition of the phenylarsonate failed to remove all of the arsenic. However, it is possible that heating in hydrogen followed by ignition at a high temperature would give the desired results. Experience gained with zirconium showed the method used to be the simpler of the two. The average of three determinations gave as a result 0.2582 g. of thoria equivalent per 25 cc., against a standard value of 0.2582. Similar work was carried out using solutions of thorium sulfate and thorium nitrate.

	ThO_2 taken, g.	ThO_2 found, g.
$Th(SO_4)_2$, av. of 4 detns.	0.3366	0.3365
$Th(NO_3)_4$, av. of 2 detns.	.2484	.2485

The Determination of Thorium by Phenylarsonic Acid in the Presence of Rare Earths

A careful study using neodymium and cerium salts revealed the fact that a double precipitation of thorium by phenylarsonic acid was necessary to remove all traces of these substances.

The procedure finally adopted was as follows. A mixture of 25 cc. of thorium nitrate and an amount of neodymium nitrate which would yield approximately the same weight of oxide as the thorium employed was diluted to 330 cc.; 75 cc. of glacial acetic acid and 5 g. of ammonium acetate were then added, the whole was heated to boiling and precipitated with 50 cc. of phenylarsonic acid solution. The precipitate was filtered off, washed, returned to the original beaker, dissolved in 30 cc. of 1:1 hydrochloric acid and the solution then diluted to 300 or 400 cc. Fifteen cc. of acetic acid was introduced and reprecipitation was brought about by the addition of a few cubic centimeters of phenylarsonic acid and a slight excess of ammonium acetate. The whole was boiled, filtered and the precipitate washed thoroughly.

This precipitate was again dissolved in 30 cc. of 1:1 hydrochloric acid the paper removed by filtration, the filtrate diluted to about 300 cc. and the thorium precipitated from a boiling-hot solution by 5 g. of oxalic acid. The precipitate was allowed to stand overnight before being filtered. Three determinations gave an average of 0.2483 g. of thoria equivalent as compared with the standard of 0.2484.

The Determination of Thorium Oxide in Monazite Sand

Twenty-five g. of the sand was digested with 50 cc. of concd. sulfuric acid for 12 hours on a hot plate. When cold, the mixture was slowly added to 500 cc. of cold water and the whole thoroughly stirred. The small residue of zircon sand, etc., was removed by filtration, and the filtrate diluted to 1 liter.

First of all, the phosphoric acid was removed in the following manner; 15 cc. of concd. nitric acid was added to a 100cc. portion of the solution and the mixture then poured into a hot solution of about 10 g. of oxalic acid. After the whole had stood for a short time the precipitate was filtered off, washed and then decomposed by boiling with concd. nitric acid. When the volume had reached about 15 cc., an excess of hot oxalic acid (10 g.) in solution was added and the whole diluted to about 200 cc. After filtering, the precipitate was again dissolved in concd. nitric acid and evaporated almost to dryness.

The residue was treated with about 300 cc. of water and all ceric cerium reduced by the careful addition of sulfurous acid. The solution was heated to boiling, treated with 30 cc. of 10% phenylarsonic acid solution and 75 cc. of acetic acid. This was followed by the slow addition of a concentrated solution of ammonium acetate until it was evident that all of the thorium phenylarsonate was precipitated, after which the mixture was digested on a hot plate for about ten minutes. The precipitate was then filtered off, washed, dissolved in 30 cc. of 1:1 hydrochloric acid, the solution diluted to about 300 cc. and treated with a little sulfurous acid. The thorium was reprecipitated by adding a few cubic centimeters of phenylarsonic acid, 75 cc. of acetic acid and enough ammonium acetate to insure complete precipitation.

This last precipitate was then dissolved in 30 cc. of 1:1 hydrochloric acid, the solution treated with 5 g. of oxalic acid and the whole diluted to about 200 cc. This was allowed to stand for at least 12 hours. Results of 6.54, 6.52, 6.50% of thoria equivalent were obtained by this method compared with an average of 6.48 by the pyrophosphate method.[3]

Summary

Zirconium phenylarsonate is an extremely insoluble substance, eminently suited for the separation of zirconium from all elements except hafnium. It has been shown that it can be quantitatively precipitated from both hydrochloric acid and sulfuric acid solutions.

Thorium phenylarsonate differs from the phenylarsonates of the rare earths, being insoluble in solutions containing large amounts of acetic acid. A method is given for the determination of thorium in monazite sand.

The authors highly recommend this reagent for the quantitative determination of zirconium and thorium.

Work is being continued with regard to the quantitative estimation of hafnium by this reagent.

DURHAM, NEW HAMPSHIRE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

PREPARATION OF DISILICON HEXACHLORIDE

BY JOSEPH B. QUIG WITH JOHN A. WILKINSON

RECEIVED DECEMBER 2, 1925 PUBLISHED APRIL 5, 1926

Introduction

In reviewing the methods that have been proposed for the preparation of disilicon hexachloride,[1] that proposed by Martin seemed the best. Gattermann and Weinlig chlorinated metallic silicon at 300° and obtained a yield of 20% but this could not be duplicated in this Laboratory. Martin

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[3] Carney and Campbell, THIS JOURNAL, **36**, 1134 (1914).

[1] (a) Friedel, *Compt. rend.*, **73**, 1011 (1871). (b) Troost and Hautefeuille, *Ann. chim. phys.*, [5] **7**, 453 (1876). (c) Gattermann and Weinlig, *Ber.*, **27**, 1943 (1894). (d) Gattermann and Ellery, *Ber.*, **32**, 1114 (1899). (e) Besson and Fournier, *Compt. rend.*, **148**, 839 (1909); (f) **149**, 34 (1909). (g) Martin, *J. Chem. Soc.*, **105**, 2836 (1914). (h) Stock, Brandt and Fischer, *Ber.*, **58**, 648 (1925).