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ZIRCONIUM SULFATE AS A REAGENT FOR THE DETECTION OF POTASSIUM[1]

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Work under way in this Laboratory indicated the possibility of using zirconium sulfate as an alternative test for the detection of potassium. Potassium sulfate has long been known as a reagent for the precipitation of zirconium.[2] No one appears to have taken the trouble to find how sensitive zirconium sulfate itself would be in the detection of potassium. Therefore the sensitiveness of a zirconium sulfate solution for potassium was investigated.

Experimental

To investigate the sensitiveness of zirconium sulfate solution as a qualitative test for potassium it was necessary to prepare the following reagents and to determine their purity.

Zirconium Sulfate Solution.—This solution was prepared by stirring powdered zirconium sulfate with distilled water for four hours. The solution was allowed to stand overnight at room temperature. It was filtered and analyzed to determine purity to preclude interfering substances. It contained no cerium earth metals, cobalt or tartrate. Quantitative analysis for zirconium by the Lundell and Knowles method[3] showed 0.2096 g. of zirconium sulfate per cc. of solution. This solution was prepared at 28°. It would deposit crystals on standing overnight but these could be dissolved by warming the bottle of solution in hot water for a few minutes.

Potassium Sulfate Solution.—A saturated potassium sulfate solution containing 0.0545 g. of elemental potassium per cc. was prepared. To preclude possible interfering substances, this solution was analyzed qualitatively and found free from hydroxyl, carbonate, sulfide, thiosulfate, phosphate, sodium and ammonium ions. Dilution of portions of this stock solution gave the more dilute solutions used.

Sodium Sulfate Solution.—To determine the effect of the sodium ion on the detection of potassium by zirconium sulfate, a saturated solution of potassium free sodium

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[1] Read before Detroit meeting, September, 1927.

[2] Fresenius, "Qualitative Chemical Analysis," C. A. Mitchell's translation of 17th edition, John Wiley and Sons, Inc., New York, **1921**, p. 182; Venable, "Zirconium and Its Compounds," Chemical Catalog Co., New York, **1922**, pp. 81–84.

[3] Lundell and Knowles, This Journal, **41**, 1801 (1919).

sulfate was prepared. Mixing of this solution with the potassium sulfate solution gave the mixtures of sodium and potassium sulfates used.

Sodium Cobaltic Nitrite Solution.—For comparison of sensitiveness of sodium cobaltic nitrite and zirconium sulfate for the detection of potassium, a solution of sodium cobaltic nitrite was prepared according to the method of Scott.[4]

General Procedure for Potassium Detection.—In all the series of experiments in which potassium was tested for by zirconium sulfate, exactly 1cc. portions of potassium sulfate solutions of varying concentrations were pipetted into dry test-tubes. Exactly 1cc. portions of zirconium sulfate solution were added. The mixtures after shaking were allowed to stand at room temperature for one hour. Then the tubes were immersed in ice water until a reaction was noticed. At the start of the run, the walls of the tubes were well rubbed with a glass rod to promote

TABLE I

SENSITIVENESS OF ZIRCONIUM SULFATE SOLUTION AS A TEST FOR POTASSIUM

Total volume, 2 cc. Zirconium sulfate, 0.2096 g. per test

Expt.	K, g. per sample	Results at room temperature	Results on cooling to 0°C.
1	0.05455	Precipitate at once	...
2	.02728	Precipitate at once	...
3	.01818	Cloudy at once	...
4	.01362	Precipitate in one-half hour	...
		Precipitate in one-half hour	
5	.00909	Slight precipitate in one-half hour	...
6	.00495	Cloudy in one hour	More cloudy in one-half hour, precipitate in one hour
7	.00260	None one hour	Cloudy in one-half hour, precipitate in one hour
8	.00176	None one hour	Cloudy in one hour, precipitate in one and one-half hours
9	.00107	None one hour	Cloudy one and one-half hours, precipitate in 2 hours
10	.00072	None one hour	Slightly cloudy in one and one-half hours, more so in two hours, precipitate in 2 and one-half hours
11	.00053	None one hour	Slightly cloudy in one and one-half hours, more so in 2 hours, precipitate in two and one-half hours
12	.00030	None one hour	Slight precipitate in one hour
13	.00007	None one hour	Slightly cloudy in two hours
14	.00000	None one hour	Slightly cloudy in two hours, precipitate in two and one-half hours
15	.00000	None one hour	Clear in two and one-half hours
16	.00000	None one hour	Slight precipitate in four hours

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[4] Scott, "Qualitative Chemical Analysis," 4th edition, 2d printing, D. Van Nostrand Co., New York City, **1923**, p. 330.

crystallization. This rubbing was repeated at half-hour intervals throughout the run.

Sensitiveness of Zirconium Sulfate Solution as a Test for Potassium.—To determine the sensitiveness of zirconium sulfate for potassium when no possible interfering ions were present, a series of experiments was made, varying the amount of potassium and keeping all other factors constant. The results are given in Table I.

Discussion.—On cooling in ice water the deposit formed in Expt. 11 containing 0.00053 g. of potassium (0.0068 molal potassium sulfate or 0.05% elemental potassium) was slightly more than in Expt. 14 containing no potassium. The deposit in Expt. 12 containing 0.3 mg. of potassium although formed after one hour's cooling did not increase in magnitude on standing. This deposit and the deposit in Expt. 13 containing 0.07 mg. of potassium were of about the same magnitude as the deposit in the blank Expt. 14. The formation of deposits in the two blanks, Expts. 14 and 16, emphasized the need of running concurrently a blank in tests for traces of potassium with zirconium sulfate.

The appearance of the precipitate varied. If it came at once on adding the reagent or after rubbing the walls of the tube with a stirring rod, it appeared to be amorphous. If it formed slowly with no agitation, it was needle shaped and collected in fan-like bundles.

An idea of the amount of potassium present in a solution could be gained from the time required for the appearance of a deposit. If 18.2 mg. of potassium was present in 2 cc. of mixture, a deposit or cloudiness was formed at once. Those solutions containing less than 18.2 mg. of potassium and more than 4.95 mg. of potassium gave a precipitate or cloudiness within an hour at room temperature. Those solutions containing 0.5 mg. to 2.6 mg. of potassium per cubic centimeter gave a precipitate only after cooling in ice water for from one to two and one-half hours depending upon the amount of potassium present.

Comparison of Sensitiveness of Zirconium Sulfate Solution for Potassium with that of Sodium Cobaltic Nitrite Test for Potassium.—To compare the sensitiveness of these two reagents, a series of tests for potassium with sodium cobaltic nitrite was made. The method of testing with sodium cobaltic nitrite was that of Scott.[5] A comparison with a blank was made where there was any doubt as to turbidity or deposit. The results appear in Table II.

Discussion.—Consideration of the time factor showed that: (1) both sodium cobaltic nitrite and zirconium sulfate gave immediate tests for potassium when 18.18 mg. of potassium was present. (2) With lower concentrations of potassium, the sodium cobaltic nitrite solution is a quicker test for potassium than zirconium sulfate solution. The presence

[5] Ref. 4, p. 151.

TABLE II

COMPARISON OF SENSITIVENESS OF SODIUM COBALTIC NITRITE TEST AND OF ZIRCONIUM SULFATE TEST FOR POTASSIUM

Total volume, 2 cc.

Expt.	K, g. per sample	Time for reaction with sodium cobaltic nitrite	Time for reaction with zirconium sulfate. Cooling to 0°C.
1	0.01818	Immediate precipitate	Immediate cloudiness at room temperature. No cooling
2	.00107	Slight precipitate in five minutes	Cloudy in one and one-half hours, cooling; precipitate in two hours, cooling
3	.00072	Slight precipitate in five minutes	Cloudy in two hours, cooling; precipitate in two and one-half hours
4	.00053	Slightly turbid in five minutes, slight precipitate in ten minutes	Precipitate in two hours, cooling
5	.00030	Slightly turbid in fifteen minutes, slight precipitate in one hour	Slight precipitate in one hour, no increase on standing. Same bulk of precipitate as blank at end
6	.00014	Slightly turbid in one hour, slight precipitate in two and one-half hours	No more test than blank
7	.00010	Very slight precipitate in five hours	No experiment run
8	.00007	Slight precipitate in twenty-three hours	No more test than blank
9	.00005	Clear, twenty-three hours	No experiment run
10	.00000	Clear, twenty-three hours	Slightly cloudy in two hours, precipitate in two and one-half hours

of 0.53 mg. to 0.3 mg. of potassium can be detected with sodium cobaltic nitrite within five to fifteen minutes, while it required one hour at room temperature and two hours' cooling to 0° to detect 0.5 mg. of potassium with zirconium sulfate solution.

As the sodium cobaltic nitrite test is usually applied according to directions of Scott[5] the absence of a precipitate with sodium cobaltic nitrite after ten to twenty minutes is considered as satisfactory proof of the absence of potassium. This work showed that as ordinarily applied the sodium cobaltic nitrite test is a little more delicate for potassium than zirconium sulfate when used for the longer time which we find desirable. Allowing the sodium cobaltic nitrite test, however, to stand for a longer time than is customary and comparing to a blank test, the sensitiveness of sodium cobaltic nitrite for potassium is 0.07 mg. of potassium as compared to 0.53 mg. of potassium with zirconium sulfate solution.[6]

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[6] Bray, THIS JOURNAL, 31, 611 (1909), obtained with the sodium cobaltic nitrite test a turbidity within one to four minutes with 0.3 mg. of potassium, while we did not secure therewith a slight turbidity until fifteen minutes and a slight precipitate in one

Effect of Sodium Ion on the Detection of Potassium by Zirconium Sulfate Solution.—In qualitative analysis potassium ions are generally associated with sodium ions, ammonium ions and various anions. While the ammonium ions and interfering anions can be removed by evaporation with hydrochloric or sulfuric acid and gentle ignition, the sodium ion remains. Therefore it is necessary to determine the extent to which the sodium ion interferes with the detection of potassium by zirconium sulfate solution. The results of this work are given in Table III.

TABLE III

THE EFFECT OF SODIUM ION UPON THE DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE SOLUTION

Total volume, 2 cc. Zirconium sulfate per test, 0.2096 g.

Expt.	K, g. per sample	Na, g. per sample	Na/K	Results at room temperature	Results on cooling to 0°C.
1	0.03632	0.0266	0.7324	Precipitate at once	...
2	.02728	.0399	1.4646	Precipitate, few minutes	...
3	.01816	.0532	2.929	Precipitate, one hour	Increased
4	.01362	.0598	4.394	Precipitate, one hour	Increased
5	.00909	.0665	7.317	None, one hour	Precipitate, one-half hour
6	.00495	.0725	14.65	None, one hour	Precipitate, one hour
7	.00304	.0748	24.58	None, one hour	Precipitate, one hour
8	.00260	.0760	29.26	None, one hour	Precipitate, one hour
9	.00210	.0767	36.19	None, one hour	Small precipitate, one hour
10	.00000	.07441	....	None, one hour	Opalescence, four hours
11	.00000	.0000	....	None, one hour	Precipitate, four hours
12	.00176	.07201	41.9	None, one hour	Precipitate, one hour
13	.00107	.07295	68.0	None, one hour	Precipitate, two and one-half hours
14	.00072	.07343	102.4	None, one hour	Precipitate, two and one-half hours
15	.00053	.07368	139.0	None, one hour	Precipitate, one and one-half hours
16	.00030	.07401	246.7	None, one hour	Precipitate, one and one-half hours
17	.00007	.07432	1061.0	None, one hour	None, two and one-half hours
18	.00000	.07441	....	None, one hour	Cloudy, one and one-half hours; precipitate, two hours

Discussion.—This work indicated that in the presence of very concentrated sodium sulfate solution, zirconium sulfate solution would detect

hour; but our results showed that by allowing the sodium cobaltic nitrite test to stand for one day, a test for 0.07 mg. of potassium would be secured while Bray did not push his test farther than 0.1 mg. of potassium, for which he obtained a precipitate in six to ten hours. We secured a test for this amount of potassium in five hours. Bray used a total volume of 10 cc., while we used a total volume of 2 cc., obtaining more sensitive results.

1.76 mg. of potassium in 2 cc. of mixture. Expt. 18, a blank, indicated that cooling for so long a time as two hours might cause a deposit to form when no potassium had been added, thus prohibiting prolonged cooling.

Comparison of the work in Table III with that in Table I indicated that: (1) the presence of sodium sulfate lowered the sensitiveness of zirconium sulfate for potassium from 0.53 mg. to 1.76 mg. (2) When potassium was present to the extent of 9 mg. or more, the presence of sodium retarded the test for potassium with zirconium sulfate about half an hour—it doubled the time. When potassium was present in amounts less than 9 mg. and 1.76 mg. or more, there was little or no difference in the time required for detection of potassium with zirconium sulfate. For amounts of potassium below 1.76 mg., the presence of sodium did not affect the time required for detection of potassium, but caused a deposit to form when no potassium had been added. As in the corresponding Experiment 12, Table I, in which no sodium was present, Expt. 16 containing 0.3 mg. of potassium gave a deposit with zirconium sulfate sooner than some of the more concentrated solutions of potassium. The amount of the deposit was of the same magnitude as that of the blank, indicating the need of a blank for comparison at low potassium concentrations.

Influence of Concentration of Zirconium Sulfate Solution on Detection of Potassium Both in the Presence and Absence of Sodium.—The stock solution was diluted to one-half strength in an attempt to eliminate precipitation in the blank. A dilute solution of the reagent would not crys-

Table IV

Influence of Concentration of Zirconium Sulfate Solution upon Test for Potassium Both in the Presence and Absence of Sodium

Total volume, 2 cc. Zirconium sulfate, 0.1048 g.

Expt.	K, g. per sample	Na, g. per sample	Na/K	Results in one hour, room temp.	Results on cooling to 0°C.
1	0.00000	....	...	Opalescence	No change, four and one-half hours
2	...	0.07441	...	Opalescence	No change, four and one-half hours
3	...	.03720	...	Opalescence	No change, four and one-half hours
4	.0026	.07485	29.26	Cloudy	Small precipitate, one hour
5	.0026	....	...	None	Small precipitate, one hour
6	.00176	.07201	41.9	None	Opalescent, one hour; precipitate, one and one-half hours
7	.00176	....	...	None	Opalescent, one and one-half hours; precipitate, two hours
8	.00072	.07343	102.4	Opalescent	Cloudy, two and one-half hours; precipitate, four and one-half hours
9	.00072	....	...	Opalescent	Increased, three hours; no precipitate, four and one-half hours
10	.0003	....	...	None	Opalescent, one hour; no change, four and one-half hours
11	.0003	.07401	246.7	None	Opalescent, one hour; no change, four and one-half hours

tallize out on standing and so the warming up, mentioned in the section on preparation of zirconium sulfate, would be avoided. The results appear in Table IV.

Discussion.—In all experiments containing sodium sulfate except the blank 3, a deposit of apparently hydrated sodium sulfate formed on cooling to 0°. This would be dissolved on warming to room temperature for a few minutes. Any potassium zirconyl sulfate which might be present was undissolved.

The degrees of opalescence in the blanks 1, 2, 3 and in 10 and 11 containing 0.3 mg. of potassium were the same. This indicated that 0.3 mg. of potassium could not be detected by 10.48% zirconium sulfate. Expt. 9, containing 0.72 mg. of potassium, gave more opalescence after three hours' cooling than the blanks.

Comparing the results given above with the corresponding results in Table I and III where the concentrated zirconium sulfate was used showed: (1) in the absence of sodium, 20.96% zirconium sulfate solution detected 0.5 mg. of potassium while 10.48% zirconium sulfate solution detected 0.7 mg. of potassium. Either solution failed to detect the presence of 0.3 mg. of potassium in 2 cc. of mixture. Dilution of the reagent did not lower the sensitiveness of zirconium sulfate for potassium, but in the presence of sodium the dilution of the zirconium sulfate increased its sensitivity for potassium from 1.76 mg. to 0.7 mg. This increase in sensitivity was due to the non-formation of a deposit in the blank which occurred when the concentrated zirconium sulfate was used. (2) In the absence of sodium, the time required for the detection of potassium by zirconium sulfate was increased about one-half hour in all experiments. In the presence of sodium, the dilution of reagent increased the time required to detect potassium half an hour in the case of 1.76 mg. of potassium only.

The absence of a misleading deposit in the blank removed the serious objection that it was not a sure test for small amounts of potassium and increased the sensitivity of the test when sodium was present.

Summary of Conclusions

1. A concentrated zirconium sulfate solution detected 0.00053 g. of potassium (0.0068 molal potassium sulfate, 0.05% elemental potassium or 0.5 mg. of potassium) or more, when no sodium was present. It detected 1.76 mg. of potassium when sodium was present.

2. Large amounts of sodium sulfate retarded the detection of potassium in concentrated solutions but had little or no effect when the amount of potassium was small.

3. Zirconium sulfate when applied for the longer time we found necessary is almost as delicate a test for potassium as is sodium cobaltic nitrite when the latter is applied in the usual way. If the latter test is allowed to

run for a longer time than is customary, it can be made more sensitive for potassium than zirconium sulfate solution.

4. With dilute solutions of potassium sulfate—0.5 mg. of potassium—a comparison blank test with water and zirconium sulfate was needed. When sodium was present, a blank using sodium sulfate and zirconium sulfate was used for comparison with the solution tested.

5. Dilution of the zirconium sulfate solution to 10.48%, or one-half strength, had little or no effect upon its sensitiveness for potassium in the absence of sodium and increased the sensitiveness for potassium from 1.76 mg. of potassium to 0.7 mg. of potassium in the presence of sodium. No deposit in the blank test was formed.

6. To detect potassium with zirconium sulfate, add to the solution to be tested an equal volume of zirconium sulfate solution. If a deposit does not form at room temperature, cool in ice water. With small amounts of potassium a comparison with a blank is necessary.

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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN LABORATORY OF THE UNITED STATES BUREAU OF CHEMISTRY AND SOILS]

THE FREE ENERGY AND FUGACITY IN GASEOUS MIXTURES OF HYDROGEN AND NITROGEN

BY ALBERT R. MERZ AND COLIN W. WHITTAKER

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Knowledge concerning the free energies and fugacities of gases in mixtures is very meager. Lewis and Randall[1] assumed, *in the absence of theoretical or experimental investigations on the subject,* that every gaseous solution is a perfect solution and therefore that at a given temperature and total pressure the fugacity of each constituent is proportional to its mole fraction or to its partial pressure. This assumption was based on the supposition "that the solution of a given pair of substances will be more nearly perfect when the density of the solution is less" and by reason of the fact that "even among liquids numerous cases occur where there is a close approach to the perfect solution."

Lurie and Gillespie,[2] applying this rule to the calculation of the equilibrium pressures of ammonia, in mixture with nitrogen, over $BaCl_2 + BaCl_2{\cdot}8NH_3$, found in the region where it could be applied that it gave results in fair agreement with the observed equilibrium pressures. This region, however, was limited to pressures of less than 17 atmospheres.

Gibson and Sosnick,[3] using the experimental results of Masson and

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

[2] Lurie and Gillespie, THIS JOURNAL, **49,** 1154 (1927).

[3] Gibson and Sosnick, *ibid.,* **49,** 2172 (1927).