

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

**THE INDIRECT VOLUMETRIC DETERMINATION OF SODIUM
BASED ON THE REDUCTION AND TITRATION OF THE
URANIUM IN MAGNESIUM SODIUM URANYL ACETATE¹**BY N. HOWELL FURMAN, EARLE R. CALEY AND IRL C. SCHOONOVER²

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Introduction

The advantages of the direct gravimetric determination of sodium as hydrated sodium magnesium uranium triacetate ($\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6.5\text{H}_2\text{O}$) have been demonstrated by Caley and Foulk.³ They have also described a rapid colorimetric method based upon color of the uranium salt; this method is limited to quantities of 5 mg. or less of sodium.

Caley⁴ obtained good results in the volumetric estimation of sodium by titration of the uranium in the solution of the triple acetate precipitate with standard sodium phosphate solution. The reduction of the uranium, followed by titration with standard oxidizing agent, should offer even greater advantages because twice as much standard solution of equivalent strength should be used, as in the sodium phosphate procedure.

Subsequent to the completion of the work which is described in this paper, Dobbins and Byrd⁵ have described a method for the indirect determination of sodium by titration of the uranium in the sodium-zinc-uranyl acetate precipitate with standard sodium hydroxide; 10 moles of sodium hydroxide are used up per mole of precipitate.

Nau⁶ proposed the indirect determination of sodium by reduction of the uranium of the triple acetate precipitate by zinc. Kahane⁷ proposed that aluminum or copper be used as a reducing agent. In both cases the reduced solution was poured or filtered away from the excess of metal. The questions of over-reduction and of oxidation of quadrivalent uranium by air in hot solutions were not studied.

In this investigation we have applied the results of a study of the potentiometric determination of uranium that has been made by Furman

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² Merck Fellow in Chemistry.

³ Caley and Foulk, *THIS JOURNAL*, **51**, 1664 (1929); in this paper the modified reagent suggested by Caley and Sickman, *ibid.*, **52**, 4247 (1930), was used. Applications of the method are described by Caley and Foulk, *J. Am. Water Works Assoc.*, **22**, 970 (1930); Caley, *Ind. Eng. Chem., Analyt. Ed.*, **1**, 191 (1929).

⁴ Caley, *THIS JOURNAL*, **52**, 1349 (1930).

⁵ Dobbins and Byrd, *ibid.*, **53**, 3288 (1931).

⁶ Nau, *Bull. soc. phar. Bordeaux*, **65**, 67 (1927); *Chem. Abstracts*, **24**, 4236 (1930).

⁷ Kahane, *Bull. soc. chim.*, [4] **47**, 382 (1930).

and Schoonover.⁸ In this study the presence of chloride was found to be undesirable, but moderate amounts of acetate or of acetic acid did not influence the accuracy of the uranium determination, when standard permanganate or ceric sulfate was used to reoxidize the tri- and quadrivalent uranium which are produced when the uranium solution is passed through the Jones reductor. Ewing and Wilson⁹ found that the presence of hydrochloric acid caused the end-point of the process $U^{III} \rightarrow U^{IV}$ to be so slow as to be impractical; they reported that the presence of acetate caused the end-point of the oxidation $U^{IV} \rightarrow U^{VI}$ to be erratic. Further tests of the effect of acetate (not detailed here), together with the numerous determinations which are presented in this paper, have convinced us that the acetate which is present in the sodium magnesium uranyl acetate precipitates is without influence upon the accuracy of the uranium titration.

The majority of the determinations here presented were made by determining potentiometrically the two inflections in the titration of the reduced uranium solution. A few determinations were made by the more rapid procedure of removing the trivalent uranium by aeration of the solution. The end of this process is detected potentiometrically; a sudden change of about 0.4 volt occurs (cell: normal calomel electrode, satd. potassium sulfate, uranium solution, Pt). The air is then displaced by a rapid stream of carbon dioxide, and the quadrivalent uranium is titrated at 85–90°.

It was found that the reduced uranium solution could be aerated to oxidize the trivalent uranium, after which a measured excess of standard ceric sulfate was added. Oxidation of the uranium to the hexavalent condition was complete in less than five minutes. The excess of ceric sulfate was determined by back-titration with ferrous sulfate (freshly standardized potentiometrically against ceric solution). This procedure, though indirect, greatly simplifies the volumetric determination of uranium. The application of this simplified method to the determination of sodium was studied.

Experimental

Materials and Apparatus.—The apparatus described by Furman and Schoonover⁸ was used. The top of the reductor was provided with a Gooch crucible holder, so that the sodium magnesium uranyl acetate could be dissolved in 2% sulfuric acid and drawn directly from the crucible into the reductor by suction.

The magnesium uranyl acetate reagent was prepared as described by Caley and Sickman.³ The sodium precipitate was washed with alcohol saturated with the precipitate, and the excess of alcohol was removed by drying. The technique described by Caley and Foulk⁴ was followed in the precipitation and gravimetric determinations of sodium, and that of Furman and Schoonover in the volumetric work.

Known sodium solutions were prepared from pure dry sodium chloride and stored in bottles of Pyrex glass.

⁸ Furman and Schoonover, *THIS JOURNAL*, **53**, 2561 (1931).

⁹ Ewing and Wilson, *ibid.*, **53**, 2105 (1931).

In the preliminary test analyses known amounts of the sodium chloride solutions were pipetted out, evaporated to 5 cc. or less, and treated with the proper amount of the magnesium uranyl acetate reagent. The amounts of sodium were determined gravimetrically, and then by titration of the solution of the precipitate after reduction of the uranium. In Table I are given the results of a number of determinations made with standard permanganate. The percentages of UO_2 in the precipitates are derived from the weights of the precipitates and the volumes of the permanganate used. It is probable that the gravimetric determinations are better values for the amounts of sodium actually present than those calculated (column 1) from the amounts of sodium solution pipetted out.

TABLE I

INDIRECT VOLUMETRIC DETERMINATION OF SODIUM WITH 0.1147 *N* KMnO_4

No.	1 Na present calcd., g.	2 Na found grav., g.	3 Na found vol., g.	4 KMnO_4 used, cc.	5 Error grav., mg.	6 Error vol., mg.	7 UO_2 in ppt., %
1	0.0200	0.02003	0.01999	45.48	0.03	-0.01	53.83
2	.0200	.02002	.01998	45.46	.02	-.02	53.83
3	.0100	.00996	.00977 ^a	22.22	-.04	-.23	52.98 ^a
4	.0100	.00999	.00986 ^a	22.42	-.01	-.14	53.20 ^a
5	.0100	.00998	.00983 ^a	22.38	-.02	-.17	53.16 ^a
6	.0100	.00999	.00999	22.74	-.01	-.01	53.92
7	.0100	.00999	.00999	22.74	-.01	-.01	53.93
8	.0100	.01000	.00998	22.73	.00	-.02	53.88
9	.0100	.01000	.01000	22.77	.00	.00	53.69
10	.0050	.00497	.00499	11.37	-.03	-.01	54.48
11	.0050	.00493	.00498	11.33	-.07	-.02	54.48
12	.0050	.00495	.00499	11.37	-.05	-.01	54.42
13	.0010	.00104	.00102	2.34	.04	.02	54.27
14	.0010	.00100	.00100	2.27	.00	.00	54.00

^a These three determinations were known to be imperfect because of loss of uranium solution by diffusion into an improperly constructed salt bridge.

A similar series of determinations was made using standard ceric solutions in the titrations. The results are presented in Table II.

TABLE II

INDIRECT VOLUMETRIC DETERMINATION OF SODIUM USING STANDARD CERIC SULFATE
Determinations 2-4 and 6-8 were made with 0.1043 *N* ceric sulfate

No.	1 Na present calcd., g.	2 Na found grav., g.	3 Na found vol., g.	4 $\text{Ce}(\text{SO}_4)_2$ used, cc.	5 Error grav., mg.	6 Error vol., mg.	7 UO_2 in ppt., %
1	0.0130	0.01309	0.01302	31.43	0.09	0.02	53.56 ^a
2	.0100	.01000	.00999	24.99	.00	-.01	53.77
3	.0100	.00999	.00998	24.97	-.01	-.02	53.84
4	.0100	.00999	.01000	25.02	-.01	.00	53.97
5	.0080	.00793	.00793	19.16	-.07	-.07	53.91 ^a
6	.0050	.00495	.00498	12.46	-.05	-.02	54.29
7	.0050	.00496	.00499	12.48	-.04	-.01	54.20
8	.0050	.00495	.00499	12.49	-.05	-.01	54.40

^a One of us (C.) made the gravimetric determination, and another (F.) the volumetric using 0.1079 *N* ceric sulfate, without information as to the amount of sodium until after the titrations had been made.

Rapid Titration of Reduced Uranium Solutions.—From thirty to forty minutes are required for the reduction of the uranium and the potentiometric titration. An atmosphere of carbon dioxide is necessary in the direct potentiometric titration. We have found that the determination of the reduced uranium may be greatly simplified, and the use of carbon dioxide dispensed with.

Procedure.—The uranium solution, at room temperature, is passed through a Jones reductor. The reduced solution is stirred for five minutes while a rapid stream of air is being passed through. The end of this process may be determined potentiometrically, although this is not necessary. A measured excess of standard ceric sulfate is added, and the solution is stirred vigorously for five minutes. The excess is then determined by back-titration with standardized ferrous sulfate solution.¹⁰ Some results of this method of determination are given in Table III. In each case 24.75 cc. of 0.2115 *N* Ce(SO₄)₂ was used.

TABLE III
DETERMINATION OF URANIUM WITH 0.2115 *N* CERIC SULFATE

	1 Uranium present, g.	2 FeSO ₄ used, cc.	3 Ce(SO ₄) ₂ used, cc.	4 Uranium found, g.	5 Error, mg.
1	0.2792	37.58	11.10	0.2795	+0.3
2	.2792	37.63	11.06	.2783	— .7
3	.2792	37.55	11.08	.2790	— .2
4	.2779	37.68	11.05	.2783	+ .4
5	.2779	37.70	11.04	.2780	+ .1
6	.2779	37.68	11.05	.2783	+ .4

Application to Sodium Determination.—The rapid titration method was applied to the determination of sodium in portions of a sodium chloride

TABLE IV
DETERMINATION OF SODIUM BY RAPID INDIRECT METHOD

Sodium present, g.	Ce(SO ₄) ₂ used by U ^{IV} cc. of 0.2080 <i>N</i>	Sodium found, g.	Error, mg.
0.0050	6.32	0.00504	0.04
.0050	6.28	.00501	.01
.0050	6.23	.00497	— .03
.0100	12.63	.01007	.07
.0100	12.62	.01006	.06
.0200	25.16	.02006	.06
.0200	25.14	.02004	.04

¹⁰ The potentiometric method was used. In some of the determinations listed in Table IV, it was found that erioglaucone indicator changed color at the potentiometric end-point, and that the presence of uranium did not interfere [see Furman and Wallace, *THIS JOURNAL*, 52, 2357 (1930)]. The indicator method was proved to be accurate for this titration by comparative study with the potentiometric method in a number of determinations which will not be described here.

solution of known concentration. The results are presented in Table IV. From 15 to 35 cc. of 0.2080 *N* ceric sulfate was added to the solutions of U^{IV} .

Applications of the Method.—One of us (S.) analyzed a silicate the composition of which was unknown to him. The samples of the material were treated in a platinum dish with hydrofluoric acid until decomposition was effected, and finally the fluorides were transposed to sulfates with a very small excess of sulfuric acid; most of the latter acid was volatilized. The sodium was then precipitated, and determined both gravimetrically and volumetrically.

	1	2	3	4
Wt. of sample, g.....	0.3334	0.3100	0.3210	0.3056
Wt. of triple acetate, g....	0.3995	0.3662	0.3785	0.3610
Na ₂ O, grav., %.....	2.46	2.43	2.42	2.43
Cc. stand. soln.....	15.48	15.00	12.98	12.42
Na ₂ O, vol. %.....	2.28	2.37	2.40	2.41

Determinations 1 and 2 were made with 0.0949 *N* ceric solution, and 3 and 4 with 0.1147 *N* permanganate solution.

The material was a Bureau of Standards feldspar containing 2.38% of Na₂O according to the Bureau. Caley found an average of 2.33% Na₂O by the direct gravimetric triple acetate method after decomposing the sample by the J. Lawrence Smith method.

The sodium present in a sample of crystallized aluminum sulfate was determined by the aeration and direct potentiometric procedures. Found: 0.220, 0.220, 0.226; present 0.231% of sodium.

The rapid procedure (aeration, addition of excess of Ce(SO₄)₂ and back-titration) was applied to the determination of sodium in a mixture of pure sodium and potassium chlorides of composition unknown to the operator (S). The ceric sulfate was 0.2080 *N*.

	1	2	3	4
Wt. of sample, g.....	0.1390	0.1410	0.1837	0.1468
Ce(SO ₄) ₂ used, cc.....	10.38	10.37	13.84	11.14
Sodium found, %.....	5.95	5.86	6.01	6.05

The material contained 5.90% of sodium (15% NaCl, 85% KCl). These results were considered to be satisfactory, especially in view of the large proportion of potassium in the sample.

Discussion.—The results which have been presented prove that permanganate or ceric sulfate solutions standardized against pure sodium oxalate may be used for the indirect estimation of sodium; with good technique the absolute error in the determination of the sodium should be less than 0.1 mg.

The variations in the percentage of UO₂ in the precipitate are of considerable interest. For the larger amounts of sodium, the percentage of

UO_2 is distributed within a small range of the value 53.79% which is calculated on the basis that the triple salt contains 6.5 molecules of water of crystallization when formed by Caley and Foulk's procedure. When small amounts of sodium are precipitated, there is apparently a change in the composition of the precipitate during washing and the percentage of uranyl is high. Caley attributes this change to partial solution of magnesium acetate during the washing. The sodium-uranium ratio appears to be practically constant for amounts of sodium as low as 1 mg. The indirect volumetric method appears to offer advantages over the gravimetric for the determination of amounts of sodium ranging from 1 to 10 mg.

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Summary

The sodium present in triple sodium magnesium uranyl acetate may be determined indirectly by reduction and titration of the uranium. The method appears to offer advantages over other methods in respect to accuracy when quantities of sodium below 10 mg. are to be determined.

The volumetric method gives significant evidence of the constancy of composition of the precipitates obtained from amounts of sodium ranging from 0.01 to 0.02 g. Although the percentage of UO_2 is somewhat higher than the theoretical value in precipitates of small weight, the ratio of sodium to uranium in these precipitates appears to be constant in the range studied.

A technique for the rapid indirect determination of uranium or of sodium has been developed.

PRINCETON, NEW JERSEY