The acid produced in this way will absorb a small amount of moisture if exposed to the air.

The mother liquors, which are occasionally dark colored, may be readily clarified by heating with norite for a few minutes and filtering off the suspended matter.

The writer wishes to take this opportunity of thanking Dr. George D. Beal for suggesting this problem, and of expressing his regret that circumstances forced the latter's withdrawal from active participation in the work at such an early date.

Summary

1. The comparative value of different reagents for the formation of a complex with silicotungstic acid has been established and the probability that the compound formed is an oxonium salt has been indirectly confirmed.

2. Salzberg's conclusion with regard to the purity of the acid when prepared according to North's directions has been verified.

3. The truth of the assumption that the acid is decomposed by twenty-four molecules of base has been established experimentally.

4. The methods of analysis have been improved.

5. A new method of isolating the acid, depending on the formation of a complex with ethyl acetate, and a new method of dehydrating it have been proposed.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. III. INFLUENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM UPON THE DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE[1]

BY RUFUS D. REED AND JAMES R. WITHROW

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We have shown the availability of zirconium sulfate as a reagent for potassium in the presence of sodium[2] and ammonium.[3] The less frequently occurring members of the fifth group, rubidium and cesium, both interfere with the detection of potassium by sodium cobaltic nitrite, perchloric acid or chloroplatinic acid. Lithium can be separated from ions of these elements by perchloric acid or chloroplatinic acid. Tread-

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[1] The authors are indebted to the Chemical Department of this University in that Professor Marion Hollingsworth of the Analytical Chemical Division of that Department furnished the rubidium and cesium chlorides used as the basis of part of this work.

[2] Reed and Withrow, THIS JOURNAL, 50, 1519 (1928).

[3] Reed and Withrow, *ibid.*, 50, 2985 (1928).

well-Hall states concerning sodium cobaltic nitrite and lithium,[4] "moderate amounts of alkaline earth elements or of lithium and sodium do not interfere." Concerning magnesium Prescott and Johnson[5] stated, "potassium and large amounts of sodium may be readily detected in the presence of magnesium." Yet because of interference with the detection of small amounts of sodium, magnesium is removed prior to testing for the fifth group, to determine whether these fifth group elements would interfere with the detection of potassium by zirconium sulfate. The sensitiveness of this reagent for potassium in the presence of lithium, rubidium, cesium and magnesium was therefore investigated.

The results indicated that in a 2-cc mixture, zirconium sulfate detected 1.0 mg. or more potassium in the presence of 50 mg. of lithium sulfate, 16.6 mg. of rubidium sulfate or 11.6 mg. of cesium sulfate. It also detected 0.5 mg. or more of potassium in the presence of 50 mg. of magnesium sulfate. With no possibly interfering ions present, the zirconium sulfate reagent detected 0.5 mg. or more potassium.

The literature indicated that while Rosenheim and Frank[6] had prepared, "by the use of rubidium and cesium sulfates, compounds analogous in external appearance and in composition" to potassium zirconyl sulfate, no one had ascertained whether the presence of lithium, rubidium, cesium or magnesium would interfere with the reaction between potassium sulfate and zirconium sulfate, though the reference indicated the probability that they would interfere.

Experimental

In order to determine the effect of lithium, rubidium, cesium and magnesium upon the detection of potassium by zirconium sulfate, the following solutions were prepared.

Potassium Sulfate Solution and Zirconium Sulfate Solution.—These solutions were prepared in exactly the same way as described in the work on effect of ammonium ion on detection of potassium by zirconium sulfate.[2] The zirconium sulfate solution analyzed for 0.0871 g. of zirconium sulfate and an excess of 0.0395 g. of sulfate ion, due to excess sulfuric acid, per cubic centimeter.

Lithium Sulfate, Rubidium Sulfate, Cesium Sulfate and Magnesium Sulfate Solutions.—These solutions were prepared by dissolving potassium-free anhydrous salts in water and diluting to known volume.

Procedure.—Solutions containing known amounts of potassium and of either lithium, rubidium, cesium or magnesium sulfate were prepared by mixing known volumes of the proper solutions. The procedure of the test was the same as given in the preceding work.[2] The results appear in the table.

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[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1920, Vol. I, p. 85.

[5] Prescott and Johnson, "Qualitative Chemical Analysis," revised by J. C. Olsen, D. Van Nostrand Co., New York, 1918, p. 242.

[6] Rosenheim and Frank, *Ber.*, 38, 812–817 (1905).

TABLE I

SENSITIVITY OF ZIRCONIUM SULFATE FOR POTASSIUM IN THE PRESENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM

Total volume 2 cc. $Zr(SO_4)_2$ per test, 0.0871 g.

Expt.	K, g.	Sulfate	G.	Results and time for precipitation
1	0.0000	Li_2SO_4	0.0550	Cloudy, 3.5 hours; same in 5 hours at 0°
2	.0010	Li_2SO_4	.0500	Sl. cloudy, 1.5 hours; more cloudy than No. 1 in 5 hours at 0°
3	.0045	Li_2SO_4	.0500	Cloudy, 1.5 hours; more cloudy than No. 2 in 5 hours at 0°
4	.0082	Li_2SO_4	.0458	Sl. ppt., 1 hour; considerable ppt. in 2.5 hours at 0°
5	.0000	Rb_2SO_4	.0199	Cloudy, 5 hours at 0°
6	.0009	Rb_2SO_4	.0166	More cloudy than blank, No. 5, in 4.5 hours at 0°
7	.0018	Rb_2SO_4	.0166	Cloudy, 1.5 hours; ppt., 3.5 hours at 0°
8	.0031	Rb_2SO_4	.0142	Cloudy, 1 hour; ppt., 3 hours at 0°
9	.0066	Rb_2SO_4	.0166	Ppt., 0.5 hour at 0°
10	.0132	Rb_2SO_4	.0142	Cloudy, 0.5 hour at room temp.; sl. ppt., 1 hour, room temp.
11	.0000	Cs_2SO_4	.0127	Cloudy, 5 hours at 0°
12	.0005	Cs_2SO_4	.0116	No difference from blank No. 11, 5 hours at 0°
13	.0010	Cs_2SO_4	.0116	More cloudy than blank No. 5, 4.5 hours at 0°
14	.0045	Cs_2SO_4	.0116	Ppt., 1.5 hours at 0°
15	.0082	Cs_2SO_4	.0116	Opalescent, 1 hour at room temp., ppt., 0.5 hour at 0°
16	.0000	$MgSO_4$	.0550	Cloudy, 5 hours at 0°
17	.0005	$MgSO_4$	.0500	More cloudy than No. 16, 5 hours at 0°
18	.0010	$MgSO_4$	.0500	More cloudy than No. 16, 5 hours at 0°
19	.0045	$MgSO_4$	.0500	Cloudy and sl. ppt., 3.5 hours at 0°
20	.0082	$MgSO_4$	.0458	Cloudy, 1 hour; ppt., 2 hours at 0°

Discussion

The results indicate that zirconium sulfate will detect 1.0 mg. or more potassium in the presence of 50 mg. of lithium sulfate (Expts. 1–4), 16.6 mg. of rubidium sulfate (Expts. 6–10) or of 11.6 mg. of cesium sulfate (Expts. 11–15). It did not detect 0.5 mg. of potassium in the presence of 11.6 mg. of cesium sulfate (Expt. 12). It detected 0.5 mg. or more potassium in the presence of 50 mg. of magnesium sulfate (Expts. 16–20). To detect 1 mg. of potassium in the presence of any members of the fifth group, a comparison with a blank run should be made concurrently. With lithium or magnesium present, comparison with a blank should be made in testing for 4.5 mg. or less potassium (Expts. 3 and 19).

Comparison of Reagents for Potassium.—In order to compare zirconium sulfate, sodium cobaltic nitrite, chloroplatinic acid and perchloric acid as reagents for the fifth group elements, a series of tests was made as tests are usually made in qualitative analysis—adding the reagent to the solutions to be tested. None of the four reagents gave a precipitate with 11% sodium acetate, 5.5% magnesium sulfate or 5.5% lithium sulfate. Sodium cobaltic nitrite solution gave a slight precipitate with a saturated lithium sulfate solution. Sodium cobaltic nitrite and chloroplatinic acid gave precipitates with 11% ammonium chloride, 1.92% rubidium sulfate and 1.16% cesium sulfate solutions as well as with 8.8% potassium sulfate solution. Perchloric acid gave a precipitate with the same solutions except the 1.16% cesium sulfate solution, but when a more concentrated cesium sulfate solution was prepared, it gave an immediate precipitate. *Zirconium sulfate gave a precipitate with the 8.8% potassium sulfate solution only.*

Reagents for the detection of potassium, other than zirconium sulfate, cannot be used in the presence of all members of the fifth group of metals. Sodium cobaltic nitrite, perchloric acid and chloroplatinic acid give a precipitate with rubidium and cesium as well as with potassium and ammonium. The perchloric acid method requires the use of absolute alcohol and the chloroplatinic acid requires the use of 80% alcohol to separate potassium from sodium and lithium.

Summary

Zirconium sulfate will detect 1.0 mg. or more of potassium in 2 cc. of reaction mixture in the presence of lithium, rubidium, cesium or magnesium ions, as well as those of sodium and ammonium. The detection of potassium by zirconium sulfate is accomplished without the use of alcohol or complicated procedure. It should always be used as the preliminary reagent, therefore, in looking for potassium, before going through the ordinary more complicated procedure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

A STUDY OF THE DETERMINATION OF CHLORIDE IN BROMIDES

BY R. K. MCALPINE

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In 1926 Berg[1] introduced an interesting modification of the usual procedure for determining chloride in the presence of bromide by using acetone in aqueous solution to absorb the bromine set free in a differential oxidation process that employed potassium bromate in dilute sulfuric acid solution. The following equation shows the reaction involved:

$$6CH_3COCH_3 + 2KBrO_3 + 4KBr + 3H_2SO_4 = 6CH_3COCH_2Br + 3K_2SO_4 + 6H_2O$$

The chloride was then titrated by a modification of the Volhard method. The experimental data in Berg's article showed that the procedure recommended worked within moderate limits and it was suggested that the nephelometer could be used to determine very small amounts of chloride.

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[1] Berg, *Z. anal. Chem.*, **64**, 342 (1926).