

XLIX.—*A Method for the Separation and Estimation of Zirconium.*

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It has already been pointed out (this vol., p. 149) that zirconium is completely precipitated from its solution in dilute sulphuric acid on addition of hydrogen peroxide alone. Hermann (*J. pr. Chem.*, **97**, 331), has described elaborate processes for the estimation of zirconium, but was unable to effect a satisfactory separation from titanium, iron, and some of the rarer earths. It was therefore desirable, in continu-

ance of the work referred to above, to ascertain whether the separation by means of hydrogen peroxide is capable of application in presence of varying amounts of such substances. Judging from Clève's results (*Bull. Soc. Chim.*, **43**, 53), there can be little doubt as to the similarity of thorium and zirconium in relation to this reagent, and where these two elements occur together they will in all probability both be precipitated on adding hydrogen peroxide to the solution; it is not proposed to consider the case of thorium in this place. Since, however, niobium and tantalum frequently accompany zirconium, the first has been included in the mixture. Solutions were made of the following composition:—

- | | | | | | |
|------|------------|---------|------|--------------------------------|-----------------------|
| (1.) | Containing | 0.02086 | gram | ZrO ₂ | per cubic centimetre. |
| (2.) | " | 0.00417 | " | " | " |
| (3.) | " | 0.00040 | " | TiO ₂ | " |
| (4.) | " | 0.00446 | " | " | " |
| (5.) | " | 0.00071 | " | Nb ₂ O ₅ | " |
| (6.) | " | 0.00625 | " | Fe ₂ O ₃ | " |

Hydrogen peroxide was added to a portion of each of these, and, except in the case of zirconium, no precipitation occurred even after several weeks. A mixture containing zirconia in larger quantity than the other constituents was made for determination from solutions 1, 3, 5, and 6. To the moderately acid solution, excess of hydrogen peroxide was added, and after standing in a stoppered flask 24 hours, the precipitated oxide was collected on a filter. It was perfectly white even after ignition, and weighed 0.4115 gram; no trace of iron or titanium could be detected in it. The filtrate was now diluted and boiled for 30 hours, the excess of the precipitating agent was thus decomposed, and a large part of the niobic and titanic oxides separated out. These were weighed together, the titanium being afterwards determined by Weller's colorimetric method and the niobium by difference. The filtrate from this still contained iron and some titanium, which were precipitated by means of ammonia. The results were—

| | Taken. | Found. |
|--------------------------------------|-------------|--------------|
| ZrO ₂ | 0.4105 gram | 0.4115 gram. |
| Nb ₂ O ₅ | 0.0103 " | 0.0240 " |
| TiO ₂ | 0.0145 " | |
| Fe ₂ O ₃ | 0.0950 " | |

A second portion was taken containing relatively less zirconia and being altogether more dilute than the above, the solutions 2, 4, 5, and 6 being used. The precipitation and analysis were carried out exactly as in the previous case.

The results were—

| | Taken. | Found. |
|--------------------------------------|--------------|-------------|
| ZrO ₂ | 0·07188 gram | 0·0745 gram |
| Nb ₂ O ₅ | 0·01450 „ | 0·0718 „ |
| TiO ₂ | 0·05288 „ | |
| Fe ₂ O ₃ | 0·03887 „ | |

The general results being thus satisfactory, a third solution was made up with a view to testing the delicacy of the separation, as it is most important to be able to determine small quantities of zirconia in presence of a large excess of other oxides. The solution occupied 32 c.c. in bulk and contained—

| | |
|--------------------------------------|--------------|
| ZrO ₂ | 0·0065 gram. |
| TiO ₂ | 0·1290 „ |
| Fe ₂ O ₃ | 0·1504 „ |

The precipitation of zirconia in this case was complete only after standing two or three days. The precipitate weighed 0·0055 gram and was free from iron and titanium. It was not considered necessary to determine the titanium and iron. As it is most desirable to have a simple and trustworthy method for the complete separation of zirconium from titanium and iron, further experiments were made in this direction.

Zirconia was precipitated by hydrogen peroxide in the presence of a very considerable excess of iron and of titanium respectively, the precipitate redissolved whilst still moist in dilute sulphuric acid, and the solution very carefully tested for these two elements. In no case was the zirconia found to contain either iron or titanium.

Properties of Zirconium Pentoxide.

The oxide described in my former paper is of course a hydrated oxide. In this form even when freshly precipitated it is insoluble in very dilute (1 per cent.) sulphuric acid or in dilute acetic acid, though on boiling for some time it partially dissolves, being probably first decomposed.

The ordinary hydrated dioxide on the other hand, especially in the freshly precipitated condition, is readily dissolved by these acids, and indeed a separation of the two oxides can be made by treating a mixture of the two with such acid. Oxalic acid dissolves both oxides quite readily, and the fact may here be emphasised that zirconia in the moist state dissolves in this acid; for although Berlin (*J. pr. Chem.*, 58, 147) has already pointed this out, the contrary is stated to be the case in a large number of authoritative text-books. In dilute

acetic acid, the pentoxide is quite insoluble, and it was therefore not unlikely that the precipitation might be more advantageously carried out in this medium than in the presence of mineral acids. A repetition of Haas' work (*Ber.*, **17**, 2249) on the peroxides of cadmium, substituting the acetate for the sulphate, showed that whereas the latter gives an oxide of the composition Cd_3O_5 , the former gives not the faintest trace of peroxide. In the case of zirconium, however, the oxide obtained by precipitation in an acetic acid solution proved to be the pentoxide and gave the ratio—

$$\text{ZrO}_2 : \text{O} :: 122 : 7.3,$$

the calculated relation for the pentoxide being—

$$\text{ZrO}_2 : \text{O} :: 122 : 8.$$

A portion of the pentoxide was now taken and dried at 100° , and the oxygen determined by the iodometric method, the zirconia by heating a separate portion over the blowpipe until the weight was constant. The water of hydration was obtained by difference.

The results were—

| | | |
|------------------------|--------|------|
| ZrO ₂ | 75.51 | — |
| O | 3.87 | 3.76 |
| H ₂ O | 20.62 | — |
| | <hr/> | |
| | 100.00 | |

Portions dried at 15° over sulphuric acid gave—

| | | | |
|------------------------|-------|-------|-------|
| ZrO ₂ | 76.81 | 74.61 | 75.66 |
| O | — | 2.44 | 3.13 |
| H ₂ O | — | 22.95 | 21.21 |

The oxide seems therefore to have the composition $\text{Zr}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, though in the dry state it is not of constant composition, and loses at ordinary temperature about one-fifth of its peroxide oxygen, and at 100° about one-half.

Clève has (*loc. cit.*) described an oxide containing more oxygen than the foregoing, which he obtained by adding ammonia and hydrogen peroxide to a salt of zirconium.

Although hitherto the several specimens of peroxide, which I have prepared, had invariably proved to be the pentoxide, I have recently obtained the higher oxide, and this also on addition of hydrogen peroxide alone.

What the conditions are under which this higher oxide is produced I am not prepared to say. I obtained it by treating the solution of the sulphate (prepared by heating the double fluoride of potassium and zirconium with sulphuric acid) *immediately* with hydrogen

peroxide before the basic potassium salt had had time to separate. In previous preparations, the solution had been allowed to stand and was filtered before adding the peroxide; it was therefore more dilute. This higher oxide is no doubt the compound described by Clève, and has the composition ZrO_3 .

In its properties, it resembles the pentoxide, behaving in the same way towards acids.

It seems, however, to be more stable, and can be dried at ordinary temperatures without undergoing decomposition. This is shown in the following experiments. The oxide was freed from moisture by placing it in a stream of air dried over caustic potash and sulphuric acid. Portions were then analysed in the same manner as the pentoxide, and the results obtained gave the following percentage composition:—

| | | | |
|----------------------------|-------|-------|------|
| ZrO_2 | 52·17 | 51·84 | — |
| O | — | 7·01 | 6·85 |
| H_2O | — | 41·15 | — |

This answers fairly well to the composition $\text{ZrO}_3 \cdot 5\text{H}_2\text{O}$. Dried at 100° , it gave—

| | | |
|----------------------------|-------|-------|
| ZrO_2 | 59·61 | 59·17 |
| O | — | 3·41 |
| H_2O | — | 37·42 |

At this temperature, therefore, it loses about 1 mol. H_2O and half its additional oxygen. The water of hydration cannot be looked on as perfectly definite in amount. Calculating for the anhydrous oxides we have the following numbers:—

| | ZrO_2 . | O. |
|----------------------------------|------------------|-------|
| Dried at 15° | 88·13 | 11·91 |
| „ | — | 11·64 |
| „ 100° | 94·55 | 5·45 |
| Calculated for ZrO_3 .. | 88·41 | 11·59 |

and for the pentoxide:—

| | ZrO_2 . | O. |
|---|------------------|------|
| Dried at 15° | 96·32 | 3·68 |
| „ 100° | 95·07 | 4·93 |
| Calculated for Zr_2O_5 .. | 93·85 | 6·15 |

Note.—In a private communication with which I have been favoured by Prof. Clève, he suggests that these peroxides may possibly contain traces of sulphuric acid, but on examination I can obtain no evidence of such contamination.