[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE DIRECT DETERMINATION OF SODIUM IN THE PRESENCE OF ALUMINUM AND CHROMIUM

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RECEIVED JULY 25, 1930 PUBLISHED NOVEMBER 5, 1930

The possibility of determining small amounts of sodium in the presence of large amounts of aluminum and chromium is of special interest due to the difficulties involved in the accurate separation of sodium from these elements. When aluminum and chromium are precipitated in the usual manner as hydroxides with the subsequent determination of sodium in the filtrate the results are far from satisfactory even with careful manipulation. Other methods of separation have been proposed but these likewise leave much to be desired. Since a direct analytical method is always desirable for the estimation of small amounts of a given element, the following experiments were performed to determine whether or not the magnesium uranyl acetate method for sodium could be applied satisfactorily to this problem.

General Procedure

In the experiments with pure salts, known volumes of standard sodium solution were added to solutions of known amounts of aluminum and chromium salts and, after evaporation to small volume, the sodium present was determined by the direct magnesium uranyl acetate method for sodium previously described.[1] The technique given in the first paper in this series was followed except for the following variations which further experience with the method has shown to be advisable. Where sulfates are present, which was the usual case in these experiments, precipitates should first be washed with two or three 5-cc. portions of reagent in order to prevent any precipitation of metallic sulfates by the alcoholic washing fluid. Experiment has shown that it is preferable to wash the sodium precipitate with a wash liquid prepared by freshly saturating 95% alcohol with the triple acetate precipitate rather than to wash with pure 95% alcohol and then apply a washing correction, since the latter varies with the amount of precipitate present and with the rapidity of washing. An important point to be noted is that the quantities of salts given in the original formula for the magnesium uranyl acetate reagent referred to the ordinary grades of uranyl acetate and magnesium acetate then obtainable on the market, the latter salt being in the form of so-called "dried" crystals containing less than the theoretical amount of water of hydration. This latter material has been found to differ in composition depending upon its source and since it has now been found possible to obtain clear crystallized magnesium acetate containing the theoretical percentage of water, it is preferable to

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[1] Caley and Foulk, THIS JOURNAL, 51, 1664 (1929).

use this salt in the preparation of the reagent. Based on the employment of salts containing the theoretical percentage of water of hydration the formula of the reagent has been modified to read as follows.

SOLUTION A		SOLUTION B	
Uranyl acetate ($2H_2O$)	90 g.	Magnesium acetate ($4H_2O$)	600 g.
Glacial acetic acid	60 g.	Glacial acetic acid	60 g.
Water	to 1000 cc.	Water	to 1000 cc.

Prepared on this basis more uniform and satisfactory results are obtained.

Materials

Standard Sodium Chloride Solution.—This solution, used as the basis of the experiments, was made by dissolving 2.5418 g. of the purified and carefully dried salt in water and making the solution up to one liter. Each cubic centimeter of this solution contained 0.0010 g. of sodium.

Aluminum Sulfate.—Since it was not found possible to obtain a sample of this salt that did not contain appreciable quantities of sodium, the material had to be especially prepared. For this purpose a quantity of U. S. Bureau of Standards melting point aluminum was dissolved in dilute sulfuric acid and $Al_2(SO_4)_3 \cdot 18H_2O$ was crystallized from this solution and dried in the usual way. The salt thus prepared gave no flame test for sodium.

Aluminum Chloride.—There was used an exceptionally pure commercial material that contained no sodium as determined by the flame test.

Chromium Sulfate.—Kahlbaum's $Cr_2(SO_4)_3 \cdot 5H_2O$ was used. The sample employed contained a slight amount of sodium as determined by the flame test and by blank determinations, but the blank was sufficiently small to permit the use of the material in these experiments. The chromium content of the salt was checked and it was found to correspond nearly to the value required by theory.

Ammonium Sulfate.—For experiments on the effect of ammonium salts on the determination of sodium in sulfate solution there was used a sample of "C. P." salt that gave no flame test for sodium.

The Determination of Sodium in the Presence of Aluminum.—In the experiments shown in Table I the calculated amount of pure aluminum sulfate was added to the measured volume of standard sodium solution and the resulting solution was brought to a volume of from five to six cubic centimeters. The reagent was then added and the determination made in the usual way. In cases where 0.500 g. of aluminum was present, it was found necessary to add the reagent to the hot solution for salts separated on cooling due to their high concentration, but since the mixture was rapidly brought to the temperature for precipitation this variation did not affect the determinations. A similar set of experiments made with aluminum chloride gave like results. In neither case was it found that the presence of the aluminum salts resulted in the separation of any undesirable phase or otherwise influenced the practical accuracy of the sodium determinations, although duplicate values as shown by the weights of precipitates failed to agree as well as similar determinations made with sodium present alone.

TABLE I

DIRECT DETERMINATION OF SODIUM IN THE PRESENCE OF ALUMINUM IN SULFATE SOLUTIONS

Aluminum present, g.	Volume of reagent, cc.	Weight of precipitate, g.	Sodium present, g.	Sodium found, g.	Difference, g.
0.500	250	1.6576	0.0250	0.0254	+0.0004
.500	200	1.6464	.0250	.0252	+ .0002
.200	250	1.6526	.0250	.0253	+ .0003
.200	250	1.6304	.0250	.0249	− .0001
.500	125	0.6631	.0100	.0101	+ .0001
.500	125	.6541	.0100	.0100	.0000
.200	125	.6577	.0100	.0100	.0000
.200	125	.6500	.0100	.0099	− .0001
.500	50	.0657	.0010	.0010	.0000
.500	50	.0659	.0010	.0010	.0000
.200	25	.0550	.0010	.0008	− .0002
.200	25[a]	.0645	.0010	.0010	.0000
.200	25[a]	.0669	.0010	.0010	.0000
.500	100	No ppt.	None	None	......

[a] In these two samples the solutions were evaporated to a volume of 3 cc. before adding the reagent.

The Determination of Sodium in the Presence of Chromium.—The results from a similar series of experiments in which chromium was present are shown in Table II. Since the chromium sulfate used did contain a small percentage of sodium (0.026% as determined by averaging a series of closely agreeing blank experiments) a corresponding correction was made

TABLE II

DIRECT DETERMINATION OF SODIUM IN THE PRESENCE OF CHROMIUM IN SULFATE SOLUTIONS

Chromium present, g.	Volume of reagent, cc.	Corr. wt. of precipitate,[a] g.	Sodium present, g.	Sodium found, g.	Difference, g.
0.500	250	1.6301	0.0250	0.0249	−0.0001
.500	250	1.6362	.0250	.0250	.0000
.200	250	1.6438	.0250	.0252	+ .0002
.200	250	1.6331	.0250	.0250	.0000
.500	125	0.6544	.0100	.0100	.0000
.500	125	.6538	.0100	.0100	.0000
.200	125	.6613	.0100	.0101	+ .0001
.200	125	.6591	.0100	.0101	+ .0001
.500	25	.0548	.0010	.0008	− .0002
.500	25	.0552	.0010	.0008	− .0002
.200	25[b]	.0609	.0010	.0009	− .0001
.200	25[b]	.0624	.0010	.0010	.0000

[a] Blank of 0.0387 g. deducted from weight of each precipitate when 0.500 g. of chromium was present and blank of 0.0155 deducted when 0.200 g. of chromium was present.

[b] In these two samples the solutions were evaporated to 3 cc. before adding reagent.

in the determined weight of each precipitate, a procedure justified by the resulting consistency of the values thus obtained and by the fact that in separate experiments solutions of chromium salts free from sodium gave no precipitate with the reagent. The results show that chromium, in sulfate solution at least, does not affect the practical accuracy of the direct sodium determination.

The Influence of Ammonium Salts in Sulfate Solutions.—Since ammonium salts are liable to be present in actual determinations, it was thought advisable to determine the effect of rather high concentrations of ammonium salts, especially in sulfate solutions, this usually being the case in direct sodium determinations involving aluminum or chromium. It was found that moderate to high concentrations of both sulfate and ammonium sometimes resulted in the precipitation of the phase $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ along with the triple acetate precipitate. Experiments on this point (Table III) showed that such concentrations of ammonium and sulfate as can ordinarily be present in 5 cc. of test solution do not result in the precipi-

TABLE III

INTERFERENCE OF AMMONIA SALTS WITH SODIUM DETERMINATIONS IN SULFATE SOLUTION

Aluminum present, g.	Chromium present, g.	Ammonium present, g.	Sulfate present, g.	Volume of reagent, cc.	Sodium present, g.	Key to amount and composition of precipitate[a]
0.200	None	0.500	2.400	25	None	II
.200	None	.500	2.400	50	None	III
.200	None	.500	2.400	100	0.0100	IV
.200	None	1.000	3.731	25	None	I
.200	None	1.000	3.731	50	None	II
.200	None	1.000	3.731	100	None	III
.200	None	1.000	3.731	100	0.0100	IV
.500	None	1.000	5.334	25	None	I
.500	None	1.000	5.334	50	None	II
.500	None	1.000	5.334	100	None	III
None	0.200	1.000	3.217	25	None	I
None	.200	1.000	3.217	50	None	III
None	.200	1.000	3.217	100	None	III
None	.200	0.500	1.885	100	0.0100	IV
None	.200	1.000	3.217	100	.0100	IV
None	.500	0.500	2.717	25	None	III
None	.500	.500	2.717	100	None	III
None	.500	1.000	4.048	25	None	I
None	.500	1.000	4.048	50	None	II
None	.500	1.000	4.048	100	None	III

[a] I. Heavy precipitate of $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. II. Slight precipitate of $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. III. No precipitate. IV. Pure precipitate of sodium magnesium uranyl triacetate giving quantitative results for the amount of sodium present.

tation of this undesirable phase providing a sufficient volume of reagent is used. The precipitation of this double salt is, of course, not peculiar to sulfate solutions containing aluminum and chromium but is a general effect governed by the concentration of magnesium, ammonium and sulfate in the solution obtained by mixing test solution and reagent. In general this source of error may be avoided safely by keeping the ammonium salt concentration down to a minimum and using an ample volume of reagent when making direct sodium determinations in sulfate solution. When working with sulfate solutions containing aluminum or chromium it is desirable on another account to keep the ammonium concentration down to a minimum since the ammonium alums are difficult to keep in solution when evaporating to the small volume required by this procedure for sodium. In working with chloride solutions containing aluminum or chromium no particular precautions need be taken in regard to the ammonium salt concentration.

Applications.—In addition to the experiments detailed above, a number of determinations of sodium have been made in commercial samples containing aluminum or chromium, including metallic aluminum, minerals and salts. Satisfactory results have been obtained in these cases, showing that the direct method for sodium may be safely applied to a diversity of materials containing these elements.

Summary

1. It has been shown that the direct magnesium uranyl acetate method for sodium is applicable in the presence of aluminum and chromium.

2. The undesirability of having a high concentration of ammonium salts when making direct sodium determinations in sulfate solution has been pointed out.

PRINCETON, NEW JERSEY