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GRAVIMETRIC DETERMINATION OF SODIUM BY THE URANYL ZINC ACETATE METHOD. II. APPLICATION IN THE PRESENCE OF RUBIDIUM, CESIUM, POTASSIUM, LITHIUM, PHOSPHATE OR ARSENATE

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In the first paper[1] of the general procedure for the determination of sodium by the uranyl zinc acetate method, it was shown that the method is quite specific for sodium, though lithium and large amounts of potassium have an interfering action. As the determination of sodium in the presence of other alkali metals is of great practical importance, we present in this paper the results of a study made in this direction. With regard to the interfering anions, we consider especially the removal of the phosphate and arsenate ions.

Rubidium and Cesium.—A solution of 100 mg. of pure rubidium chloride and cesium chloride, respectively, in 1 cc. of water does not give a precipitate with 10 cc. of the reagent after long standing. It was shown that Kahlbaum's salts of these elements contained a trace of sodium: the rubidium chloride, 0.45%; the cesium chloride, 0.13%. The general procedure outlined in the first paper is to be followed in determining sodium in rubidium and cesium compounds.

Potassium.—In the first paper it was shown that if a solution contains more than 50 mg. of potassium per cc., potassium uranyl zinc acetate will be precipitated; therefore, in cases where sodium is to be determined in large amounts of potassium, the larger part of the latter has to be removed.[2] It is not necessary to remove all of the potassium in a quantitative way, as small amounts of this element do not interfere with the sodium determination. For the precipitation of the larger part of potassium, we used ammonium perchlorate in a medium of 72% alcohol. A test for purity of the ammonium perchlorate is made by dissolving 1 g. of the salt in 10 cc. of the reagent. A clear solution should be ob-

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[1] Barber and Kolthoff, THIS JOURNAL, **50**, 1625 (1928).

[2] In order to avoid any misunderstanding, it may be remarked that if more than 50 mg. of potassium per cc. is present, the solution can be correspondingly diluted, provided that in the precipitation of sodium for each cc. of solution 10 cc. of the reagent is used. If the ratio of sodium to potassium is very unfavorable, the application of the above procedure would require large amounts of reagent and therefore would be uneconomical and impracticable.

In the general procedure for the precipitation of sodium, it should be noted that as long as a ratio of 1 cc. of solution to 10 cc. of reagent is maintained, satisfactory results will be obtained. Each 10 cc. of reagent will completely precipitate from 1 cc. of solution 8 mg. of sodium. If 5 cc. of solution were used, 50 cc. of reagent should be added. This amount of reagent would precipitate, if present, 40 mg. of sodium.

tained with no separation of crystals after standing for one hour. If the perchlorate contains sodium, the latter can be removed easily by recrystallization from water.

Procedure

One gram of potassium chloride is dissolved in 5 cc. of water. To this add a hot solution of 2 g. of ammonium perchlorate in 3 cc. of water and 25 cc. of 95% alcohol. Cool the mixture to room temperature, filter and wash the precipitate five times carefully with 2-cc. portions of 95% alcohol. Evaporate the filtrate to dryness, take the residue up in 1 cc. of water and add 10 cc. of reagent. If the potassium salt contains more than 1% of sodium, the residue should be taken up in more water and an aliquot part weighed out. As a matter of fact, one may start in this case with less potassium salt. A qualitative test for sodium in the potassium salt will give an approximate idea of the amount of sodium present (see first paper). The following table shows that traces of sodium down to 0.1% may be determined in potassium chloride with an accuracy of 1 to 2%.

TABLE I

DETERMINATION OF TRACES OF SODIUM IN THE PRESENCE OF 1 G. OF POTASSIUM CHLORIDE

NaCl, g.	Wt. of ppt., g.	NaCl calcd. from ppt., g.	NaCl, g.	Wt. of ppt., g.	NaCl calcd. from ppt., g.
0.01414	0.3667	0.01394	0.0064	0.1692	0.0064
.01289	.3367	.01280	.0057	.1540	.0058
.01197	.3104	.01180	.0055	.1477	.0056
.01063	.2812	.01068	.0046	.1160	.0044
.0085	.2278	.0086	.0044	.1164	.0044
.0079	.2103	.0080	.0043	.1073	.0041
.0079	.2036	.0077	.0039	.1003	.0038
.0077	.2028	.0077	.0037	.0954	.0036
.0077	.2034	.0077	.0023	.0597	.0023
.0070	.1794	.0068	.0020	.0520	.0020

It should be mentioned that the outlined procedure is useful for the qualitative detection of traces of sodium in potassium salts. In that case it is not necessary, of course, to wash the potassium perchlorate with alcohol.

In the way described 0.005% of sodium can easily be detected in potassium salts.

Lithium.—Many more difficulties were encountered in the determination of sodium in the presence of lithium. Lithium triple salt is very slightly soluble. A solution of 0.2 mg. of lithium in 1 cc. of water with 10 cc. of reagent forms a crystalline deposit after a few hours' standing. The reaction would be more sensitive if the reagent was saturated to the lithium compound. We are planning to make a study on the application of the reagent for the determination of lithium.

For the determination of sodium in the presence of lithium, the latter has to be quantitatively removed. We first tried the alcohol–ether method of S. Palkin,[3] but did not find this method suited to our purpose as in his

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[3] Palkin, THIS JOURNAL, 38, 2326 (1916).

procedure all the alkali metals have to be in the form of chlorides. Commercial salts of lithium and even C. P. products appeared to contain sulfate as an impurity; it is necessary to remove this anion, as lithium sulfate is insoluble in the alcohol–ether mixture. The extraction method in the regular course of analysis will give satisfactory results. In cases where traces of sodium have to be determined in lithium compounds, we prefer to remove the latter in the form of an insoluble salt; therefore, we precipitated lithium as the fluoride.

In our first experiments we attempted to purify C. P. products of lithium chloride according to the alcohol–ether method of Palkin.[3] The purified salt still contained traces of sodium.[4] A better product for our purpose was obtained by precipitation of lithium as a carbonate with pure ammonium carbonate.

The separation of sodium from lithium by the fluoride method is a tedious procedure. Though the solubility of lithium fluoride in water is small, alcohol should be added to precipitate the lithium quantitatively. However, if too much alcohol is added, or if too much lithium is present, some sodium may be carried down by the precipitate. On the other hand, if too little alcohol is added, too high results are found due to incomplete precipitation of lithium. Under special conditions a compensation of errors may lead to results agreeing with the theoretical.

TABLE II

SEPARATION OF LITHIUM FROM SODIUM

Concn. of alcohol, %	NaCl, g.	LiCl, g.	NaCl found, g.	Error, %
10	0.05712	0.10	0.05887	+3.0
15	.05903	.05	.06224	+5.4
15	.05850	.22	.05840	−0.2
15	.06004	.33	.05828	−3.0
20	.06048	.22	.05743	−5.0
25	.05860	.22	.05495	−6.6
25	.06145	.24	.05607	−9.0
30	.05741	.22	.05029	−12.5
40	.06935	.10	.06709	−3.3

In the final procedure a 10% solution of ammoniacal ammonium fluoride was used. (The reagent should be kept in paraffined or hard rubber bottles.) The ammonia has to be added to decompose fluosilicate, which occurs as an impurity even in chemically pure products of ammonium fluoride and interferes in the separation, and also to prevent the action of the fluoride on glass. A 25% solution of hydrochloric acid and 95% alcohol are the other reagents.

Though ammonium fluoride does not precipitate with uranyl zinc acetate, it prevents the precipitation of sodium; therefore, the fluoride

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[4] Compare, also, T. W. Richards and H. H. Willard, THIS JOURNAL, **32**, 4 (1910).

has to be removed before the sodium is precipitated with the reagent. This can be done easily by evaporation with hydrochloric acid. The ammonium fluoride and hydrochloric acid should be tested for purity. In a platinum crucible place about 1 g. of ammonium fluoride, add 10 cc. of 25% hydrochloric acid and evaporate to dryness. Add to the residue 5 cc. of the reagent and transfer to a test-tube. The solution should be clear after standing for one-half hour. The ammonium hydroxide used has to be sodium free. Evaporate 5 cc. to dryness and test residue with the reagent. All the solutions of ammonia tested contained sodium. It was necessary to redistil and keep in paraffined bottles.

Procedure

To not more than 0.1 g. of the salt add 10 cc. of water and 5 cc. of 95% alcohol. After the salt has dissolved, add 5 cc. of the ammonium fluoride solution. Allow to stand for twenty hours, or longer, and then filter off the precipitate through a glass filter crucible. The lithium fluoride is washed five times with 2-cc. portions of a 50% alcohol solution containing 0.5% of ammoniacal ammonium fluoride. The filtrate and wash liquor are evaporated carefully in a platinum crucible and the residue is evaporated three times with 5-cc. portions of hydrochloric acid. The residue is now transferred with water to a weighing bottle of known weight. The solution is evaporated to a volume of 2 to 5 cc. and weighed after cooling. An aliquot part is weighed out and the sodium determined by the regular procedure.

If amounts of sodium of the order of 1.5% or less have to be determined in lithium salts, one may start with 0.5 g. of salt and treat this according to the above procedure. Finally, the residue is taken up in 2 cc. of water and 20 cc. of uranyl zinc acetate reagent is added. In this way we found that sodium could be determined with an accuracy of 1 to 2%.

TABLE III

SEPARATION OF LITHIUM FROM SODIUM

Concn. of alcohol, %	NaCl, g.	LiCl, g.	NaCl found, g.	Error, %
25	0.06306	0.02	0.06321	+0.2
25	.05894	.08	.05888	− .1
25	.05941	.10	.05917	− .4
25	.1135	.10	.1138	+ .3
25	.005936	.35	.00607	+2.0
25	.003994	.38	.00392	−2.0

In Tables II and III the analyses show that when the alcohol concentration is 25%, good results are obtained if the ratio between weight of sodium chloride taken and weight of lithium chloride is 1 to 1 or less where the weight of sodium chloride is 100 mg., or less. However, as soon as the ratio between the weight of sodium chloride and weight of lithium chloride becomes 1 to 2, sodium is carried out of the solution by the lithium fluoride precipitate and low results are obtained. On the other hand, results within 2% of the theoretical were obtained when a few mg. (4–6 mg.) of sodium chloride was present with a much greater quantity (350 mg.) of lithium fluoride.

All of our experimental work in 25% alcohol solution gave consistently low values for sodium when the sodium chloride–lithium chloride content in 20 cc. of solution was 100 mg., or less, of sodium chloride to 125 mg., or more, of lithium chloride (see Table II), but when the lithium chloride content was 100 mg., or less, excellent results were obtained (see Table III). Consequently, the amount of lithium chloride should not be greater than 100 mg. in 20 cc. of 25% alcohol solution unless small amounts, a few mg., of sodium are to be determined in lithium salts. In this case, 0.3 to 0.4 g. of lithium chloride may be present.

Phosphate and Arsenate.—Phosphate and arsenate give a precipitate with the uranyl zinc acetate reagent. We first tried to remove these ions with a dilute solution of the reagent. (Sodium does not precipitate under these conditions.) However, this procedure cannot be recommended as the slimy precipitate absorbs sodium and too low results are obtained. It is better to remove the phosphate and arsenate by precipitation with magnesia mixture in cold solution to which an excess of ammonia has been added. The filtrate and the wash liquor are evaporated to dryness and the sodium is determined according to the regular procedure. Again, the reagents must be free from sodium and the usual precautions for precipitating phosphate or arsenate with magnesia mixture must be observed.

In our experiments we used monopotassium phosphate and dipotassium arsenate. Both salts were recrystallized three times from water. In the following table we show that satisfactory results are obtained.

TABLE IV

SEPARATION OF PHOSPHATE AND ARSENATE FROM SODIUM

K_2HPO_4, g.	NaCl, g.	NaCl, found, g.	Error, %	K_2HAsO_4, g.	NaCl, g.	NaCl found, g.	Error %
0.076	0.01143	0.01180	+3.0	0.033	0.01182	0.01182	0.0
.087	.01220	.01220	0.0	.086	.01259	.01260	+ .1
.034	.01199	.01210	+1.0	.048	.01124	.01130	+ .5
.019	.01048	.01053	+0.5				

Summary

The determination of sodium in the presence of the alkali metals, phosphate or arsenate has been investigated and the following ascertained.

1. Cesium and rubidium in amounts of 0.1 g. do not interfere.
2. Interfering amounts of potassium may be removed by precipitation with ammonium perchlorate in 72% alcoholic solution.
3. Lithium must be removed quantitatively. Ammonium fluoride in 25% alcoholic solution is used to precipitate the lithium.
4. Phosphate and arsenate interfere and are removed by precipitation with magnesia mixture.

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