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

Normal-Propylarsonic Acid as a Reagent for the Determination of Zirconium

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Phenylarsonic acid has been shown by Rice, Fogg and James[1] to be a satisfactory reagent for the determination of zirconium in the presence of certain elements. Knapper, Craig and Chandlee[2] found that in the absence of zirconium this reagent could be used for the determination of tin but could not find conditions that would permit the determination of one in the presence of the other. Investigation of a large number of aromatic arsonic acids yielded only arsanilic acid[3] as a reagent that would effect this separation. Since close observation of conditions was necessary in using this reagent attention was turned to the alkylarsonic acids.

Procedure.—Prepare a solution containing the zirconium as chloride in 10% by volume of hydrochloric acid. The solution is heated to boiling and the zirconium is precipitated as a white flocculent precipitate, not difficult to filter, by the addition of 25 cc. of a 5% water solution of *n*-propylarsonic acid. The mixture is boiled for two to three minutes, cooled and the precipitate washed by decantation and then on the filter paper with cold water until free from chloride.

The zirconium is weighed as the oxide. The precipitate is ignited in a porcelain crucible over a low Bunsen flame until the carbon is burned off and is then heated over a full Meker flame to constant weight. No difficulty is encountered in volatilizing the arsenic although the time could undoubtedly be shortened by heating in an atmosphere of hydrogen.

Nine determinations on solutions prepared from carefully purified zirconyl chloride (hafnium content not determined), whose zirconium content had been established by the selenious acid method, using samples containing approximately 0.1 g. of zirconium dioxide and with the acidity of the solutions ranging from 1 to 10% of hydrochloric acid, gave results with an average deviation of 1 part per thousand.

Tin, Thorium, Other Elements.—No modification of the procedure as given was necessary for the determination of zirconium in the presence of tin, thorium or the list of elements which follows. All determinations were made in solutions containing 10% by volume of hydrochloric acid and approximately 0.1 g. of zirconium dioxide. The residues burned white in every case and were not further tested.

Three determinations in solutions containing 0.12 g. of tin oxide, three other determinations in solution containing simultaneously 0.05 g. of tin and thorium oxides and another three determinations in solutions containing simultaneously 0.04 to 0.05 g. of thorium, titanium and tin oxides all gave results with an average deviation of approximately 1 part per thousand.

Seven analyses in solutions containing simultaneously 0.01 to 0.2 g. of tin, manganese, nickel, iron, aluminum, vanadium, chromium, titanium, copper, cerium and thorium oxides gave results with an average deviation of 1.1 parts per thousand.

Four analyses containing simultaneously 0.04 to 0.6 g. of magnesium, zinc, uranium, molybdenum, cobalt, beryllium and cadmium oxides gave results with an average deviation of 1.2 parts per thousand.

Antimony and Bismuth.—A satisfactory separation of zirconium from antimony and bismuth was not obtained, the results being high in 10% hydrochloric acid solution and low in higher acid concentrations.

Influence of the Sulfate Radical.—Other investigations[4] have shown the effect of the presence of sulfate on the completeness of precipitation of zirconium with various reagents.

In the present work it was found that zirconium could be determined with an average deviation of 1 part per thousand in solutions containing not more than 4.5% by volume of sulfuric acid. With higher acidities the results were low. This acidity is not high enough to provide for the determination of zirconium in the presence of the group of elements from which separation is readily obtained in the presence of 10% hydrochloric acid.

Allylarsonic Acid.—Without modifying the procedure in any other respect it was found that allylarsonic acid could be substituted for *n*-propylarsonic acid for the determination of zirconium alone or when present in solutions containing simultaneously 0.04 to 0.1 g. of thorium, titanium and tin oxides. The same limitations of acidity, 10% of hydrochloric acid or 4.5% of sulfuric acid, were necessary. The average deviation of the results was 1.1 to 1.3 parts per thousand.

Allylarsonic acid was not satisfactory for the determination of zirconium in solutions containing simultaneously the large group of elements for which results have been given, using *n*-propylarsonic acid. Since the latter reagent proved so satisfactory further investigation of individual separations with allylarsonic acid was not made.

Summary

1. *n*-Propylarsonic acid has been shown to be a satisfactory reagent for the direct determination of zirconium in the presence of a number of elements, including tin, from which a separation has not heretofore been obtained by reagents of this type.

2. Some properties of allylarsonic acid as an analytical reagent have been described.

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(1) Rice, Fogg and James, THIS JOURNAL, **48**, 895 (1926).
(2) Knapper, Craig and Chandlee, *ibid.*, **55**, 3945 (1933).
(3) Craig, unpublished work.
(4) R. Ruer, *Z. anorg. Chem.*, **42**, 87 (1904); Simpson and Schumb THIS JOURNAL, **53**, 921 (1931).