and was of such a truly quantitative character that it was thought that the atomic weight of phosphorus might readily be determined in this way. This investigation is now in progress. It will give the ratio of P : NaF. As sodium fluoride is readily converted into sodium chloride the ratio of P : NaCl is the one that is being determined. Incidentally, this will also give the ratio of F : Cl.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ACTION OF SALICYLIC ACID UPON THE METALLIC ACIDS.[1]

BY JOHN HUGHES MULLER.

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On exposing the hydrates of columbium, tantalum and titanium to the action of a number of organic acids salicylic acid alone showed a marked difference in its behavior with them. An excess of salicylic acid was slowly added to a solution of sodium columbate and a precipitate, gelatinous in form and orange-yellow in color resulted. Continued digestion of this precipitate at boiling temperature caused it to become bright yellow in color and to lose much of its gelatinous form. After washing with water containing some salicylic acid to prevent hydrolysis, the precipitate was dried and the percentage of columbium present determined by the ignition of weighed quantities, thus converting them to columbic oxide. The precipitation of the columbium was complete.

On precipitating an alkaline tantalate solution with salicylic acid the precipitate, while gelatinous, was colorless. This reaction was also quantitative.

Warm solutions of ammonium hydroxide and potassium hydroxide decompose these salicylates of columbium and tantalum. They are insoluble in ether, methyl alcohol, ethyl acetate, chloroform, carbon tetrachloride, carbon bisulfide, and petroleum ether.

The presence of an alkali fluoride prevents the precipitation of columbium or tantalum by salicylic acid. Orthotitanic acid dissolves in salicylic acid in the presence of fluorides to an almost colorless solution and in their absence to an intensely yellow colored salicylate. Zirconium and thorium hydroxides are difficultly soluble in aqueous salicylic acid while after ignition the corresponding oxides are practically insoluble.

Known amounts of each of the oxides of columbium, tantalum, zirconium and thorium were mixed with weighed amounts of titanic oxide and these mixtures then fused with 5 grams of potassium carbonate, the fusions being taken up in from 350–400 cc. of water at 60° and treated with 14–15 grams of salicylic acid, the solution being heated for three to

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[1] From the author's Ph.D. thesis.

four hours at the boiling temperature. The precipitates were allowed to settle, filtered rapidly and washed with boiling water. The concentrated filtrates were treated with ammonium hydroxide, when the titanium was precipitated, washed and ignited to oxide. These precipitates were invariably contaminated with alkali salicylates which could not be removed by washing. They were therefore fused with potassium bisulfate and the corresponding oxides obtained in the usual manner.

Titanic Oxide and Columbic Oxide.

Cb_2O_5 taken.	Cb_2O_5 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.3042	0.3047	0.2989	0.2989	3
0.3080	0.3075	0.3204	0.3204	3
0.3489	0.3486	0.0200	0.0187	2
0.3040	0.3046	0.0530	0.0530	3
0.3001	0.3005	0.0020	0.0019	2
0.2980	0.2981	0.0011	0.0012	1
0.3022	0.3025	0.0063	0.0060	2
0.4000	0.4000	0.0006	0.0006	1

Titanic Oxide and Tantalic Oxide.

Ta_2O_5 taken.	Ta_2O_5 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.3050	0.3054	0.4010	0.4015	4
0.3019	0.3021	0.1020	0.1021	3
0.5020	0.5021	0.0006	0.0006	1
0.3046	0.3051	0.0515	0.0512	2
0.5020	..	0.0153	0.0155	2
0.5040	0.5048	0.0005	0.0005	1

Titanic Oxide and Thorium Oxide.

ThO_2 taken.	ThO_2 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.4998	0.4997	0.1030	0.1035	2
0.0590	0.0595	0.3027	0.3026	3
0.9658	0.9658	0.0020	0.0019	1
0.7377	0.7380	0.0027	0.0025	1
0.9658	0.9659	0.0005	0.0006	1
0.7380	0.7380	0.0009	0.0010	1

Titanic Oxide and Zirconium Oxide.

ZrO_2 taken.	ZrO_2 found.	TiO_2 taken.	TiO_2 found.	Number of fusions.
0.3035	0.3024	0.3016	0.3030	2
0.0996	0.0990	0.5000	0.4991	3
0.0726	0.0715	0.5719	0.5730	3
0.4481	0.4472	0.0047	0.0050	2

The intense color produced by the addition of salicylic acid to alkaline titanates suggested a colorimetric determination of this metal, while the characteristic nature of the reaction pointed to its possible estimation in the presence of oxides, none of which produce a marked coloration with the same acid.

A 0.5000 gram portion of titanic oxide was fused with 5 grams of potassium carbonate, the melt taken up in warm water and treated with an excess of salicylic acid. Refusion of the small residue and repetition of the process brought all the oxide into solution. The combined solutions were diluted to exactly 500 cc. at 20–23°. 100 cc. of this intensely colored solution were removed and diluted to 1 liter, which latter volume then contained 0.1 gram of titanium dioxide and still exhibited an intense yellow color inclining to orange. A set of standards was prepared by dilution of known volumes of this stock solution, carrying out the dilution as far as practicable, noting the intensity and permanence of the color reaction as compared to the quantity of oxide present.

Grams of TiO_2 per 100 cc....	0.1	0.01	0.005	0.0025	0.0010	0.0005	0.00025	...	0.0001	0.00005
Color of solution.	Orange-red	Orange	Deep yellow	Bright yellow	Yellow	Light yellow	Sulfur-yellow	...	Pale yellow	Faint yellow

The solutions were kept in 100 cc. Nessler tubes (2 cm. in diameter). The last two faded considerably on standing for several days, but the addition of a little aqueous salicylic acid was found to render the more dilute solutions just as permanent in color as those of greater concentration. Standing for one month with no special precautions, other than exclusion of dust, caused no appreciable change in color intensity. Blanks, containing sodium salicylate and salicylic acid which had been boiled for several hours, were compared with the highest dilution, *i. e.*, 0.00005 gram TiO_2 per 100 cc. A distinct difference was still observable. Two other sets of standards were now made, using double the amount of alkaline flux in one case, and double the excess of salicylic acid in the other. No difference in color intensity could be found, the three sets being exactly similar in appearance. Very small amounts of hydrofluoric acid or fluorides interfered with the delicacy of the reaction. Appreciable quantities absolutely destroyed the yellow color. Traces of iron interfered, producing the familiar purple color used in the detection of this acid and other phenolic compounds. The presence of zirconium gave a brownish cast to the solutions, sufficiently deep to make a determination of titanium in the presence of this oxide quite impossible. Columbic oxide interfered. Tantalic oxide did not seriously affect the results, although tending to give high results for titanium.

Alkaline molybdates gave a yellow color closely resembling that caused by a titanate. The oxides of thorium, tantalum, lanthanum, cerium and yttrium did not cause the slightest interference in the colorimetric determination. Small quantities of neodymium, praseodymium, and a mixture of erbium and terbium oxides did not give a color with salicylic acid; larger amounts developed colors that obscured the yellow.

Experiments with small quantities of columbic oxide (0.002–0.002) gave colorless filtrates, after precipitating in the usual way with salicylic acid. This is additional evidence that dissolved columbic oxide was not the cause of the brownish color imparted to the filtrates from the columbium determinations. The author cannot repress the conviction that an unknown substance, only noticeable in large amounts of the columbic oxide, was the cause of the brownish color. In the following tables titanium was determined colorimetrically, while the columbic and tantalic oxides were estimated by difference.

TITANIC OXIDE AND COLUMBIC OXIDE.

Cb_2O_5 taken.	TiO_2 taken.	Cb_2O_5 found.	TiO_2 found.	Number of fusions.
0.3025	0.1000	0.3045	0.0980	3
0.3110	0.0105	0.3102	0.0113	2
0.5032	0.0010	0.5028	0.0019	1
0.0101	0.0500	0.0091	0.0510	2
0.0050	0.0005	0.0048	0.0007	1

TITANIC OXIDE AND TANTALIC OXIDE.

Ta_2O_5 taken.	TiO_2 taken.	Ta_2O_5 found.	TiO_2 found.	Number of fusions.
0.3105	0.0205	0.3103	0.0207	2
0.4439	0.0020	0.4441	0.0018	1
0.5050	0.0005	0.5049	0.0006	1
0.3000	0.0005	0.3000	0.0005	1
0.0502	0.0010	0.0499	0.0011	1

TITANIC OXIDE AND THORIUM OXIDE.

ThO_2 taken.	TiO_2 taken.	ThO_2 found.	TiO_2 found.	Number of fusions.
1.0020	0.0500	1.0010	0.0510	3
0.5001	0.0206	0.5002	0.0205	2
0.8763	0.0010	0.8759	0.0014	1
1.0002	0.0008	0.9999	0.0011	1

The results for titanium in the presence of columbium are high. To correct these errors the solutions were heated to boiling, and the color due to titanium discharged by the addition of ammonia, again comparing the residual color with the standards. The brownish solutions were, however, not comparable with the pure yellow of the standards, and in consequence the colorimetric estimation of titanium in this mixture had to be given up.

On the other hand, tantalic oxide did not interfere, enabling a very rapid determination of small quantities of titanic oxide without the necessity of the ammonium hydroxide precipitation.

The results with thorium were high, probably because of the large amounts of thorium or traces of impurity in the oxide.

This colorimetric method is evidently of little practical value, owing to the interference of the common contaminants of titanic oxide. It may, however, be conveniently used for the very accurate determination of nearly pure titanic oxide, and especially for the detection of this oxide in the acid earths. As a test for titanium in the absence of molybdenum and iron, the delicacy of the reaction considerably exceeds any reaction for this metal with which the writer is acquainted. As little as 0.00005 gram of titanic oxide in 100 cc. shows a pale yellow, while 0.0001 gram in the same volume produces a very marked and permanent sulfur-yellow color. In the presence of large quantities of columbium or zirconium the brownish yellow color produced might be mistaken for the yellow of titanium, but this yellow color of titanium solutions is immediately discharged by ammonia, while the brownish yellow color due to columbium or zirconium is permanent in alkaline solution, and only appreciable when a large quantity of the last-mentioned metals are present.

Ten grams of sodium tungstate dissolved in 200 cc. of water gave no precipitate with salicylic acid. Ten grams of sodium molybdate, containing 66.66 per cent. MoO_3, were treated in the same manner as the tungstate. The behavior was almost the same as that of the tungstate. The solution, however, was deep yellow, while a lighter colored very similar amorphous substance separated when the solution was concentrated to a small volume (25–30 cc.).

The tungsten and molybdenum solutions failed to give a precipitate with ammonium hydroxide while the alkaline solutions remained colorless. The above reactions seemed to indicate a possible separation of these two metals from titanium by precipitation of the salicylic acid solution with ammonium hydroxide. Likewise the solubility of the molybdate and tungstate in salicylic acid suggested the removal of columbic and tantalic oxides from molybdenum and tungsten.

Molybdic oxide in large quantity completely prevented the precipitation of columbium by salicylic acid. The attempt to separate titanium from both tungsten and molybdenum, by this method, gave incomplete precipitation and turbid filtrates, which could not be cleared by a second or third filtration.

The separation of tungsten and columbium was more satisfactory, giving values not far from quantitative, requiring for success, however, a relatively small amount of tungsten.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

AN EMPIRICAL RELATION BETWEEN THE CONFIGURATION AND ROTATION OF SUGARS.

BY ERNEST ANDERSON.

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It has long been known that some sugars rotate polarized light very