The only change in the table of atomic weights is in the case of scandium; from 44.1 to 45.1; which appears to be fully justified by the evidence.

Signed, F. W. CLARKE,
T. E. THORPE,
G. URBAIN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

A NEW METHOD FOR THE DETERMINATION OF ZIRCONIUM.

BY MELVIN M. SMITH AND C. JAMES.

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The increased commercial development of zirconium and its compounds during the last two or three years has called for far more accurate determinations of the dioxide than nearly all the older methods would give. Heretofore, in practically every instance the study of the quantitative separation of an element, keeps ahead of its industrial application. It seems reasonable to state, in the case of the element under discussion, that, up to the present time, there has been only one method, that employing nitroso-phenylhydroxylamine (cupferron), which has given absolutely reliable results.

Sodium thiosulfate has probably been the precipitant most commonly employed until comparatively recently. This method separates zirconium from iron very nicely when carried out under the proper conditions. However, since thorium, aluminum, titanium and phosphoric acid were precipitated by this reagent also, the results obtained were often as much as several per cent. too high.

Precipitation as the phosphate by sodium phosphate in the presence of hydrogen peroxide possesses an advantage in that titanium is held up. A considerable excess of hydrogen peroxide must be present and a second precipitation is advised. Unfortunately the solubility of the phosphate is affected by sulfuric acid; the second precipitation involves several tedious operations and the precipitate is not any too well defined.

The cupferron method, which is an excellent one, precipitates both zirconium and titanium together, iron having been previously removed. The solution should have 10% of free sulfuric acid present. If the original material contains only a few per cent. of phosphoric acid, a negligible amount of the latter will be found in the precipitate. The amount of titanium dioxide present must be determined either colorimetrically by hydrogen peroxide or by zinc reduction and subsequent titration. Tantalum and columbium, which occur in some varieties of zirkite, are precipitated by cupferron in the presence of large amounts of conc. sulfuric acid. It is, therefore, necessary to make sure that these elements are absent.

The other methods described for the estimation of zirconium leave much to be desired.

While the cupferron method is a very good one, it is not very simple, and in addition the reagent is very costly. Having these facts ever in mind, the authors commenced a search for suitable reagents. Several interesting ones have been found and work upon one of them is described below.

It was noticed that when selenious acid was added to boiling solutions of zirconyl chloride made acid with hydrochloric acid precipitates of basic selenite would form even in very dilute solutions. The composition of the selenite probably varied according to the conditions of this experiment, as was noticed by Nilson in 1875. Selenious acid moreover gave no precipitates with solutions of aluminum, or the rare earths. In the case of ferric chloride a precipitate formed in nearly neutral solution but not in a dilute acid solution. This last observation appeared to be especially interesting for it is here that the cupferron method fails. Thorium is precipitated in dilute acid solutions of the chloride. However this element does not appear to occur in zirkite to any appreciable extent.

Purification of Zirconyl Chloride.—Crude zirconium hydroxide was dissolved in conc. hydrochloric acid and the solution evaporated. When the volume had been considerably reduced, a quantity of conc. hydrochloric was added and the whole allowed to crystallize. The crystals were then placed upon a Büchner funnel and well washed with 1 : 1 hydrochloric acid. The chloride was further purified by 2 more crystallizations from 1 : 1 hydrochloric acid. The material was then examined for both iron and titanium by adding ammonium thiocyanate and hydrogen peroxide to separate portions of a solution. In neither case could any coloration be detected.

Preparation of Selenious Acid.—This acid was prepared by treating selenium with conc. nitric acid until oxides of nitrogen ceased to be evolved. The solution was evaporated to dryness and the selenium dioxide purified by sublimation. The oxide was then dissolved in water and the solution diluted until the liquid contained approximately 12.5% of selenious acid.

Zirconyl Chloride Solution.—A certain amount of zirconyl chloride was weighed out and dissolved in distilled water so as to give about 8 g. of zirconium oxide per liter.

A comparison of the amount of oxide contained in 25 cc. of the solution was made by precipitating the zirconium by ammonium hydroxide, cupferron and selenious acid with the following results.

Ammonium Hydroxide.—25 cc. of zirconyl chloride solution was diluted to 100 cc. and ammonium hydroxide added to the boiling liquid until it smelled of ammonia. The resulting precipitate was filtered off, washed, dried, ignited to oxide and weighed. Two runs gave 0.2111 g. and 0.2107 g., respectively.

Nitroso-phenyl-hydroxylamine, Cupferron.—25 cc. of the solution was evaporated to fumes with 15 cc. of conc. sulfuric acid in a Kjeldahl flask. The cooled residue was taken up with water, diluted to 150 cc., cooled to 10° and precipitated with a 6% solution of the cupferron. The precipitate was filtered off, washed first with 10% hydrochloric acid and then with 5% ammonium hydroxide, after which it was dried, ignited and weighed. Two different portions gave 0.2102 g. and 0.2106 g., respectively.

Selenious Acid.—In the case of this reagent precipitations were made under varied conditions. For the first tests 25 cc. of the original solution was diluted to 100 cc., precipitated by the addition of about 20 cc. selenious acid solution and the whole heated to boiling. The precipitate was filtered off, washed with hot 2% hydrochloric acid, dried and ignited. Three results gave 0.2106 g., 0.2107 g. and 0.2105 g., respectively.

The next trials were made upon 25 cc. of solution diluted from 100 to 250 cc. in the presence of 5% of conc. hydrochloric acid. Under these conditions the figures yielded were 0.2109 g., 0.2106 g., and 0.2109 g. The filtrate was found to be free from zirconium, the ignited precipitate contained no selenium.

Sulfuric acid solutions are not suited to the use of the selenious acid reagent. The material should be in the form of the chloride and the free acid should not exceed 7% of hydrochloric acid (sp. gr. 1.200). Precipitation from 7% hydrochloric acid and washing with water containing 3% of hydrochloric acid gave good results, since no zirconium was found in the filtrate or wash water. The selenite appeared to be distinctly soluble in solutions containing 10% of free acid, as the following results show. 25 cc. of zirconium chloride solution was used in each experiment.

Hydrochloric acid. %.	Zirconium oxide found. G.
0	0.2106
do	0.2107
do	0.2105
5	0.2109
do	0.2106
do	0.2109
10	0.2060
do	0.2044

Separation of Zirconium from Aluminum.—A solution of aluminum chloride was prepared by dissolving pure aluminum chloride in water. It was standardized by precipitating with ammonium hydroxide, washing and igniting to form the oxide. One cc. of the solution was equivalent to 0.0183 g. of aluminum oxide.

In order to find out whether the presence of aluminum would affect the determination of zirconium as the selenite, various portions of the solutions were mixed and diluted with 150 to 200 cc. of water. Hydrochloric acid was added to bring the concentration to 5%. The whole was then heated to boiling and precipitated by about 20 cc. of selenious acid. The precipitate was washed with a hot 2% hydrochloric acid solution. The aluminum hydroxide was precipitated from the filtrate by adding ammonium chloride and ammonium hydroxide in the usual manner. The results obtained were as follows.

Al_2O_3 taken. G.	Al_2O_3 found. G.	ZrO_2 taken. G.	ZrO_2 found. G.
0.0366	0.0360	0.2108	0.2106
0.1830	0.1831	0.2108	0.2106
0.7320	0.7326	0.2108	0.2107
0.1830	0.1831	0.04216	0.0421

Separation of Zirconium from Rare Earths.—Solutions of chlorides of the rare earths give no precipitates with a solution of selenious acid. Cerium should be in the cerous condition.

A solution of the chlorides of the rare earths was prepared and standardized. One cc. of the solution was equivalent to 0.0083 g. of oxides.

The operations were carried out in a manner similar to those described under aluminum. Although the rare earths might easily have been precipitated as the oxalates, no determination was made. The following figures were obtained.

Rare earth oxides taken. G.	ZrO_2 taken. G.	ZrO_2 found. G.
0.2490	0.2108	0.2108
0.0249	0.2108	0.2107

Separation of Zirconium from Iron.—These 2 elements may be easily separated by means of hydrogen sulfide in ammoniacal ammonium tartrate solution, sodium thiosulfate, etc. This involves the use of some additional method for the removal of such other elements as aluminum, the rare earths, etc. Ferric chloride made slightly acid with hydrochloric acid is precipitated by selenious acid. This precipitate is readily dissolved by hydrochloric acid, and it was found that in 5% hydrochloric acid solution ferric chloride is not precipitated by selenious acid.

A solution of ferric chloride was prepared and standardized by precipitation by ammonium hydroxide in the presence of ammonium chloride. One cc. of the solution was equivalent to 0.00222 g. of ferric oxide, Fe_2O_3.

Twenty-five cc. of zirconyl chloride solution, 20 cc. of ferric chloride solution and 7.5 cc. of conc. hydrochloric acid were mixed and diluted to about 150 cc. The liquid was then heated, precipitated by selenious acid and filtered. The precipitate was washed with a boiling 2% hydrochloric acid. The precipitate and paper were returned to the original beaker owing to the fact that iron could be seen in the zirconium selenite. A measured volume 1 : 1 hydrochloric acid was added and the mass heated carefully for a time. Water was then added until the hydrochloric acid content was reduced to 5%. Any zirconium that might have remained in solution was next thrown out by adding about 20 cc. of selenious acid. The insoluble selenite was removed, washed and ignited. The resulting oxide which possessed a reddish tint, weighed 0.2145 g. instead of 0.2111 g. A similar run involving the use of 10 cc. of ferric chloride gave 0.2128 g. of oxide, and another in which 5 cc. was employed gave 0.2115 g. of oxide. Although these results were far from encouraging, it was decided to see what one precipitation in very dilute solution would do, for in the operations described above it was noticed that the selenite never entirely dissolved in the strong acid, and that certain portions of the ignited precipitate was very red, while others were white.

Twenty-five cc. of zirconyl chloride, 10 cc. of ferric chloride and 20 cc. of conc. hydrochloric acid were mixed, diluted to about 400 cc. and precipitated by 30 cc. of selenious acid. The whole was then boiled and filtered. The precipitate was washed with 2 to 3% hydrochloric acid and ignited. This time the oxide weighed 0.2112 g. as compared with the standard figure of 0.2111. In the next experiment 25 cc. of zirconyl chloride, 20 cc. of ferric chloride and 40 cc. of conc. hydrochloric acid were diluted to about 750 cc. and precipitated by 40 cc. of selenious acid. The ignited oxide weighed 0.2125 instead of 0.2111 g. These results indicate that if the amount of iron oxide in the combined iron-zirconium oxides is about 20% there will be a very slight error. As the amount of iron decreases, the error will become less and finally disappear when the figure reaches about 10% oxide of iron. Since practically all commercial zirconia ore contains much less than this latter value, a single precipitation is sufficient. In certain special cases it might become necessary to repeat the operation or else to remove the iron by another method.

Separation of Zirconium from Titanium.—Selenious acid throws down titanium along with zirconium and it is necessary to make a correction for this. This may easily be carried out either colorimetrically by hydrogen peroxide when small amounts are present or by titration after reduction in the Jones reductor if larger quantities are found.

It was found that zirconium could be precipitated, in the cold or boiling, as the selenite, in the presence of an excess of hydrogen peroxide free from titanium. The filtration can be carried out much better in the cold, since the evolution of oxygen in the pores of the filter paper causes the precipitate to run through.

In order to test the accuracy of the separation, 25 cc. of zirconyl chloride solution and 5 cc. of titanium sulfate were mixed, diluted and precipitated by ammonium hydroxide in the presence of ammonium chloride. The hydroxides were filtered off, washed, returned to the original beaker and warmed with 10 cc. of conc. hydrochloric acid. After standing a short time an equal volume of water was added and the whole heated to boiling. The solution was diluted further, filtered and the residue of filter paper well washed. An excess of hydrogen peroxide was added, the liquid diluted to about 500 cc. and precipitated by an excess of selenious acid. The precipitate was filtered off and washed with water containing 2% of hydrochloric acid and a little selenious acid.

TiO_2 taken. G.	ZrO_2 taken. G.	ZrO_2 found. G.
0.0463	0.1022	0.1019
0.0463	0.1022	0.1016

Separation of Zirconium from Phosphoric Acid.—If phosphoric acid is present it will be precipitated along with the members of the iron group by ammonium hydroxide in the presence of ammonium chloride. Upon dissolving the precipitate in hydrochloric acid zirconium phosphate will remain insoluble and be lost if the paper pulp is filtered off. On the other hand if the phosphate is not removed the determination will be too high. If this substance is found, it must be collected, decomposed by fusion with an excess of sodium carbonate, boiled out with water, the residue washed, dissolved in hydrochloric acid and added to the main portion.

Determination of Zirconium in Zirconia Ore.—1.2408 g. of zirconia ore was fused with 12 to 15 g. of potassium hydrogen fluoride in a platinum dish. The potassium hydrogen fluoride was prepared by treating potassium fluoride with a slight excess of hydrofluoric acid and evaporating over a very small flame until a clear fused mass was obtained. After allowing it to cool, it was broken up. The mixture of zirconia ore and fluoride was carefully heated by a very small flame. When the mixture became fused it was stirred with a platinum rod, and the size of the flame was gradually increased. After the whole had become solid and white, it was heated over a powerful burner until it just fused to a clear liquid. The lowest possible temperature for this operation was always used. The cooled melt was next treated with about 50 cc. of 1 : 1 sulfuric acid, gently heated until nearly all water was removed, and then more strongly heated until abundant fumes were evolved. The cold residue was boiled with water, cooled and diluted to 250 cc. 100 cc. of this solution was diluted, boiled and precipitated by ammonium hydroxide in the presence of ammonium chloride. The hydroxides were filtered off and well washed. The filter paper and the precipitate were treated with 36 cc. of conc. hydrochloric acid and about 40 cc. of water, boiled, diluted to 700 cc. and precipitated by selenious acid.[1] The insoluble selenite was removed

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[1] If phosphoric acid is present, the insoluble phosphate must be filtered off and treated as mentioned under phosphoric acid.

by filtration, washed with 3% hydrochloric acid, dried and ignited. The resulting oxides weighed 0.4286 g. 50 cc. of the solution treated in a similar manner gave 0.2141 g. These quantities represented 86.36 and 86.40% respectively, of zirconium and titanium oxides.

Average by selenious acid	86.38%
By cupferron was	86.36%

0.2591 g. of another sample of zirconia ore gave 0.1939 g. of oxides of zirconium and titanium, or 74.84%, while the average given by cupferron was 74.70%.

The method described above was found to be very rapid, simple and accurate for the determination of zirconium. The reagent, selenious acid, is cheap.

The determination of thorium by means of selenious acid and the determination of tantalum and columbium by means of cupferron are being investigated at the present time.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTIONS. (PRELIMINARY PAPER.)

BY S. A. BRALEY AND J. LOWE HALL.[1]

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In a study of the equilibria existing between mixed salt solutions and liquid amalgams, Smith and Ball[2] have noted that, with equivalent mixtures of sodium and potassium chlorides in solution, the ion-fraction of the potassium gradually decreases with increasing total salt concentration. In other studies on sodium-strontium[3] and potassium-strontium[4] mixtures similar results have been obtained. Several explanations may be offered to account for this behavior and the present work has been carried out for the purpose of throwing some light upon the subject by comparing the calculated values (on the basis of the isohydric principle) with the determined values of the transference numbers at various equivalent salt concentrations.

G. M. J. McKay,[5] by the use of transference experiments in mixed solutions of potassium chloride and potassium sulfate, 0.2009 *N* with respect to each, has shown that the ratio of the ionization factors of the 2 salts in the mixture is 1.372, whereas the ratio as calculated from the

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[1] The authors wish to thank Dr. T. R. Ball for originally suggesting the problem and starting the work upon it.

[2] Smith and Ball, THIS JOURNAL, **39**, 179 (1917).

[3] Smith and Braley, *ibid.*, **39**, 1545 (1917).

[4] Smith and Rees, *ibid.*, **40**, 1802 (1918).

[5] McKay, *ibid.*, **33**, 308 (1908).