

[CONTRIBUTION FROM THE UNIVERSITY OF NORTH CAROLINA]

## A VOLUMETRIC METHOD OF DETERMINING SODIUM

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The development of a rapid and accurate volumetric method of determining sodium has been the subject of study of many investigators. Practically all of the volumetric methods thus far developed are based upon the precipitation of the sodium as sodium magnesium uranyl acetate and the subsequent titration of the uranium content of the triple salt. Caley<sup>1</sup> has proposed a volumetric method of estimating sodium, in which the sodium content of the sample is precipitated as sodium magnesium uranyl acetate, and the uranium content of the triple salt titrated with standard disodium phosphate using potassium ferrocyanide as an outside indicator. Although the method gives concordant results, it suffers disadvantage of an outside indicator, and it is necessary that special precautions be taken that none of the precipitate comes in contact with the indicator. Kahane<sup>2</sup> and Nau<sup>3</sup> have proposed volumetric methods in which the sodium is precipitated as sodium magnesium uranyl acetate, the uranium of the triple salt reduced and then titrated with standard permanganate.

The volumetric method outlined below is based upon the precipitation of sodium as sodium zinc uranyl acetate in the usual way and the subsequent titration of the uranium by standard sodium hydroxide. This volumetric method is quite rapid and simple.

## Preparation of Reagents

	ZINC URANYL ACETATE		
Solution A			Solution B
Uranyl acetate, c. p.	85 g.	Zinc acetate, c. p.	200 g.
Acetic acid (99.5%)	50 cc.	Acetic acid (99.5%)	25 cc.
Distilled water	400 cc.	Distilled water	250 cc.

Each solution was prepared by mixing the constituents in a Pyrex beaker and heating to a temperature just below the boiling point until all of the solid had dissolved, then the two solutions were mixed and allowed to stand in a Pyrex container for several hours so that any sodium in the reagents would be precipitated, leaving a solution saturated with the triple salt. The solution was then filtered into a Pyrex container and preserved.

**Sodium Hydroxide and Hydrochloric Acid.**—Standard solutions of  $N/2$  sodium hydroxide and  $N/2$  hydrochloric acid were prepared by the usual methods of standardization.

## Experimental

**Method of Analysis.**—Samples of the sodium salt which should not contain more than 20 to 25 mg. of sodium are weighed into 150-cc. Pyrex beakers and dissolved in 2

<sup>1</sup> Caley, *THIS JOURNAL*, 52, 1349 (1930).

<sup>2</sup> Kahane, *Bull. soc. chim.*, [4] 47, 382-404 (1927).

<sup>3</sup> Nau, *Bull. soc. phar., Bordeaux*, 65, 67 (1927).

to 3 cc. of distilled water. If dilute solutions are to be analyzed for sodium, aliquots of the solution which will contain approximately this quantity of sodium should be taken and evaporated to about 3 cc. Then twenty to thirty cc. of the precipitating agent or 1 cc. for each mg. of sodium present, is added and precipitation induced by stirring. Due to the fact that sodium zinc uranyl acetate is appreciably soluble above 20°, the temperature of the solution should be maintained below this point, preferably by placing the beakers in a pan of cracked ice. The beakers should remain in contact with the ice for an hour or longer, and should be stirred at intervals during this time. The beakers are then removed and the solution filtered through a Gooch crucible by means of suction. Any adhering precipitate is washed from the beakers by using small portions of the mother liquor. In order to do this effectively, it was found expedient to use a small wash bottle such as a 12-cm. test-tube as the volume of the precipitating agent seldom exceeds 30 cc. The precipitate is washed three or four times using 2-cc. portions of 95% alcohol which has been saturated with the triple salt, and then dissolved in about 100 cc. of distilled water. Five drops of phenolphthalein are added to the solution, and standard sodium hydroxide run in from a buret until an excess is indicated by the appearance of the characteristic red coloration. A yellow precipitate, which will settle very readily, is formed upon the addition of the base. The solution is then heated to incipient boiling. If the red coloration disappears during the course of the boiling, again 3 to 5 cc. of the base is run in and the solution heated for about five minutes. This treatment is continued until the red coloration persists after five minutes of incipient boiling. The heating is done in a covered beaker, and any adhering liquid is washed from the watch glass and the excess base titrated with standard hydrochloric acid. The end-point should be ascertained by allowing the precipitate to settle after each addition of hydrochloric acid and viewing the supernatant liquid above the precipitate.

It was surprising to note in some of the preliminary titrations that instead of eleven equivalents of hydroxyl being required for each molecule of the triple salt, approximately ten equivalents were used. Consequently the milliequivalent weight of sodium chloride was determined and the values obtained are recorded in Table I.

TABLE I  
MILLIEQUIVALENT WEIGHT OF SODIUM CHLORIDE

0.005846	0.005841
.005854	.005844
.005852	.005848
.005835	Average, 0.005845

**Standardization of Base.**—After seeing that the milliequivalent weight of sodium chloride as determined above is almost exactly one-tenth of its normal value, it appeared possible to standardize a solution of sodium hydroxide against sodium chloride using the above procedure. The validity of the method was tested by weighing definite samples of sodium chloride so as to have about 20 to 25 mg. of sodium, and following the procedure as outlined above. The data listed in Table II for the standardization of sodium hydroxide against sodium chloride show an almost identical normality with that found by the acidimetric methods of standardization.

The reliability of the method for the determination of sodium was tested by weighing definite samples of c. p. sodium chloride and following the procedure as outlined above. The results are shown in Table III.

TABLE II  
EXPERIMENTAL RESULTS

Solution 1		Solution 2	
Sample, g.	N of base	Sample, g.	N of base
0.0498	0.5409	0.0523	0.5514
.0595	.5413	.0851	.5520
.0736	.5407	.0559	.5517
.0634	.5412	.0539	.5502
.0600	.5404	.0518	.5508
.0545	.5400	.0681	.5511
Average, 0.5405		Average, 0.5512	
Against succinic acid, 0.5405		Against succinic acid, 0.5513	

TABLE III  
RESULTS WITH SODIUM CHLORIDE

Series 1		Series 2	
Titrated with 0.5512 N NaOH		Titrated with 0.5405 N NaOH	
Sample, g.	Sodium, %	Sample, g.	Sodium, %
0.0559	39.31	0.0545	39.41
.0539	39.42	.0491	39.35
.0581	39.38	.0654	39.30
.0681	39.36	.0736	39.32
.0851	39.31	.0612	39.30
.0523	39.35	.0498	39.32
Average, 39.35		Average, 39.33	

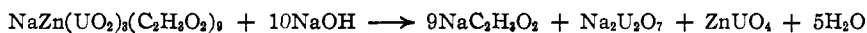
The theoretical value of sodium in sodium chloride is 39.34%.

### Discussion

The effectiveness of this method depends, in a large measure, upon the complete precipitation of the sodium, and all precautions should be taken to this end. Special attention should be paid to the concentration of the precipitating agent, the volume of solution from which the sodium is to be precipitated, and to the temperature, because the error from these sources is greater than any of the others.

In order to approach actual experimental conditions, it may be advisable to standardize the base against sodium chloride rather than an acid. Although, as the data show, the results should be the same, some persons may not detect the end-point at the same colorations, and by standardizing the base against a sodium salt this error would be eliminated. It was found that  $N/2$  sodium hydroxide was the most suitable as the volume usually required was from 15 to 30 cc. on an ordinary sample. The precipitate settles very readily and little time is consumed in this operation; however, it should be called to the attention of the experimenter that a small amount of the suspended precipitate should not be mistaken for the red color of the indicator. After a little practice no difficulty should be encountered in this respect.

While the literature does not afford any information as to the behavior of zinc with uranium salts under the conditions of this method, it was found that under similar conditions, magnesium, barium, calcium and strontium all form insoluble uranates. Consequently, it might be safe to predict that zinc would form a similar compound under these conditions since it occurs in the same group in the periodic table. By taking some sodium di-uranate, suspending it in water, and adding an equivalent quantity of zinc acetate, it was proved qualitatively that zinc enters into combination with uranium because the zinc disappeared from the solution in the form of a precipitate and sodium appeared in the solution in its place. Therefore, the following equation is proposed to show how ten hydroxyls are required for each molecule of the triple salt:



This equation fits in exactly with the experimental facts.

The practical advantages of the volumetric method over gravimetric methods have already been pointed out by Caley. In addition to them, this method offers the following advantages: the ratio of the base to the triple salt being 10:1, the possibility of error is further reduced, since the uranium content of the triple salt alone is titrated, it is independent of the degree of hydration of the triple salt, which is still uncertain; no difficulty should be encountered in using this method as it is nothing more than an acid and base titration using phenolphthalein as an inside indicator.

An attempt will be made to apply this method to the sodium magnesium uranyl acetate precipitate.

### Summary

A rapid and accurate volumetric method of determining sodium has been developed, in which the sodium is precipitated as sodium zinc uranyl acetate, and the uranium content of the precipitate titrated by means of sodium hydroxide.

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