4. Six per cent. potassium iodide must be employed when sodium thiosulfate solutions are standardized with potassium permanganate. Standing is not necessary. The acid concentration may be 0.1 *M* sulfuric.

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ZIRCONIUM. IV. PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

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This paper is devoted to a study of the completeness of precipitation of zirconium by other phosphates. In testing for completeness of precipitation of potassium by zirconium sulfate it was found that this reagent also gave a precipitate with sodium cobaltic nitrite. Therefore, it became necessary to remove the zirconium before testing for potassium. As phosphates have been used for quantitatively determining zirconium and as Noyes and Bray[1] have shown that phosphates do not interfere with the detection of potassium by sodium cobaltic nitrite, the completeness of removal of zirconium by phosphates prior to testing for potassium was investigated.

The results indicated that a five-fold excess of ammonium phosphate, phosphoric acid or microcosmic salt in the presence of 0.344 molal sulfuric acid were all efficient in removing zirconium but that sodium phosphate was inefficient except when used in forty-fold excess. The presence of added acid was necessary.

Literature

Phosphates.—Sodium phosphate,[2] ammonium phosphate,[3] microcosmic salt[4] and phosphoric acid[5] have been used to determine zirconium quantitatively in the presence of sulfuric acid. Biltz and Mecklenburg[6] recommend the qualitative detection of zirconium by sodium phosphate in the presence of hydrochloric or nitric acid, as sulfuric acid slowed up the reaction.

Conditions for the Precipitation of Zirconium Phosphate.—Marden and Rich[2] recommend "a slight excess of sodium phosphate" in the presence of 10% sulfuric acid. Lundell and Knowles[3] recommend an excess of 10 to 100 times the calculated amount of ammonium phosphate in

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[1] Noyes and Bray, This Journal, **31**, 634 (1909).

[2] Marden and Rich, *J. Ind. Eng. Chem.*, **12**, 654 (1920).

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

[4] Steiger, *J. Washington Academy of Science*, **8**, 637 (1908).

[5] Marden and Rich, Bureau of Mines, Bulletin No. 186, 75–77 (1921).

[6] Biltz and Mecklenburg, *Z. angew. Chem.*, **25**, 2110 (1912).

the presence of 2 to 20% tepid sulfuric acid. Less than 0.5% sulfuric acid caused the formation of basic zirconium phosphate. Noyes, Bray and Spear[7] found that an excess of sodium phosphate was needed to remove practically all of the zirconium from solution. Steiger[4] stated that the zirconium was completely removed by microcosmic salt except when the acidity was from 5 to 10% sulfuric acid. Marden and Rich investigated the yield of zirconium phosphate by precipitation with various phosphates and concluded[5] "that $(NH_4)_2HPO_4$, Na_2HPO_4 or H_3PO_4 gave equally good results." If one chooses results from their determinations given in the table, agreeing results are secured, but the average of their determinations of zirconium by sodium phosphate is less than the average of either the ammonium phosphate or phosphoric acid results.

While zirconium has been determined quantitatively by all four phosphates, their efficiency in removing zirconium completely in the presence of hydrochloric, nitric and sulfuric acids of varying concentrations was still subject to question. It was decided, therefore, to investigate the completeness of removal of zirconium by these phosphates.

Experimental

Reagents.—The zirconium sulfate solution contained 0.1134 g. of zirconium sulfate per cc. The approximate strengths of the acids were determined by specific gravity. The phosphates were analyzed for phosphate by the magnesium pyrophosphate method according to Treadwell and Hall.[8]

General Procedure.—To 1-cc. portions of zirconium sulfate solution in the presence of no added acid and also hydrochloric, nitric or sulfuric acid, a solution of either phosphoric acid, sodium phosphate, microcosmic salt or ammonium phosphate was added. After standing for two hours or overnight the solutions were filtered through closest grained filter paper and washed four times with cold water. Early experiments showed that if medium texture paper was used the zirconium phosphate would pass through the paper. To make any precipitate more noticeable, the filtrate and washings were concentrated upon a sand-bath to 10 or 20 cc. Then concentrated ammonium hydroxide was added to neutralize the acid. If the solution gave no deposit, it was warmed and allowed to stand to see if a tardy precipitate would form.

Sodium phosphate as a reagent for precipitation of zirconium was investigated more minutely than the others as it would not interfere with the detection of potassium after zirconium was removed. The efficiency of all four reagents is shown in the table.

Discussion

In Expts. 1 to 4 where no acid was added the precipitate settled slowly and filtered with difficulty. In Expts. 5 to 25 where acid was added the precipitate settled readily and filtered much more rapidly than where no acid was added. Evidently acid must be added to secure a proper

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[7] Noyes, Bray and Spear, THIS JOURNAL, **30**, 559–560 (1908).

[8] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1915, Vol. II, p. 474.

TABLE I

PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

Expt.	Added acid Kind	Added acid G.	Total vol., cc.	Ppt. calcd., P_2O_5	Calcd. factor as excess, P_2O_5	Test in filtrate for zirconium by NH_4OH Na_2HPO_4	H_3PO_4	$NaNH_4HPO_4$	$(NH_4)_2HPO_4$
1	None	....	50	0.5696	10.0	Ppt.	Ppt.	Ppt.	Sl. ppt.
2	None	....	200	2.2792	40	....	Clear No. ppt.	....	....
2a	None	....	50	2.2792	40.0	....	Few dark flocks	....	....
3	None	....	100	5.6980	100.0	....	Clear No ppt.	Sl. ppt.	....
4	None	....	200	1.1396	20.0	....	Dark ppt.	....	....
5	HCl	0.410	54	0.0929	1.33	Ppt.	....	....	....
6	HCl	.410	54	.0929	1.33	Ppt.	....	....	....
7	HCl	.373	50	.1139	2.00	Ppt.	....	....	....
8	HCl	9.325	50	.1139	2.00	Ppt.	....	....	....
9	HCl	0.373	50	.5696	10.00	Ppt.	Ppt.	Ppt.	Ppt.
10	HCl	1.230	152	2.0907	36.7	Sl. ppt. overnight	....	....	....
11	HCl	0.373	50	1.1396	20.0	....	Sl. ppt.	Sl. ppt.	Sl. if any ppt.
12	HCl	.373	50	2.8490	50.0	....	No ppt. clear	....	....
13	HNO_3	.358	50	0.2321	4.05	Sl. ppt. on standing	....	....	....
14	HNO_3	8.717	50	.2321	4.05	Ppt. on standing	....	....	....
15	HNO_3	4.3585	50	1.9658	32.4	Ppt. on standing	....	....	....
16	HNO_3	0.896	50	0.5696	10.0	Ppt. on standing	Sl. ppt.	Ppt.	Sl. ppt.
17	HNO_3	.8966	50	1.1396	20.0	....	Clear No ppt.	Clear No ppt.	Sl. if any ppt.
18	H_2SO_4	.1634	50	0.5405	9.48	....	....	....	Ppt. standing
19	H_2SO_4	.817	50	.2849	5.00	....	Cloudy	Ppt.	Clear No ppt.
20[a]	H_2SO_4	.817	50	.5696 .5405	10.0	Ppt. on standing	Sl. ppt.	Clear No ppt.	Clear No ppt.
21	H_2SO_4	1.634	50	.2849	5.0	....	Clear No ppt.	Clear No ppt.	Slight if any ppt.
22	H_2SO_4	1.6417	50	.4642	8.15	Ppt. on standing	....	....	....
23	H_2SO_4	1.634	50	.5698	10.0	....	Clear No ppt.	Clear No ppt.	Clear No ppt.
24	H_2SO_4	3.2324	100	.3215	40.05	No ppt.	....	....	....
25	H_2SO_4	8.17	50	.5718	10.0	....	....	Sl. cldy.	Clear No ppt.

[a] The amount of ammonium phosphate used in Expt. 20 was not 0.5696 g. of P_2O_5 as in the other three cases but 0.5405 g. of P_2O_5. All other conditions were the same.

physical condition of the precipitate. In Expts. 18 to 25, where sulfuric acid was present, the precipitate formed only after standing for a few seconds, while in all other cases, Expts. 1 to 17, where either none or hydrochloric or nitric acid was present, it formed as soon as any precipitant was added. This agreed with the observation of Biltz and Mecklenburg.[6]

In Expt. 5 the zirconium was precipitated from hot solution while in Expt. 6 the precipitation was made from solution at room temperature, all other conditions being equal. The bulk of precipitate was greater in the filtrate from 5 than from 6, possibly indicating that zirconium was more completely removed when precipitation was made at room temperature than from hot solution. All other precipitations were made at room temperature.

Effect of Added Acid.—In Expts. 5 to 12 where hydrochloric acid was present, only one condition—Expt. 12, 0.204 *N* hydrochloric acid—succeeded in removing all of the zirconium. An excess of 50 times the calculated amount of phosphoric acid was needed for this. Expts. 13–17, where 0.269 *N* nitric acid was present, indicated that in Expt. 17, 20 times the calculated needed amount of phosphoric acid, microcosmic salt or ammonium phosphate would remove all of the zirconium from solution. Expts. 18–25, in which sulfuric acid was present, indicated that either phosphoric acid, microcosmic salt or ammonium phosphate—Expts. 20, 21, 23—when used in excess of 5 to 10 times the calculated needed amount would remove all of the zirconium from solution in the presence of 0.817 g. (0.168 molal or 0.334 normal) to 1.634 g. (0.334 molal or 0.668 normal) of sulfuric acid per 50 cc. of solution. Expt. 25 showed that as much as 8.17 g. of sulfuric acid per 50 cc. of solution did not prevent the complete removal of zirconium by 10 times the calculated amount of ammonium phosphate. These results indicated that the presence of sulfuric acid, while retarding the appearance of a precipitate, was more beneficial than either hydrochloric or nitric acid in aiding the removal of zirconium by phosphates.

Efficiency of Various Phosphates.—Sodium phosphate—Expts. 19 to 23—was less efficient than phosphoric acid, microcosmic salt or ammonium phosphate in removing zirconium from solution. However, the amount of zirconium left in solution by sodium phosphate was very small and the precipitate of zirconium phosphate formed only after standing. The bulk of the deposits, in the ammonium phosphate column, marked "slight if any" amounted to but a few flakes which would be unweighable on ignition and might have been shreds of filter paper.

Summary

1. The efficiency of sodium phosphate, phosphoric acid, ammonium phosphate and microcosmic salt as precipitants for zirconium has been investigated and the last three were found to be equally efficient and more efficient than sodium phosphate. Even sodium phosphate removed practically all of the zirconium.
2. The phosphates were found most efficient in the presence of 0.344 to 0.668 *N* sulfuric acid and less efficient in the presence of 0.269 *N* nitric acid or 0.204 *N* hydrochloric acid.
3. Although record was found in the literature of the formation of

basic zirconium phosphate in the absence of added acid, no record was found indicating incompleteness of precipitation of zirconium under these conditions. Investigation showed that phosphates are not efficient in removing zirconium in the absence of added acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAPE TOWN]

THE SINGLE POTENTIAL OF THE COPPER ELECTRODE

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The determination of the normal single potential of a copper electrode has been attempted by many investigators with very discordant results and at the present time its value is not known with certainty within a possible error of 40 millivolts. This work was undertaken, therefore, with the object first of finding the reasons for the variation in the results obtained, and, second, if possible, of removing or circumventing the disturbing factors and determining the true value.

Possible sources of error or of variability of results are: (1) impurities in the electrode, (2) impurities in the electrolyte, (3) variations in the nature of the electrode surface, (4) changes in constitution of electrolyte during measurement, (5) chemical action between electrode and electrolyte producing any or all of the conditions (1) to (4).

1. Most investigators have exercised great care to ensure that the copper electrodes used were free from traces of other metals. Unfortunately one of the most dangerous impurities, hydrogen, which is very frequently present and has a profound potential-disturbing capacity, has been ignored. If two copper plates cut from the same sheet be immersed in dilute acid and a current passed for a few seconds, a potential difference of several millivolts is produced which may persist for several hours. By introducing a third electrode cut from the same sheet at the same time it may be shown that this potential change is mainly due to the cathode.

This cannot be due to deposition of copper on the cathode since the effect is quite unchanged if the three electrodes are placed in separate compartments connected only by narrow tubes.

Lewis and Lacey[1] used electrolytic copper sponge for the determination of the single potential of copper and this was undoubtedly contaminated with hydrogen.

Their attempt to show that occluded hydrogen was not taking part in the electrode process was very unconvincing. They found that the presence of 0.0005 *M* sulfuric acid in the solution had no effect upon the e.m.f.

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[1] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).