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

ZIRCONIUM. V. DETECTION OF TRACES OF POTASSIUM IN THE PRESENCE OF ZIRCONIUM[1]

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Zirconium sulfate can be used to detect potassium,[2] but the completeness of precipitation of potassium by zirconium sulfate is not easily measured, as zirconium sulfate also gives a precipitate with sodium cobaltic nitrite. Obviously zirconium must be eliminated, if present, prior to testing for potassium, so a study of delicate methods of detection of traces of potassium under these conditions was made. The results indicated that while phosphates will remove the zirconium, they interfere with the subsequent detection of traces of potassium. Ammonium hydroxide, however, was found to remove all of the zirconium without interfering materially with subsequent detection of potassium. Also a quicker and less objectionable method was found to be the transformation of the zirconium into a complex ion with tartaric acid, and after adjusting the acidity with sodium hydroxide and acetic acid, testing for potassium with sodium cobaltic nitrite.

Discussion of Literature

Zirconium can be removed by phosphates in excess under proper conditions.[3] Bray[4] found that dilute sodium phosphate solution gave no precipitate with sodium cobaltic nitrite; but according to solubility records[5] approximately 39 cc. of water at 20° would be needed to dissolve the 7.5 g. of sodium phosphate which we found was needed to remove 0.1134 g. of zirconium sulfate used in the test. If the original concentration of potassium was 1 mg. per cc., this dilution would lower the concentration to 0.02 mg. per cc.—a smaller concentration than sodium cobaltic nitrite will detect.[2]

Smaller concentrations of phosphoric acid, microcosmic salt or ammonium phosphate would remove the zirconium but the interfering ammonium salts would have to be expelled before testing for potassium. The gelatinous zirconium phosphate might adsorb any traces of potassium salts. The use of ammonium hydroxide to remove the zirconium risked the same objections.

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[1] Presented at the Columbus Meeting of the American Chemical Society, April 25, 1929.

[2] Reed and Withrow, THIS JOURNAL, **50**, 1515 (1928).

[3] Reed and Withrow, *ibid.*, **51**, 1311 (1929).

[4] Bray, *ibid.*, **31**, 634 (1909).

[5] Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 2d ed., 1919, p. 662.

The possibility of avoiding these dangers of loss of potassium by volatilization or adsorption, by the elimination of zirconium as a complex ion was suggested by the statement of Fresenius,[6] "tartaric acid prevents the precipitation (of zirconium) by alkalies."

Experimental

Detection of Potassium after Removal of Zirconium.—Samples containing 0.113 g. of zirconium sulfate, varying amounts of potassium and 1.634 g. of hydrogen sulfate were prepared. Some were treated with an excess of 5 times the calculated needed amount of either phosphoric acid, ammonium phosphate or microcosmic salt. To avoid evaporation of large amounts of solution the final volume was kept at 50 cc. After standing for several hours the solutions were filtered and the filter washed four times with cold water. The filtrate and washings were evaporated to a sirup. This was transferred with washing to a platinum crucible, the evaporation continued to dryness and the residue ignited short of red heat until no more fumes were noticed. If a drop of a solution prepared by adding 1 cc. of water to the residue gave no test for ammonium salts with Nessler's reagent, the remainder was neutralized with sodium hydroxide, about 3 cc. of 30% acetic acid was added and then an equal volume of sodium cobaltic nitrite solution. Preliminary experimentation showed that if this excess acid was not added a flaky precipitate was obtained whether potassium was present or not. This amount of acetic acid did not prevent the detection of 0.3 mg. of potassium in a test solution. Other samples were treated with ammonium hydroxide instead of phosphates to remove the zirconium and the filtrates were tested for potassium in the same way except that no acetic acid was added. The results appear in Table I.

TABLE I

DETECTION OF POTASSIUM BY SODIUM COBALTIC NITRITE AFTER REMOVAL OF ZIRCONIUM

Expt.	K, g. per sample	Results of test for potassium by $Na_3Co(NO_2)_6$ after removing zirconium by			
		H_3PO_4	$NaNH_4HPO_4$	$(NH_4)_2HPO_4$	NH_4OH
1	0.00053	Flaky ppt.	Flaky ppt.	Clear, sev. hrs.	Ppt., 4 min.
2	.00031	Clear, 20 min.; cloudy, 2 hrs.	Ppt., 45 min.	Clear, no ppt., sev. hrs.	Ppt., 5 min.
3	.00012	Clear, no ppt., 1 hr.	Clear, no ppt., 1 hr.	Clear, no ppt., sev. hrs.	Sl. ppt., standing hrs.
4	.00000	Clear, no ppt., 15 min.; cloudy, 1 hr.	Clear, 1 hr.	Clear, 20 min.; cloudy, 40 hrs.	Clear, no ppt., 1 day
5	.00176	......	......	Ppt. at once	

Discussion.—The precipitates (Run 1) where zirconium had been removed by phosphoric acid or microcosmic salt were flaky and brownish, not the usual yellow color of potassium cobaltic nitrite. They resembled the precipitates obtained (preliminary work) by adding sodium cobaltic nitrite to a solution of phosphoric acid neutralized by sodium hydroxide which had added thereto but a small excess of acetic acid.

The results in Cols. 2, 3 and 4, where zirconium was removed by phosphates prior to testing for potassium, indicated that either the zirconium phosphate adsorbed the potassium or the prolonged heating, needed to

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[6] Fresenius, "Qualitative Chemical Analysis," translated by C. A. Mitchell, John Wiley and Sons, Inc., New York, 1921, 17th German ed., p. 181.

drive off the excess acids and ammonium salts, volatilized most or all of the potassium. When zirconium was removed by ammonium hydroxide (Col. 5), prior to testing for potassium, there were no such difficulties in detecting potassium. Therefore phosphates are not suitable and *ammonium hydroxide is suitable for removing zirconium prior to testing for potassium by sodium cobaltic nitrite.*

Detection of Potassium in the Presence of Zirconium by Changing the Zirconium into a Non-Interfering Complex Ion with Tartaric Acid.—Preliminary experimentation showed that if a 2-cc. solution of zirconium sulfate be treated with 0.3 g. of tartaric acid and the acidity controlled by neutralizing with 25% sodium hydroxide, making slightly acid with acetic acid, no precipitate is obtained with sodium cobaltic nitrite. If any potassium was added, a test for it was obtained. To determine the sensitiveness of sodium cobaltic nitrite for potassium under these conditions, a series of experiments was run. The manipulation was exactly as described above. The amount of zirconium sulfate was 0.1131 g. per test, the tartaric acid 0.3 g. and the amount of potassium varied. The results appear in Table II.

TABLE II

SENSITIVENESS OF SODIUM COBALTIC NITRITE FOR POTASSIUM WHEN ZIRCONIUM IS PRESENT IN COMPLEX ION

Expt.	K, g. per sample	Results of test for potassium with $Na_3Co(NO_2)_6$	
		Presence of zirconium	Absence of zirconium K_2SO_4 alone present
1	0.00107	Cloudy at once; ppt., 5 min.	Ppt., 5 min.
2	.00072	Cloudy, 5 min.	Sl. ppt., 5 min.
3	.00053	Cloudy, 10 min.	Very sl. ppt., 10 min.
4	.00030	Very sl. cloudy, 15 min.; ppt., 1.5 hrs.	Very sl. ppt., 10 min.
5	.00014	Very sl. cloudy, 1.5 hrs.; no ppt., 2 hrs.	Ppt., 2.5 hrs.
6	.00000	No ppt.; clear, 1.5 hrs.	Clear, no ppt., 23 hrs.

Discussion.—The suppression of zirconium by tartaric acid did not prevent the detection of 0.3 mg. of potassium (Expt. 4) by sodium cobaltic nitrite. The slight difference between the time for appearance of a precipitate in the test for potassium in the presence (Expt. 4) and absence of zirconium was doubtless due to dilution of potassium solution from 1 cc. to 3 cc. with zirconium present.

This method of suppression of zirconium ions is much to be preferred to removal of zirconium by either phosphates or ammonium hydroxide prior to testing for potassium by sodium cobaltic nitrite, as it is shorter and avoids danger of adsorption or volatilization of potassium.

Summary

1. The use of phosphates to remove zirconium prior to testing for potassium by sodium cobaltic nitrite is not advisable because of loss or dilution of potassium.

2. When phosphoric acid is neutralized with sodium hydroxide and the solution tested with sodium cobaltic nitrite, a misleading precipitate is secured unless a considerable excess of acetic acid is added.

3. Zirconium can be removed by ammonium hydroxide and potassium detected in the filtrate by sodium cobaltic nitrite, after eliminating the ammonium.

4. The best and shortest way of eliminating zirconium prior to testing for potassium by sodium cobaltic nitrite is by throwing the zirconium into a complex ion with tartaric acid and controlling the acidity with sodium hydroxide and acetic acid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED VERDE COPPER COMPANY]

THE SYSTEM SODIUM SULFIDE-FERROUS SULFIDE[1]

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This investigation deals with the composition diagram of the system Na_2S-FeS obtained from cooling curves on melts of several compositions and by microscopic examination of polished surfaces of frozen samples of the melts. The principal interest from an industrial standpoint was in the liquidus curves and no great effort was made completely to determine the nature of the phases or phase changes at temperatures beneath the liquidus. Therefore the phase diagram as presented is incomplete but contains the reasonable conclusions and certain inferences that seem to be justified by the data.

Preparation of Sodium Sulfide.—Several methods for preparing pure sodium sulfide were considered: reduction of sodium sulfate with carbon; the Hugot[2] method of reacting with sulfur on a solution of sodium in liquid ammonia with subsequent evaporation of excess ammonia; the Hugot method of reacting on molten sodium with hydrogen sulfide; the Sabatier[3] method of dehydrating the hydrated salt, $Na_2S{\cdot}9H_2O$; and the reaction[4] obtained by heating sodium carbonate in sulfur vapor. All of these methods were tested by Friedrich,[5] who found that a reasonably pure product could be obtained by heating the hydrated salt in a rapid stream of hydrogen. The hydrated salt first melts in its water of crystallization, solidifying when the mass has reached about 70% of sodium sulfide by weight and leaving a porous mass from which the remainder of the

[1] The preparation of materials and cooling curves was carried on in the Pacific Experiment Station of the U. S. Bureau of Mines, at Berkeley, California.

[2] Hugot, *Compt. rend.*, **129**, 388 (1899).

[3] Sabatier, *Ann. chim. phys.*, [5] **22**, 66 (1881).

[4] Vauquelin, *ibid.*, [2] **6**, 32 (1817).

[5] Friedrich, *Metall und Erz*, **11**, 79 (1914).