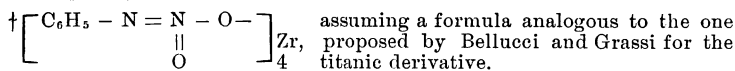


ART. IX.—*The Separation of Zirconium from Iron and Aluminum with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron")*; by WILLIAM M. THORNTON, Jr., and E. M. HAYDEN, Jr.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccix.]

IN connection with a study of potassium ferrocyanide, Schröder\* has stated that both titanium and zirconium could be quantitatively precipitated by the "cupferron" reagent from their acidified solutions and that experiments were in progress for estimating these two elements. Schröder gave no experimental data and, as far as the authors of this paper can ascertain, has not published further upon the subject. Bellucci and Grassi† have shown the "cupferron" reagent to be a quantitative precipitant for titanium and that a clean separation of titanium from aluminum could be brought about in solutions notably acid with either sulphuric or hydrochloric acid. Following the work of Bellucci and Grassi, one of us‡ has pointed out that, after throwing down the iron as ferrous sulphide from a solution containing sufficient ammonium tartrate to hold up titanium, and after acidifying the iron free filtrate, the titanium can be quantitatively precipitated by the "cupferron" reagent notwithstanding the presence of tartaric acid; and, further, that, if the above-mentioned filtrate be strongly acidified with sulphuric acid and contain also a sufficient quantity of tartaric acid, titanium can be quantitatively separated from both aluminum and phosphoric acid in one operation.§ On account of the great similarity in chemical nature between titanium and zirconium it appeared probable that in a similar way zirconium could be parted from the three substances mentioned above. Experiments with a view to accomplishing these separations were very successful as far as iron and aluminum were concerned. In the case of phosphoric acid, however, it was found that the zirconium derivative of nitrosophenylhydroxylamine,† even when the former was



present with the zirconium in relatively small quantities, carried down very appreciable masses of phosphoric acid; although the test solution contained 40<sup>cm³</sup> of sulphuric acid (1:1) and 5 gm. of tartaric acid in a total volume of 400<sup>cm³</sup>.

\* Zeitschr. anorg. Chem., lxxii, 89, 1911.

† Gazzetta Chimica Italiana, Anno xliii, Parte I, 570, 1913.

‡ This Journal, xxxvii, 173, 1914.

§ Ibid., xxxvii 407, 1914.

On account of the great difficulty in handling these two substances when together in solution the authors decided to abandon the attempt to separate them in aqueous solution but to recommend instead that, in the analysis of phosphatic materials containing zirconium, the phosphoric acid be separated at the beginning of the analysis by fusion with sodium carbonate and a little sodium nitrate and leaching with water, whereupon sodium phosphate dissolves, leaving the residual sodium zirconate which is soluble in sulphuric acid.\*

Two solutions of zirconium sulphate were used in these experiments. The first was prepared by dissolving Merck's zirconium sulphate in dilute sulphuric acid, filtering, and making up to definite volume. Four experiments were made with the object of setting the standard of this solution. In experiments (a) and (b) the zirconium was thrown down in the hot solution by redistilled ammonium hydroxide—the precipitation being performed in a platinum basin. In experiments (c) and (d) the zirconium was precipitated by the "cupferron" reagent from a volume of 400<sup>cm</sup><sup>3</sup> containing 20<sup>cm</sup><sup>3</sup> of sulphuric acid (made by diluting acid of sp. g. = 1.84 with an equal volume of water). The following results were obtained :

| Zirconium sulphate solution |  | Zirconium oxide |         |
|-----------------------------|--|-----------------|---------|
| (a)                         | 25 <sup>cm</sup> <sup>3</sup> = 25.9545 grm. | 0.1088 grm.     | 0.4157% |
| (b)                         | 25 <sup>cm</sup> <sup>3</sup> = 25.9415 grm. | 0.1089 grm.     | 0.4198% |
| (c)                         | 25 <sup>cm</sup> <sup>3</sup> = 25.978 grm.  | 0.1091 grm.     | 0.4200% |
| (d)                         | 25 <sup>cm</sup> <sup>3</sup> = 25.975 grm.  | 0.1089 grm.     | 0.4192% |

Since the values obtained in (b) and (c) by two different methods agree so closely, (c) was arbitrarily taken as correct. The second solution was prepared by acting on twice crystallized potassium fluozirconate with sulphuric acid (1:1), warming gently until all hydrofluoric acid had been displaced, pouring into cold water, and making up to definite volume. This solution was standardized by precipitation with the "cupferron" reagent, which had already been shown to agree well with results obtained by the reliable ammonium hydroxide precipitation. Duplicate determinations gave the following results :

| Zirconium sulphate solution |   | Zirconium oxide |         |
|-----------------------------|---|-----------------|---------|
| (a)                         | 25 <sup>cm</sup> <sup>3</sup> = 26.550 grm. | 0.1101 grm.     | 0.4147% |
| (b)                         | 25 <sup>cm</sup> <sup>3</sup> = 26.559 grm. | 0.1099 grm.     | 0.4138% |

The mean of these two values was taken as correct.

The first series of experiments was performed with the object of ascertaining satisfactory conditions for the separation of zirconium from aluminum. Known quantities of zirconium

\* See Hillebrand, Bull. U. S. Geological Survey, No. 422, p. 139, 1910.

and aluminum were taken by weighing off portions of the standardized zirconium solution and dry recrystallized ammonium aluminum sulphate respectively. The solution was made neutral to methyl orange with ammonium hydroxide, which had been redistilled and kept in bottles of Jena glass. Measured volumes of sulphuric acid (1 : 1) were then added and the solution made up to 400<sup>cm</sup><sup>3</sup>. About 20<sup>cm</sup><sup>3</sup> of a 6 per cent "cupferron" solution was added gradually with constant stirring. Thereupon the zirconium came down as a very bulky and flocculent white precipitate. Without much delay the precipitate was filtered on paper with the aid of gentle suction and washed thoroughly with hydrochloric acid (made by diluting 100<sup>cm</sup><sup>3</sup> of acid of sp. g. = 1.20 to one liter). The precipitate was placed in a tared platinum crucible, dried at 110° C., and carefully ignited to zirconium oxide. Table I contains the results of four experiments.

TABLE I.  
The Separation of Zirconium from Aluminum.

| No. | ZrO <sub>2</sub><br>taken<br>gram. | Al <sub>2</sub> O <sub>3</sub><br>taken<br>gram. | ZrO <sub>2</sub><br>found<br>gram. | Error<br>gram. | H <sub>2</sub> SO <sub>4</sub><br>(1 : 1)<br>cm <sup>3</sup> | Volume<br>of soln.<br>cm <sup>3</sup> |
|-----|------------------------------------|--|------------------------------------|----------------|--|---------------------------------------|
| 1.  | 0.1091                             | 0.1127   | 0.1090                             | −0.0001        | 40   | 400                                   |
| 2.  | 0.1088                             | 0.1127   | 0.1090                             | +0.0002        | 40   | 400                                   |
| 3.  | 0.1086                             | 0.1127   | 0.1090                             | +0.0004        | 60   | 400                                   |
| 4.  | 0.1091                             | 0.1127   | 0.1094                             | +0.0003        | 60   | 400                                   |

In the second series of experiments zirconium was separated from iron. Known quantities of iron were introduced by weighing off portions of Kahlbaum's ferrous ammonium sulphate. Since the technique is the same for the separation of zirconium from iron only as for the separation of zirconium from both iron and aluminum, the procedure will be described below for the more general case. Table II embodies the results of two experiments.

TABLE II.  
The Separation of Zirconium from Iron.

| No. | ZrO <sub>2</sub><br>taken<br>gram. | Fe <sub>2</sub> O <sub>3</sub><br>taken<br>gram. | ZrO <sub>2</sub><br>found<br>gram. | Error<br>gram. | Tartaric<br>acid<br>gram. | H <sub>2</sub> SO <sub>4</sub><br>(1 : 1)<br>cm <sup>3</sup> |
|-----|------------------------------------|--|------------------------------------|----------------|---------------------------|--|
| 5.  | 0.1088                             | 0.1018   | 0.1091                             | +0.0003        | 2                         | 40   |
| 6.  | 0.1090                             | 0.1018   | 0.1093                             | +0.0003        | 2                         | 40   |

In the third series of experiments known mixtures of iron, aluminum, and zirconium were analyzed. The iron and aluminum were introduced into the solution by weighing dry portions of ferrous ammonium sulphate and ammonium aluminum

sulphate just as was done in the two series above. In Table III are put forth the results of four experiments.

TABLE III.

The Separation of Zirconium from Iron and Aluminum.

| No. | ZrO <sub>2</sub><br>taken<br>grm. | Fe <sub>2</sub> O <sub>3</sub><br>taken<br>grm. | Al <sub>2</sub> O <sub>3</sub><br>taken<br>grm. | ZrO <sub>2</sub><br>found<br>grm. | Error<br>grm. | Tartaric<br>acid<br>grm. | H <sub>2</sub> SO <sub>4</sub><br>(1:1)<br>cm <sup>3</sup> | Volume<br>of soln.<br>cm <sup>3</sup> |
|-----|-----------------------------------|---|---|-----------------------------------|---------------|--------------------------|--|---------------------------------------|
| 7.  | 0.1087                            | 0.1018  | 0.05635   | 0.1086                            | -0.0001       | 2                        | 40   | 400                                   |
| 8.  | 0.1089                            | 0.1018  | 0.05635   | 0.1088                            | -0.0001       | 2                        | 40   | 400                                   |
| 9.  | 0.1101                            | 0.2036  | 0.1127  | 0.1110                            | +0.0009       | 2                        | 40   | 400                                   |
| 10. | 0.1100                            | 0.2036  | 0.1127  | 0.1103                            | +0.0003       | 2                        | 40   | 400                                   |

The technique of the analysis is here connectedly given. Tartaric acid is added to the solution in amount equal to five times the aggregate weight of the three bases to be held by it in solution. It is desirable that the initial volume of the test solution should not much exceed 100<sup>cm</sup><sup>3</sup>. To facilitate reduction of the iron the solution is made neutral to litmus paper with ammonium hydroxide and then acid again with 2<sup>cm</sup><sup>3</sup> of sulphuric acid (1:1). Hydrogen sulphide is then passed in until the iron has all been reduced to the ferrous state. The solution is now made slightly ammoniacal and more hydrogen sulphide introduced till the iron has been completely thrown out as ferrous sulphide, leaving the solution, however, alkaline to test-paper. The ferrous sulphide is thrown on a filter and washed ten times with very dilute colorless ammonium sulphide. The filtrate is acidified with 40<sup>cm</sup><sup>3</sup> to 60<sup>cm</sup><sup>3</sup> of sulphuric acid (1:1) and the hydrogen sulphide thus liberated boiled out. The solution is then cooled (best by iced water), the volume made to 400<sup>cm</sup><sup>3</sup>, and the "cupferron" reagent added gradually in the cold with constant stirring. Without delay the filtration is proceeded with, using a paper filter and mild suction. The filtrate should be tested as to completeness of precipitation by adding thereto a few drops of the reagent. A white turbidity will appear immediately if the solution still contain zirconium—otherwise a small white precipitate of nitrosophenylhydroxylamine which disappears on standing. After a little experience the analyst will have no difficulty in distinguishing these two precipitates, which are very different in appearance. The precipitate is washed at least twenty times with hydrochloric acid (100<sup>cm</sup><sup>3</sup> of acid of sp. g. = 1.20 diluted to one liter), agitating the filter contents as much as possible and not allowing the washing fluid to run through too fast to accomplish much solvent work. After having been sucked free from drainage liquid at the pump, the precipitate along with the filter is placed in a tared platinum crucible and dried

at 110° C. If it be desired to save time, the ignition can be started with the precipitate moist—exercising great care, however, to avoid loss by spattering. With the lid not quite covering the crucible, the volatile matter is cautiously smoked off, the residual carbon burned away, the Meker burner applied for one half hour, and the zirconium oxide weighed. The ignition should be repeated, of course, until a constant weight is obtained.

In order to determine to what extent the zirconium derivative of nitrosophenylhydroxylamine includes fixed alkalis when salts of the latter are present in the solution, zirconium determinations were made in the presence of a large excess of potassium sulphate. The mode of experimentation was the same as that employed in the case of the separation of zirconium from aluminum. Table IV shows the results of two experiments.

TABLE IV.

The Separation of Zirconium from Potassium.

| No. | ZrO <sub>2</sub><br>taken<br>gram. | K <sub>2</sub> O<br>taken<br>gram. | ZrO <sub>2</sub><br>found<br>gram. | Error<br>gram. | H <sub>2</sub> SO <sub>4</sub><br>(1:1)<br>gram. | Volume<br>of soln.<br>cm <sup>3</sup> |
|-----|------------------------------------|------------------------------------|------------------------------------|----------------|--|---------------------------------------|
| 11. | 0.1088                             | 2.7027                             | 0.1097                             | +0.0009        | 40   | 400                                   |
| 12. | 0.1089                             | 2.7027                             | 0.1096                             | +0.0007        | 40   | 400                                   |

It will be observed that the gain of weight undergone by the zirconium is not very large, and when one considers that the amount of potassium present (calculated as oxide) is nearly twenty-five times as great as the zirconium (also reckoned as oxide), the tendency of the precipitate to carry down alkalis need not be regarded as serious.

It remains now only to call attention to the chief points of merit possessed by this method of analysis. The precipitation of zirconium by the "cupferron" reagent is quantitative. From solutions strongly acidified with sulphuric acid, a clean separation of zirconium from aluminum can be effected. Tartaric acid does not interfere with the precipitation so that the acidified filtrate from the ferrous sulphide is in fit condition for the separation of zirconium from aluminum—a fact which obviates the necessity for oxidizing the organic oxyacid. The precipitate comes down immediately in flocculent and readily filterable condition, is little prone to include alkalis, and after drying can be converted into zirconium oxide of a high degree of purity. The manipulation is extremely simple and the sources of error are few.

May 26, 1914.