No. of experiment.	Wt. of commercial KCN taken, g.	K_2O found, g.	Theory for K_2O on 92% KCN and 8% K_2CO_3 basis, g.	Error in g.	Error in %.
1	0.1490	0.1075	0.1073	+0.0002	+0.19
2	0.1128	0.0808	0.0812	—0.0004	—0.49
3	0.1389	0.0995	0.0998	+0.0003	+0.3
4	0.2198	0.1574	0.1572	+0.0002	+0.13
5	0.2708	0.1942	0.1936	+0.0006	+0.31

Carbonates, nitrates and iodides lose their acid radicals on gentle heating with this flux. Cyanides, as seen from the above table, do the same in the presence of an oxidizing agent. Other halogens, when suspected of being present in commercial cyanides, will leave a definite and weighable oxide on the application of a small blowpipe flame.[1] This flux may therefore be applied with advantage for the estimation of residual basic oxides in cyanides which are weighed with the flux.

AMES, IOWA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUTLER UNIVERSITY.]

THE USE OF CUPFERRON (PHENYLNITROSO-HYDROXYLAMINE AMMONIUM) IN: I. THE QUANTITATIVE SEPARATION OF ZIRCONIUM, TITANIUM, IRON, MANGANESE AND ALUMINUM. II. THE ANALYSIS OF ZIRCON AND BADDELEYITE.

BY JAMES BROWN.

Received July 2, 1917.

The work described in this paper was undertaken with the purpose of ascertaining the applicability of the cupferron reagent to the analysis of zirconium minerals. The minerals investigated thus far have been samples of zircon and baddeleyite purchased in powdered form from a mineral dealer. A preliminary analysis showed the zircon to consist of silica, zirconium, titanium, iron and aluminum. The baddeleyite was found to consist of the same elements as the zircon, plus small amounts of manganese and water. Baudisch[2] has shown that cupferron may be used as a quantitative precipitant for iron, and the iron determined by ignition to the oxide. His work has been confirmed by several investigators. Baudisch also separated iron from manganese by the use of cupferron in the analysis of minerals. Bellucci and Grassi[3] have shown the cupferron reagent to be a quantitative precipitant for titanium, and that this element can thereby be separated quantitatively from aluminum in acid solution. Thornton and Hayden[4] have found that cupferron may also be used in separating titanium from aluminum and phosphoric acid

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[1] Kuzirian, *Am. J. Sci.*, 36, 301 (1913).

[2] *Chem. Ztg.*, 33, 1293–1300 (1909).

[3] *Gazz. chim. ital.*, 43, I, 570 (1913).

[4] *Am. J. Sci.*, [4] 37, 173 (1914).

quantitatively after iron has first been removed by use of ammonium sulfide in a solution containing ammonium tartrate. Thornton and Hayden[1] have used a similar method to separate iron, zirconium, and aluminum. It was proposed to combine these methods with the necessary changes and additions to analyze the minerals mentioned.

In order to test the accuracy of the proposed method, tests were first made with solutions containing known quantities of the elements found in the minerals. The procedure was as follows: Weighed amounts of standard solutions of zirconium, titanium, iron, manganese and aluminum, as the sulfates or chlorides were mixed. The mixtures were treated with ammonium hydroxide in faint excess, sulfuric acid (1 : 1) was then added in slight excess, then 25 cc. additional sulfuric acid (1:1) were added, and the solution was made up to 150 cc. The solution was then cooled by the use of ice-water; 100 cc. of 6% aqueous solution of the cupferron reagent were added slowly with constant stirring. This was a large excess. The liquid was filtered without delay, using a filter paper and mild suction. The precipitate was washed at least twenty times with hydrochloric acid (100 cc. of acid of sp. gr. 1.20, diluted to one liter). The filtrate and washings were saved for the determination of aluminum and manganese. The cupferron precipitate was washed five times with a dilute solution of ammonium hydroxide. The filter paper and precipitate were partly dried at 80°, placed in a weighed platinum crucible, heated gently at first until the paper and precipitate no longer gave off gases, then ignited with the full heat of a Méker burner. The ignition was continued for one-half hour after the carbon of the paper was removed. This time was usually sufficient to obtain a constant weight, though the ignition should, of course, be repeated until a constant weight is obtained. The ignited precipitate gives the oxides of ferric iron, zirconium and titanium.

The separation and determination of the iron, zirconium and titanium were accomplished as follows: The oxides obtained above were fused with potassium bisulfate and dissolved in dilute sulfuric acid. The iron was precipitated as the sulfide from this solution by the use of tartaric acid, hydrogen sulfide, and ammonium hydroxide in the usual way. The filtrate was treated for titanium and zirconium as in the following paragraph; the iron sulfide was dissolved in nitric acid, precipitated as ferric hydroxide, ignited and weighed as the oxide.

To determine the titanium and zirconium the filtrate from the iron precipitate was acidified with hydrochloric acid, evaporated almost to dryness, and treated in a Kjeldahl flask with sulfuric and nitric acids to remove all tartrate. The resulting liquid was diluted with water and treated for the titanium and zirconium determinations. For this purpose the author

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[1] *Am. J. Sci.*, [4] **38**, 137 (1914).

used under different conditions the colorimetric method of Weller,[1] and the volumetric potassium permanganate method of Pisani,[2] modified by Newton,[3] for titanium; the zirconium was determined as difference, or by the phosphate method of W. F. Hillebrand.[4] Which of these methods was used depended principally upon the amount of titanium present. When the larger amounts of titanium were present, Method A or B, as follows, was used; when the smaller amounts of titanium were present, Method C, as follows, was used:

Method A.—The titanium and zirconium were precipitated as the hydroxides by the use of ammonium hydroxide, filtered, ignited, and weighed as the oxides. These oxides were dissolved by the fusion with potassium bisulfate and treatment with dilute sulfuric acid. The titanium was determined by reduction and titration with an approximately 0.05 *N* potassium permanganate solution, following the directions of Newton.[5] The zirconium was taken as the difference. Results were recorded in analyses, numbers I to III, inclusive, of Table I.

Method B.—The oxides of zirconium and titanium were weighed together and dissolved as in Method A. The zirconium was precipitated as the phosphate and separated from titanium by the use of disodium phosphate and by hydrogen peroxide in a solution acid with sulfuric acid according to the direction of W. F. Hillebrand. As noted by Hillebrand the zirconium phosphate precipitate usually carries down some titanium with it. To complete the separation the fusion with sodium carbonate and subsequent treatment were used. When the dried filter paper and precipitate of phosphate were placed in the platinum crucible surrounded as nearly as possible with the sodium carbonate and then ignited, and the fusion took place without any deleterious effect of reduced phosphate on the platinum crucible. The melt was then dissolved by fusion with potassium pyrosulfate and treatment with dilute sulfuric acid. The zirconium was reprecipitated by the use of disodium phosphate and hydrogen peroxide as before and allowed to stand overnight. The liquid was then filtered and the precipitate washed. The zirconium phosphate thus freed from all titanium was fused with sodium carbonate, extracted with water, filtered, washed, fused with potassium bisulfate, dissolved in dilute sulfuric acid, precipitated with ammonium hydroxide, filtered, ignited, and weighed as the dioxide. The filtrate from the sodium carbonate fusion of the zirconium phosphate, when acidified with dilute H_2SO_4, then rendered faintly alkaline with ammonia and heated for some time on the water bath, gave in most cases a slight white flocculent precipitate. This seemed

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[1] *Ber.*, 15, 2593 (1882).

[2] *Compt. rend.*, 59, 298; *Chem. News*, 10, 218 (1864).

[3] *Am. J. Sci.*, [4] 25, 130 (1908).

[4] "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 422, p. 141.

[5] *Loc. cit.*

to be greater in amount than a faint precipitate given by a blank test made with the reagents used. The cause of this has not been ascertained. The literature states that zirconium hydroxide is slightly soluble in excess of sodium carbonate. Whether this holds true under the conditions above described the author cannot state at present. The precipitate may have been due to accidental causes. Since it was small in amount and the results obtained were quantitative, no further investigation was made in connection with this work, although the author plans to do so in the near future. If some of the zirconium goes into solution means should be found to determine it. The determination of the titanium in the filtrate from the zirconium phosphate is also under investigation. Another question which seems worthy of consideration is whether the zirconium phosphate or the residue obtained when it is fused with sodium carbonate may be weighed and taken for the zirconium content. The determination of zirconium would be appreciably shortened in either case. This point also is under investigation. Results are recorded in analyses, numbers IV to VI, inclusive, of Table I.

A comparison of the values of titanium and zirconium obtained by Methods A and B in Tables I and II show that the direct determinations, and determinations by loss of weight for titanium and zirconium, agree within desirable limits.

Method C.—The titanium was determined colorimetrically by the use of hydrogen peroxide, according to Weller's method. The same portion of solution was then used to determine the zirconium as in Method B, after the acidity had been reduced to about 1%.

Separation and Determination of Aluminum and Manganese.

The filtrate from the cupferron precipitate was evaporated to small volume, 100 to 200 cc. of concentrated nitric acid being added during the evaporation in portions of 50 cc. This destroys the larger amount of the excess cupferron and hydrochloric acid. The evaporation was continued to a small volume. The resulting liquid was treated by one of the two following methods, A or B:

Method A.—This method has been used when large amounts of manganese are present. The manganese was precipitated according to the well-known treatment with nitric acid and potassium chlorate, the residual cupferron being destroyed and all manganese precipitated if the treatment is continued sufficiently. The author has found from one to three treatments with potassium chlorate and nitric acid sufficient to precipitate all manganese. The combined filtrates from the oxides of manganese were used for the determinations of aluminum, this element being precipitated by ammonium hydroxide and weighed as the oxide in the usual way. The oxides of manganese were dissolved in sulfurous and hydrochloric acids. The excess of sulfur dioxide was removed by heating.

The manganese was then determined as the pyrophosphate according to the method of Gooch and Austin.[1]

Results of this method are recorded in analyses, numbers I to VI, inclusive, of Table I.

Method B.—When small amounts of manganese were present the following procedure was found quite satisfactory: The filtrate from the cupferron precipitate was evaporated to a small volume and treated with concentrated sulfuric and nitric acids in the usual way, to remove all cupferron. The liquid was then treated with ammonium chloride and ammonium hydroxide in excess. The precipitate was dissolved in HCl, and again treated with ammonium chloride and ammonium hydroxide in excess. Continued treatment in this way gives a precipitate of aluminum hydroxide, free from all manganese, the manganese being found in the combined filtrates. This is in accordance with a standard procedure. The aluminum is ignited and weighed as the oxide in the usual way.

The manganese was precipitated by the use of ammonium persulfate and ammonium hydroxide, ignited and weighed as Mn_3O_4, according to the standard method. Results by this method are given in analyses, numbers VII to X, inclusive, of Table I, the manganese being expressed as MnO_2.

TABLE I.

Analysis of Mixed Solutions of Known Contents.

Number of analysis.	Fe_2O_3 found, g.	Fe_2O_3 taken, g.	ZrO_2 found, g. by PO_4 method.	ZrO_2 found, g. by difference.	ZrO_2 taken, g.
I	0.0859	0.0856	....	0.1130	0.1128
II	0.0891	0.0893	....	0.1105	0.1102
III	0.1024	0.1025	....	0.2029	0.2028
IV	0.0699	0.0673	0.2123	....	0.2120
V	0.0472	0.0470	0.2219	....	0.2221
VI	0.0925	0.0927	0.2304	....	0.2306
VII	0.1128	0.1123	0.1108	....	0.1107
VIII	0.1011	0.1007	0.1750	....	0.1748
IX	0.1367	0.1362	0.1939	....	0.1941
X	0.1789	0.1787	0.2159	....	0.2160

	TiO_2 found, g. colorimetric method.	TiO_2 found, g. $KMnO_4$ method.	TiO_2 found, g. by difference.	TiO_2 taken, g.	Al_2O_3 found, g.	Al_2O_3 taken, g.	MnO_2 found, g.	MnO_2 taken, g.
I	....	0.0540	....	0.0542	0.1057	0.1054	0.1257	0.1254
II	....	0.0585	....	0.0582	0.1046	0.1048	0.1204	0.1208
III	....	0.0689	....	0.0692	0.1127	0.1129	0.1048	0.1049
IV	....	....	0.0628	0.0631	0.1248	0.1240	0.1182	0.1186
V	....	....	0.0545	0.0549	0.1046	0.1044	0.1232	0.1223
VI	....	....	0.0751	0.0749	0.1185	0.1180	0.1063	0.1065
VII	0.00534	....	....	0.00535	0.1042	0.1040	0.0053	0.0051
VIII	0.00505	....	....	0.00502	0.1133	0.1135	0.0058	0.0056
IX	0.0108	....	....	0.0106	0.1749	0.1748	0.0149	0.0152
X	0.0114	....	....	0.0113	0.1045	0.1043	0.0168	0.0166

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[1] *Am. J. Sci.*, [4] 6, 233 (1898).

The author has tried modifying the above procedure by precipitating the iron and manganese by ammonium sulfide in the presence of ammonium tartrate, separating the iron and manganese by the basic acetate method; and precipitating the zirconium and titanium by adding cupferron to the acidified filtrate from the sulfide precipitate. The aluminum is found in the filtrate from the cupferron precipitate. This method seems simpler in many ways than the above. The method seems promising and the author hopes to report favorably later, but has no conclusive data at present.

The Analysis of Zircon.

As stated above, the sample of this mineral analyzed contained only silicon, zirconium, titanium, iron and aluminum. The method of analysis was as follows: Approximately 0.5 g. of the mineral was taken. This was placed in a platinum crucible of 25 to 30 cc. capacity, 5 g. of anhydrous sodium carbonate added and thoroughly mixed with the mineral. The mixture was then heated, at first gently, then at the full heat of a number four Méker burner for twelve hours. No effort was made to determine the minimum time required for the complete fusion, although the author's experience indicated that a prolonged treatment was necessary. The melt was transferred to a platinum evaporating dish, treated with water and hydrochloric acid, evaporated, and dried at 120° in the usual way. The residue was treated with dilute HCl, and filtered. The filtrate was retreated twice to remove silica still in solution. The combined filtrates were treated for the determination of the bases, as in the second paragraph below. The combined insoluble residues of impure silica were ignited to constant weight with a few drops of sulfuric acid, then ignited with 2 cc. of 40% hydrofluoric acid and 1 cc. of concentrated sulfuric acid, the treatment being repeated to constant weight. The sulfuric acid is used to prevent volatilization of titanium and zirconium in accordance with the experience of previous experimenters. The weight of material volatilized is taken as the correct weight of silica. To this is added a small amount of silica recovered later from the aluminum precipitate.

After the volatilization with hydrofluoric and sulfuric acids, an insoluble residue was always found. This was dissolved by fusion with potassium bisulfate and treatment with dilute sulfuric acid, and added to the liquid for the determination of the bases as in the following paragraph:

The solution of the bases was treated as follows: It was evaporated almost to dryness to remove large excess of acid. Water was added with hydrochloric acid, if necessary to hold all the bases in solution. The solution was transferred to a small flask and ammonium hydroxide added in faint excess. Then hydrogen sulfide was introduced to saturation, followed by ammonia in faint excess. The precipitate was filtered off, washed thoroughly with dilute white ammonium sulfide, then dissolved in dilute HCl. The filtrate from the ammonium sulfide treatment was evaporated to a small volume. This resulted usually in the precipitation of small amounts of hydroxides of bases. The precipitate was filtered off, washed with ammonium sulfide and chloride solution and dissolved in hydrochloric acid, as with the first precipitate from the ammonium sulfide treatment. The two solutions in hydrochloric acid were united, and treated as in the following paragraph. In this way the platinum dissolved from the crucible and evaporating dish was left as the sulfide upon the filter paper and the bases were removed from the alkalies used in the treatment thus far. Thornton and Hayden[1] and others have noted the tendency of the cupferron precipitate to retain alkalies. This interference is avoided by the procedure here followed.

The solution of bases was treated with a few drops of concentrated nitric acid to oxidize the iron. Sulfur, if present, was filtered off, the solution evaporated almost to dryness with hydrochloric acid to remove nitric acid. The liquid was treated with ammonium hydroxide in faint excess, then with sulfuric acid (1 : 1), an excess of 25 cc. being added. The solution was made up to 150 cc., and the cupferron reagent added as in the treatment of the known solutions above. The cupferron precipitate was treated as there described for the determination of iron, titanium and zirconium, Methods A and B being used for the last two elements after the removal of the tartrate. The filtrate was treated as in the following paragraph for aluminum:

The filtrate from the cupferron precipitate was evaporated almost to dryness. If considerable amounts of ammonium salts were present these were removed by evaporating with aqua regia. From the evaporated liquid, any cupferron still present was removed by heating with concentrated sulfuric and nitric acids in the usual way. The aluminum was then precipitated by use of ammonium hydroxide and weighed as the oxide.

This aluminum oxide was then treated according to the directions of W. F. Hillebrand[2] to determine small amounts of silica which are always, or usually, present (in most cases from 2 to 4 mg.). The aluminum oxide and silica contents of the minerals are corrected in accordance with the silica here found.

TABLE II.—ANALYSIS OF ZIRCON.

Weight of sample taken, g.	SiO_2 found, %.	Fe_2O_3 found, %.	ZrO_2 found, % by difference.	ZrO_2 found, % PO_4 method.	TiO_2 found, % MnO_4 method.	TiO_2 found, % by difference.	Al_2O_3 found, %.	Total found, %.
0.5000	27.84	1.99	...	54.16	...	10.59	5.44	100.02
0.5002	27.49	2.15	...	54.33	...	10.46	5.23	99.66
0.5005	27.56	2.07	...	54.23	...	10.38	5.35	99.59
0.5009	27.36	2.10	54.41	...	10.41	...	5.44	99.72
0.5009	27.45	2.05	54.26	...	10.50	...	5.61	99.87
0.5006	27.32	2.09	54.29	...	10.41	...	5.72	99.83

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[1] *Loc. cit.*

[2] "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* **422**, pp. 105–107.

Table II gives the results obtained with the sample of zircon used. The percentages of the different elements agree closely, and total close to 100 in all cases.

Analysis of Baddeleyite.

As noted above, the sample of this mineral analyzed contained silicon, zirconium, titanium, iron, manganese, aluminum and water. The treatment was the same as with zircon with the following changes: To remove the bases from the platinum and alkalies, the solution was treated with ammonia and hydrogen sulfide in a flask as described above. The flask was filled to the neck with water and allowed to stand 24 hours or more. The precipitate was then filtered off, washed thoroughly with a solution containing colorless ammonium sulfide and ammonium chloride. The precipitate was dissolved from the paper by the use of dilute hydrochloric acid, saturated with hydrogen sulfide.[1] The solution is heated to remove hydrogen sulfide, a few drops of concentrated nitric acid added to oxidize iron, sulfur filtered off, if present, the liquid evaporated to a small volume to remove excess nitric acid, and treated with ammonium hydroxide, sulfuric acid, and cupferron reagent as with the solutions of known content above. The cupferron precipitate is treated for iron, zirconium, and titanium as in the following paragraph. The filtrate from the cupferron precipitate is treated with aluminum and manganese as in the second paragraph below.

Determination of Iron, Titanium and Zirconium in Baddeleyite.—The cupferron precipitate ignited to give oxides of iron, zirconium and titanium is treated as above to dissolve it, and to separate and determine the iron. The filtrate from the iron sulfide precipitate is treated for titanium and zirconium by Method C above after removal of the tartrate as directed with the solutions of known content.

Determination of Manganese and Aluminum in Baddeleyite.—The filtrate from the "cupferron" precipitate is evaporated with the addition of 100 to 200 cc. of concentrated nitric acid, added 50 cc. at a time. The determination of manganese and aluminum is then made as in Method B above for the known solutions. The aluminum oxide is corrected for the silica contained as in the analysis of zircon.

Determination of Water in Baddeleyite.—This mineral contained small amounts of water which were readily expelled. The determinations were made by ignition with a Méker burner of the mineral in a Penfield tube. Portions of the mineral weighing about 0.5 g., not used for the rest of the analysis, were taken. The mean of six different determinations was regarded as the correct value. The different determinations agreed within 0.3%.

The results obtained with baddeleyite are given in Table III, following.

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[1] See Hillebrand, "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 422, p. 115.

TABLE III.—ANALYSIS OF BADDELEYITE.

Weight of sample. g.	SiO_2 found, %.	Fe_2O_3 found. %.	ZrO_2 found, % PO_4 method.	TiO_2 found. % calorimetrically.	Al_2O_3 found, %.	MnO_2 found, %.	H_2O found, % (average).	Total found. %.
0.5016	15.83	2.31	71.46	0.78	5.24	0.98	2.94	99.54
0.5017	15.73	2.55	71.15	0.76	5.56	0.92	2.94	99.61
0.5006	15.46	2.66	71.23	0.75	5.82	1.12	2.94	99.98
0.5006	15.72	2.44	71.35	0.75	5.46	0.75	2.94	99.41

Summary.

The above results show that the cupferron reagent may be used in acid solution for the quantitative precipitation of iron, titanium, and zirconium from solutions containing these elements mixed with aluminum and manganese. The first three of these elements may be separated by standard methods, as by the procedures outlined above. The aluminum and manganese may be determined by standard methods after the removal of the excess cupferron.

Analyses were made both of mixed solutions of pure salts and of minerals, with accurate results.

Recognition is due R. B. Moore, of the United States Bureau of Mines, for suggesting the analysis of zirconium minerals as an inviting field for investigation.

INDIANAPOLIS, IND.

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

THE COLORIMETRIC DETERMINATION OF MANGANESE BY OXIDATION WITH PERIODATE.[1]

BY HOBART H. WILLARD AND LUCIEN H. GREATHOUSE.

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Historical.

The determination of manganese by comparing the color intensities of solutions of the permanganate ion has been a practical method for the rapid estimation of small amounts for about forty-five years. W. Crum[2] first suggested the possibility of using in this way the oxidation of manganous salts to permanganate by means of lead dioxide in nitric acid solution, but P. Pichard[3] was the first to work out the details for a complete method. A number of communications appearing in the thirty years following Pichard's work, proposed or discussed methods which utilized the same principles. Reactions involving other colored compounds of manganese have been proposed (references 4, 8, 13, 14, 15 in the bibliography) but have never found much favor.

[1] Read at the meeting of the American Chemical Society in Cincinnati, April, 1914.

[2] *Ann.*, 55, 219 (1845).

[3] *Compt. rend.*, 75, 1821 (1872).