Summary

1. Accurate electromotive force measurements of the cells

$$Ag \mid AgCl \mid NaCl\,(m) \mid Na_xHg \mid NaCl\,(0.1) \mid AgCl \mid Ag$$

have been made at 0, 12.5, 15, 20, 25, 30, 37.5 and 40°.

2. The first order difference of the electromotive force varies linearly with the temperature. This fact helps considerably in obtaining the electromotive forces at 5° temperature intervals and affords a very accurate method of obtaining the constants of the equation which expresses the variation of the electromotive force with the temperature.

3. By a graphical method based upon first order differences, the temperature coefficients of electromotive force have been computed, as well as the partial molal heat content decrease of transfer from the concentrated to dilute solutions. This quantity is negative at the lower temperatures and becomes less negative as the temperature rises, reaching zero and assuming positive values in the vicinity of 40°. Since this change takes place uniformly, positive values are to be expected at the higher temperatures. If this is the case, then the activity coefficient will pass through a maximum and decrease with increasing temperature.

4. The activity coefficients at 0, 25 and 40° have been computed by Hückel's equation.

5. Accurate values of the activity coefficients at 0, 5, 10, 15, 20, 25, 30, 35 and 40° have been computed. At constant composition, they increase somewhat with the temperature and reach a maximum at about 40°.

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ERRORS INVOLVED IN THE DETERMINATION OF MINUTE AMOUNTS OF SODIUM BY THE MAGNESIUM URANYL ACETATE METHOD

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In former papers in this series[1] attention was directed almost entirely to the errors involved in the direct determination of amounts of sodium ranging from one milligram upward. As far as the writer is aware, no systematic experiments have been made on the determination of smaller amounts than this by the particular procedure considered here. Due to the fact that the method has been applied to the determination of amounts of sodium below one milligram in various materials, it seemed advisable to make a systematic series of analyses in order to determine the errors in-

[1] (a) Caley and Foulk, THIS JOURNAL, **51**, 1664–74 (1929); (b) Caley, *ibid.*, **52**, 1349–53 (1930); (c) Caley and Sickman, *ibid.*, **52**, 4247–51 (1930).

herent in such estimations. In the following experiments the general procedure outlined in previous papers was followed using as a reference standard a carefully prepared solution of sodium chloride each cubic centimeter of which was equivalent to 0.10 mg. of sodium. Special modifications of the general method, used for experimental purposes in the following test analyses, are given in the proper places. It should be mentioned here, however, that in these determinations the precipitates were in all cases collected and weighed in medium-porosity, sintered-glass filtering crucibles instead of in Gooch crucibles as previously recommended. For this particular precipitate the use of glass crucibles has been found to lead to greater accuracy and convenience, especially the latter, since the salt can be dissolved out by simple washing with water leaving the vessels, after drying, unchanged in weight and ready for the next determination.

Precipitation with Regular Reagent.—In the first series of experiments, the results of which are shown in Table I, a 5-cc. volume of solution containing the stated amount of sodium was taken for each determination, 100 cc. of magnesium uranyl acetate reagent[1c] was added and the determination was completed in the usual way with particular regard to the condition of vigorous motor stirring which was found especially essential to the initiation of the separation of the triple acetate precipitate in these experiments involving such small amounts. Due to the delay sometimes encountered before precipitation began, the stirring time in all these determinations was extended to one hour. The results shown are not from selected determinations but are all the values obtained in one set of experiments. When it is considered that this is not intended as a micromethod it will be seen that the results obtained down to and including the 0.20 mg. quantity are, in general, satisfactory with the possible exception of the first value for the 0.30 mg. amount. It was found that amounts of sodium less than 0.20 mg. cannot be determined by the general method previously recommended.

TABLE I

DETERMINATIONS OF MINUTE AMOUNTS OF SODIUM

Reagent used	Sodium present, mg.	Ppt., mg.	Sodium found, mg.	Error, mg.	Reagent used	Sodium present, mg.	Ppt., mg.	Sodium found, mg.	Error, mg.
Reg.	0.50	29.1	0.45	−0.05	Sat.	0.20	11.2	0.17	−0.03
Reg.	.50	36.9	.56	+ .06	Sat.	.20	17.4	.27	+ .07
Reg.	.50	31.9	.49	− .01	Sat.	.20	16.4	.25	+ .05
Sat.	.50	37.3	.57	+ .07	Reg.	.10	2.6	.04	− .06
Sat.	.50	38.3	.59	+ .09	Reg.	.10	2.5	.04	− .06
Reg.	.30	13.6	.21	− .09	Sat.	.10	1.7	.03	− .07
Reg.	.30	21.2	.32	+ .02	Sat.	.10	3.5	.05	− .05
Reg.	.20	11.4	.17	− .03	Sat.	.10	7.2	.11	+ .01
Reg.	.20	13.3	.20	.00	Sat.	.10	2.6	.04	− .06
Reg.	.20	15.0	.23	+ .03					

Precipitation with Saturated Reagent.—In view of the fact that the usual procedure was found to fail at a certain point, it was thought that a more concentrated reagent would bring about the quantitative precipitation of lower amounts of sodium notwithstanding the large total volume of solution involved. A reagent of the composition given below was therefore prepared, the two solutions being formed and mixed in the usual manner.

Solution A		Solution B	
Uranyl acetate ($2H_2O$)	100 g.	Magnesium acetate ($4H_2O$)	700 g.
Glacial acetic acid	60 g.	Glacial acetic acid	60 g.
Water	to 1000 cc.	Water	to 1000 cc.

Since this reagent is one of practically the maximum possible concentration, it is designated in the following experiments as saturated reagent. When used in a series of determinations similar to those first mentioned it is apparent, from the values shown in Table I, that the saturated reagent does not aid much in the quantitative precipitation of even 0.10 mg. of sodium and that it has the disadvantage of tending to make the results for the larger amounts high in value. The error in this direction caused by the use of the more concentrated reagent was found to be due largely to the difficulty of preventing slight supersaturation of the saturated reagent with triple acetate precipitate in the course of its preparation. It should be noted, however, that this highly concentrated reagent has been found to have practical application in cases where it is not possible to reduce the solution from a given sample to the required volume of 5 cc. or less. Experiments have shown that the addition of a suitable volume of saturated reagent to a larger volume of solution (not more than 10 cc.) gives values for sodium determinations made by this method that are as satisfactory as those obtained by the usual procedure. The first four experiments shown in Table II are illustrative of this point. The first two determinations indicate the low results obtained when an attempt is made to estimate the

Table II

Determinations under Varied Conditions

Reagent used	Solution volume, cc.	Sodium present, mg.	Ppt., mg.	Sodium found, mg.	Error, mg.
Reg.	10	0.20	0.9	0.01	−0.19
Reg.	10	.50	23.5	.36	− .14
Satd.	10	.20	11.8	.18	− .02
Satd.	10	.50	34.6	.53	+ .03
Reg.	1	.10	5.6	.09	− .01
Reg.	1	.10	5.9	.09	− .01
Reg.	5	.20[a]	11.5	.18	− .02
Reg.	5	.50[a]	40.3	.62	+ .12
Satd.	5	.20[a]	25.3	.39	+ .19
Satd.	5	.50[a]	43.4	.66	+ .16

[a] 100 mg. of potassium also present.

given amounts of sodium by precipitation in a solution volume of 10 cc. with 100 cc. of regular reagent. The second pair of experiments shows the substantially correct results obtained with saturated reagent under the same conditions with respect to the amounts of sodium present and volumes used.

Determinations with Small Volumes of Solution and Reagent.—By reducing the volume of solution employed in a determination, or, preferably, both the solution volume and the reagent volume in the same proportion, no difficulty is experienced in determining 0.10 mg. of sodium as illustrated by the two typical results shown in Table II, which were obtained by precipitation in 1.0 cc. of solution with 25 cc. of reagent. Even smaller amounts can be determined thus, so that in some cases the use of these smaller volumes may be a desirable procedure. In general, however, when operating on actual samples, the use of less than the recommended 5 cc. of solution and 100 cc. of reagent is often impractical due to interference caused by (a) the presence of sparingly soluble or soluble salts in amounts sufficient to render impossible the reduction of the solution to a smaller volume, (b) the presence of other than small amounts of potassium or (c) the simultaneous presence of sulfates and ammonium salts. Since the practical accuracy of direct methods using either magnesium uranyl acetate reagent or zinc uranyl acetate reagent hinges upon the avoidance of gross errors caused by the precipitation of any phase except the desired one, the increased sensitivity or accuracy obtained through the use of smaller volumes is reached only at the risk of errors greater than those intended to be avoided, especially when analytical samples of the usual weight are taken.

Determinations in the Presence of Potassium.—Since the case might often arise of determining these small weights of sodium in the presence of amounts of potassium many times larger, it was thought advisable to make experiments on this point although it has already been demonstrated that up to certain limits potassium does not, in general, interfere in this method. In Table II are shown four typical results that indicate the effect of an amount of potassium either two hundred or five hundred times the weight of sodium being determined. Apparently in such extreme cases the errors tend to be positive ones and they are more marked when saturated reagent is used, another reason for employing a reagent of the proper recommended concentration for determinations by this procedure. With less disproportionate ratios between the amounts of potassium and sodium correspondingly smaller errors occur and the results are then similar to those obtained with sodium present alone.

Results on Actual Samples.—Numerous test analyses have indicated that low percentages of sodium may be directly determined satisfactorily in various materials, the errors occurring being similar to those found in the

preceding experiments. Results obtained on a sample of reagent grade chromium sulfate (green modification) are shown in Table III. In order to place samples of this salt, having the given weights, in sufficiently small volumes of solution it was found necessary to dissolve them in hot water, then add the reagent with rapid mixing and finally complete the determinations in the usual way. This variation is often a necessary expedient when large samples must be taken. In the first set of experiments (A) in the table is recorded a series of results obtained by this procedure using varying sample weights, varying volumes of solution and the usual volume of reagent. In order to obtain some idea as to whether or not the satisfactorily duplicated results of series A were actually an accurate measure of the percentage of sodium in the material, a second series of determinations (B) was made by a method devised to test this point. In these an accurately measured volume of sodium chloride solution containing 1.00 mg. of sodium was added to each sample before precipitation. A weight of sodium magnesium uranyl triacetate corresponding to this amount of added sodium was then subtracted from the total weight of precipitate obtained in each case leaving the precipitate weights shown, which presumably represent the amounts of sodium originally present in the samples.

TABLE III

DETERMINATIONS OF SODIUM IN REAGENT GRADE CHROMIUM SULFATE

Series	Sample, g.	Soln., volume, cc.	Ppt., g.	Sodium, %
	1.0000	2–3	0.0106	0.016
	2.0000	4–5	.0277	.021
A	2.3170	5	.0303	.020
	2.3170	5	.0266	.018
	2.5000	5	.0297	.018
	0.9268	2–3	.0125	.021
B	0.9268	2–3	.0110	.018
	2.3170	5	.0285	.019
	2.3170	5	.0281	.019
	2.0000	5	.0366	.028
C	2.0000	5	.0360	.028
	1.0000	2–3	.0141	.022
	2.5000	5	.0411	.025

It will be seen that the results found in this manner agree satisfactorily among themselves and with those of the previous series, thus demonstrating that the values obtained by the direct method in the first instance were substantially correct. The final series of experiments shown in Table III were made to see if high results are liable to ensue when a reagent of excessively high concentration is employed for determinations made on actual samples and the results confirm the findings obtained on pure sodium chloride solutions recorded in the first part of the paper.

To determine whether or not different workers can obtain concordant values in the direct determination of low percentages of sodium, a sample of "C. P." crystallized aluminum sulfate of well-known make was examined independently by three analysts. Analyst A had previous experience with the procedure while the other two analysts had not used it before. The satisfactory concordance of results thus independently arrived at is demonstrated by the sets of values shown in Table IV.

TABLE IV

RESULTS OBTAINED INDEPENDENTLY ON THE SAME SAMPLE OF "C. P." ALUMINUM SULFATE BY DIFFERENT ANALYSTS

Analyst	Sample, g.	Ppt., g.	Reported values for sodium To third decimal, %	To second decimal, %
A	2.0000	0.3043	0.233	0.23
	2.0000	.3132	.240	.24
B	2.0000	.3035	.232	.23
	2.0000	.2992	.229	.23
C	1.5911	.2378	.229	.23
	1.6830	.2471	.225	.23

Determinations made on various other materials where this method is applicable have shown, in general, that satisfactory results are obtained as long as the quantity of sodium present is not less than 0.2 mg., a matter that can usually be regulated by the size of the sample taken.

Summary

Experiments on pure solutions and on commercial samples have shown, in general, that small amounts of sodium may be determined satisfactorily by the direct magnesium uranyl acetate method as long as the amount present does not fall below 0.2 mg. Lesser weights may be determined in special cases by the use of unusually small volumes of solution and reagent.

The use of a more concentrated reagent leads to high results with the usual procedure and is not helpful in the quantitive precipitation of minute quantities of sodium.

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