cal case, the authors were unable to detect any effect when the tubes were so clean that complete wetting occurred. On contamination of the tubes with solutions of oleic acid in benzene, finite pressures could be supported. Slight contaminations have more effect than larger ones within certain limits. The results suggest that Jamin action arises in cylindrical tubes because of hysteresis of contact angles. The greatest pressure P' which can be sustained is calculated to be

$$P' = \frac{2\sigma n}{r}(\cos \Theta'_2 - \cos \Theta'_1) + A$$

where Θ'_2 and Θ'_1 are the maximum and minimum values which the contact angles assume, n the number of bubbles in the chain, σ the surface tension, r the radius of the tube and A atmospheric pressure.

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THE VOLUMETRIC ESTIMATION OF SODIUM

BY EARLE R. CALEY

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The direct gravimetric magnesium uranyl acetate method for sodium, which is satisfactory when only a few sodium determinations are required, does not readily lend itself to making a series of such determinations rapidly. While it is true that colorimetric modifications of this method are capable of fulfilling this requirement, they suffer from the disadvantage of a limited range. The procedure given below is the result of experiments directed toward devising a rapid volumetric method suitable for making a series of sodium determinations.

The principles underlying this volumetric method are simple. The sodium is separated from the other elements in the same manner as described in a previous paper[1] but, instead of drying and weighing the precipitate of sodium magnesium uranyl tri-acetate, the latter is dissolved in water containing 4–5% of acetic acid and the uranium is titrated with a standard solution of sodium phosphate using potassium ferrocyanide as an outside indicator. Under the proper conditions the uranium is quantitatively precipitated as di-uranyl hydrogen phosphate, while the magnesium remains in solution. Since the uranium and sodium contents of this precipitate have been shown to be in fixed, definite ratio when it is formed under the correct conditions, a measure of the sodium present is thus obtained. While the titration of uranium with phosphate solution using an outside indicator is not an especially accurate procedure, the errors involved are greatly divided by reason of the favorable weight ratio (31.07:1) of uranium to sodium in the triple acetate precipitate. The result is that

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[1] Caley and Foulk, THIS JOURNAL, **51**, 1664–1674 (1929).

sodium can be quite satisfactorily determined by this volumetric process, as the experimental results show.

Reagents Required

Standard Sodium Chloride Solution.—2.5415 g. of pure and completely dried sodium chloride is dissolved in water and made up to a volume of one liter in a calibrated flask. This solution contains 1 mg. of sodium per cc.

Magnesium Uranyl Acetate Reagent.—This reagent is prepared in the manner described in a former paper.[1]

Standard Sodium Phosphate Solution.—Thirty-five grams of crystallized disodium hydrogen phosphate is made up to one liter. One cc. of this solution theoretically corresponds to 0.00075 g. of sodium. It should be standardized against measured portions of the standard sodium chloride solution.

Potassium Ferrocyanide Paper.—For recognizing the end-point it was found preferable to use potassium ferrocyanide test paper instead of the usual solution, this form giving a sharper end-point. The paper is prepared by immersing large strips of heavy white filter paper in fresh 10% potassium ferrocyanide solution and drying them. It keeps indefinitely in a dark bottle.

Procedure.—The precipitation of the sodium and the washing of the precipitate are carried out as directed in the preceding paper.[1] After washing, the suction is continued for two to three minutes in order to remove most of the adhering alcohol. The precipitate and the asbestos felt of the crucible are then transferred to a small beaker, 2–2.5 cc. of glacial acetic acid is added and the precipitate dissolved in 40–50 cc. of hot water, care being taken also to dissolve any precipitate adhering to the sides of the crucible. The solution thus obtained is heated to 90° and titrated at once with the standard sodium phosphate solution, using potassium ferrocyanide test paper as an outside indicator.

Discussion of the Procedure.—For data regarding the allowable limits of other elements that can be present and for manipulative details on this precipitation reference should be made to the former paper.[1]

It is essential to keep the volume of the solution to be titrated down to 50 cc. When quite small amounts of sodium are to be determined it is preferable to use a volume of 25 cc. Experiments demonstrated that the use of larger volumes introduced a two-fold error due to the solubility of the precipitate and the indistinctness of the end-point. The precipitation of uranium as uranyl phosphate is only complete and rapid in hot solution. The maintenance of a temperature of 90° is not so essential at the beginning of the titration but it must be raised to this point or slightly more at the end in order to insure complete precipitation and the attainment of the correct end-point. The end-point of this titration requires some degree of care and practice but with proper precautions there should be no difficulty. Only the clear liquid free from any suspended precipitate of uranyl phosphate should be taken for testing since, as Kolthoff[2] has previously shown,

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[2] I. M. Kolthoff and H. Menzel, "Volumetric Analysis," Vol. II, p. 257. Translated by N. H. Furman, John Wiley and Sons, Inc., New York, **1929**.

this precipitate is capable of reacting with potassium ferrocyanide and giving after some seconds the characteristic brown color of uranyl ferrocyanide. For the purpose of rapidly withdrawing one or two drops of clear fluid for testing, the writer has found that a simple filtration pipet[3] is a great convenience. The end-point in this titration is the disappearance of the characteristic brown color when a drop of the filtered liquid is allowed to come in contact with potassium ferrocyanide test paper, but it is essential to allow the same time interval to elapse in each case when observing the result of a test since with very dilute uranium solutions the reaction takes place after different time intervals in accordance with the concentration of uranium in the solution. Attempts were made to use certain phenols, which give characteristic color reactions with uranium, as inside indicators in this titration but all of these color reactions were found to be much less sensitive than the reaction between uranyl salts and potassium ferrocyanide. In general, the best results are obtained if exactly the same procedure is followed for making determinations that is used for standardizing the sodium phosphate solution.

Experimental Results

After devising the above procedure a series of tests was made to determine its value and reliability in actual use. A sodium phosphate solution was first prepared and standardized. Table I shows the values obtained on standardization.

TABLE I

STANDARDIZATION OF THE SODIUM PHOSPHATE SOLUTION

Trial no.	Vol. of standard NaCl soln. used, cc.	Sodium titrated, g.	Volume of standard soln. req., cc.	Value of each cc. of sodium phosphate soln. in terms of sodium, g.
1	20.00	0.0200	27.92	0.000716
2	20.00	.0200	28.00	.000714
3	20.00	.0200	27.90	.000717
4	20.00	.0200	27.97	.000715
5	10.00	.0100	13.95	.000717
6	10.00	.0100	14.00	.000714
			Mean value	0.000715

While the results in the separate experiments in the standardization show a not inconsiderable percentage deviation from the mean value, the absolute differences in terms of grams of sodium are so small that these variations are of no practical consequence within the range covered by the method.

This standardized solution was then used to determine the sodium in known amounts of pure sodium chloride. The results appear in Table II.

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[3] For description see E. R. Caley, *Ind. Eng. Chem.*, *Anal. Ed.*, **2**, 77 (1930).

TABLE II

TEST ANALYSES ON KNOWN AMOUNTS OF PURE SODIUM CHLORIDE

Sodium present, g.	Standard soln. req., cc.	Sodium found, g.	Diff., g.	Sodium present, g.	Standard soln. req., cc.	Sodium found, g.	Diff., g.
0.0250	34.60	0.0247	−0.0003	0.0100	13.95	0.0100	0.0000
.0250	34.73	.0248	− .0002	.0050	7.10	.0051	+ .0001
.0200	27.95	.0200	.0000	.0050	7.00	.0050	.0000
.0200	27.90	.0199	− .0001	.0020	3.00	.0021	+ .0001
.0100	14.03	.0100	.0000	.0020	2.95	.0021	+ .0001
.0100	13.93	.0100	.0000	.0010	1.45	.0010	.0000
.0100	13.95	.0100	.0000	.0010	1.50	.0011	+ .0001
.0100	13.90	.0099	− .0001	.0005	0.90	.0006	+ .0001
.0100	14.00	.0100	.0000	.0005	1.05	.0007	+ .0002

These results were considered to be satisfactory although further experiments showed that the method is not always reliable for amounts below 1.0 mg. due to the influence of the end-point error. The procedure, however, leads to useful results down to 0.5 mg. if care is taken to use only a small volume for titration and to standardize the solution with amounts of sodium approximating those being determined.

A further test of the value of this method was made on samples of various materials containing known amounts of sodium. The results appear in Table III. In the case of the sodium potassium tartrate the purified material was simply dissolved in water and the determination made according to the procedure given. The calcium carbonate was first dissolved in hydrochloric acid and this solution was evaporated nearly to dryness. Then the residue was dissolved in water and the determination made on the latter solution. Standard sample No. 1 of the U. S. Bureau of Standards, stated to contain 0.33% of sodium oxide, was used to test the method on rock material. These samples were decomposed by the J. Lawrence Smith method. The sintered mass was extracted with water as usual and the

TABLE III

THE VOLUMETRIC ESTIMATION OF SODIUM IN VARIOUS SUBSTANCES

Material used	Sample taken, g.	Standard soln. req., cc.	Sodium found, %	Sodium present, %
Crystallized sodium potassium tartrate	0.2973	33.70	8.10	8.15[a]
	0.2608	29.85	8.18	
"C. p." calcium carbonate	2.0000	4.05	0.14	0.12[b]
	2.0000	4.25	0.15	
Argillaceous limestone, Bureau of Standards Sample No. 1	0.5010	2.05[c]	0.33 (Na_2O)	0.30 (Na_2O)[b]
	1.0000	3.70[c]	0.32 (Na_2O)	0.32 (Na_2O)[b]
				0.33 (Na_2O)[d]

[a] Based on the theoretical composition. [b] Determined by the gravimetric magnesium uranyl acetate method. [c] This includes the blank on the reagents which amounted to 0.33 cc. This blank was found gravimetrically and then expressed in terms of the titrating solution. [d] According to the U. S. Bureau of Standards.

extract was acidified with hydrochloric acid and evaporated to dryness. The determinations were then made on the water solutions of these residues without removing the calcium. With the exception of the sodium potassium tartrate, the sodium content of each substance was also determined by the gravimetric magnesium uranyl acetate method as a check on the accuracy of the results.

The above results were considered to be satisfactory evidence of the usefulness of the method. It should be mentioned that these values were obtained in a fraction of the time that would be required to obtain the sodium content of such materials by any of the older methods. This volumetric procedure has certain advantages not possessed even by the gravimetric magnesium uranyl acetate method. There is no need, for example, to free the original solution from insoluble and inert suspended matter when using the volumetric method. The error arising from the determination of sodium in the presence of barium when using a reagent containing considerable sulfate is then eliminated for this same reason. Perhaps the greatest practical advantage of this volumetric procedure lies in the fact that sodium may be determined in the presence of small amounts of phosphates without their preliminary removal before proceeding to the sodium determination.

Summary

A rapid volumetric method for the determination of sodium has been described based upon its precipitation as sodium magnesium uranyl acetate and the titration of the uranium content of the precipitate by means of a standard phosphate solution.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

ADDITION COMPOUNDS OF COPPER HALIDES AND SILVER NITRATE WITH BENZYL SULFIDE[1]

BY EUGENE HARVEY HUFFMAN WITH G. MCP. SMITH

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Introduction.—The previously known addition compounds of benzyl sulfide and inorganic metal salts are few in number. Löndahl[2] prepared and analyzed $PtCl_2 \cdot 2(C_7H_7)_2S$, $PtBr_2 \cdot 2(C_7H_7)_2S$, $PtI_2 \cdot 2(C_7H_7)_2S$, $Pt(OH)NO_2 \cdot 2(C_7H_7)_2S$, $Pt(NO_2)_2 \cdot 2(C_7H_7)_2S$ and $PtCl_4 \cdot 2(C_7H_7)_2S$. Herrmann[3] obtained two compounds of the composition $AuCl_2 \cdot (C_7H_7)_2S$ and $AuCl \cdot (C_7H_7)_2S$, and Smith[4] prepared the gold halide compounds $AuBr_2 \cdot (C_7H_7)_2S$,

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[1] Thesis presented to the Graduate School of the University of Washington, in partial fulfilment of the requirements for the degree of Master of Science.

[2] H. Löndahl, *J. prakt. Chem.*, [2] **38**, 521 (1888).

[3] F. Herrmann, *Ber.*, **38**, 2813 (1905).

[4] G. McP. Smith, THIS JOURNAL, **44**, 1769 (1922).