The authors wish to express their appreciation to Dr. D. A. MacInnes for many helpful suggestions and constructive criticisms in the preparation of this manuscript.

Summary

1. A modification of the moving boundary method for determining transference numbers, in which rising boundaries are used, has been studied. In this new method the boundary starts at the surface of the metal electrode, which furnishes the "indicator" ions by electrochemical solution of the metal.

2. When applicable the new method furnishes a simpler means of obtaining boundaries than has been so far proposed. The method also avoids the necessity of making measurements with indicator solutions of varying concentration, since it has been shown experimentally that there is, with this method, automatic adjustment to the condition, $C/C' = T_c/T'_c$. (C and C', and T_c and T'_c, are, respectively, the normality and cation transference number of the leading and indicator solution.)

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A GRAVIMETRIC AND COLORIMETRIC METHOD FOR THE DIRECT DETERMINATION OF SODIUM

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It is a curious and interesting fact that no satisfactory method for the direct determination of sodium had ever been produced before the recent appearance of the paper by Barber and Kolthoff,[1] and it is also interesting to note that the present independent experimental study of the same subject had just been completed when the above paper was published. Barber and Kolthoff precipitated the sodium with zinc uranyl acetate.. The method described here is analogous but uses magnesium uranyl acetate.[2] The sodium is thrown down as magnesium sodium uranyl acetate, $NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2 \cdot (C_2H_3O_2)_2 \cdot 6^1/_2H_2O$, which can then either be dried and weighed or, if small in amount, dissolved in water and measured colorimetrically.

This method, which was first suggested by Streng[3] for the qualitative detection of sodium, was also studied by Miholic[4] and Blanchetière[5] and

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[1] H. H. Barber and I. M. Kolthoff, THIS JOURNAL, **50**, 1625 (1928).

[2] Weiland, *Mitt. Kali-Forsch. Anst.*, **1927**; *C. A.*, **22**, 3600 (1928), used this reagent but gives a formula of the precipitate containing nine molecules of water. We did not have access to his original paper.

[3] A. Streng, *Z. wiss. Mikroskop.*, **3**, 129–130 (1886).

[4] S. S. Miholic, *Bull. Acad. Sci. Zagrab.*, **1920**, 16–23.

[5] A. Blanchetière, *Bull. soc. chim.*, **33**, 807–818 (1923).

later by Barber and Kolthoff, who rejected it partly because of the poor results obtained by other investigators (see paper of Barber and Kolthoff for references) and partly because of their own failure to obtain by its means a precipitate that was stable on prolonged drying. Our own preliminary experiments amply bore out the experience of the previous workers, but fortunately they also suggested the reasons why these early investigators failed to get the desired results. These causes of failure will be given in detail below but they can be summed up here by the general statement that it happened to be a method which required closer attention than is usually given to such details as temperature, stirring and concentration of precipitant. The early investigators failed to consider these points and consequently rarely obtained quantitative results.

A comparison of the Barber and Kolthoff method with the one offered here shows the former to be the more precise if limited to the precipitation of small amounts of sodium (0.008 g. or less) and the latter to be superior in handling larger amounts, up to 0.050 g.

Preparation of the Magnesium Uranyl Acetate.—The following was found to be the most satisfactory method of preparing the reagent.

Solution A		Solution B	
Crystallized uranyl acetate	85 g.	Crystallized magnesium acetate	500 g.
Glacial acetic acid	60 g.	Glacial acetic acid	60 g.
Distilled water	to 1000 cc.	Distilled water	to 1000 cc.

Each solution is separately heated to about 70° until all the salts are dissolved and then the two solutions are mixed at this temperature and allowed to cool to 20°. The large vessel containing the mixed reagent is next placed in water at 20°, and held at this temperature for an hour or two until the slight excess of salts is crystallized out. The reagent is finally filtered through a dry filter into a dry bottle. The solution thus prepared apparently suffers no alteration upon standing and is permanent for all practical purposes when kept away from direct sunlight. A separate portion of some of the first lot of reagent kept in a clear glass bottle exposed to diffused daylight for eight months showed no change in activity or appearance at the end of this time.

General Gravimetric Procedure

The neutral solution containing the sodium, preferably as the chloride, should be reduced to a volume of 5 cc. or less, if there is no separation of salts. A volume of reagent corresponding to the probable sodium content of the solution is then rapidly added and the two solutions are mixed. The flask containing the mixed solution is next partly immersed in a water-bath maintained at 20° and the solution vigorously stirred for thirty to forty-five minutes. The precipitate is then immediately filtered into a Gooch crucible using gentle suction, and after all of the solution has run through the precipitate is washed with successive 5-cc. portions of 95% alcohol. The crucible with its precipitate is finally dried in an air oven at 105 to 110° for thirty minutes and weighed.

The weight of the precipitate, plus one milligram for each 5 cc. of alcohol used in washing, times 0.0153, gives the sodium content of the original solution.

By reason of the large volume and weight of the precipitate formed, 25 mg. of sodium is the maximum amount that should be present, although with care 50 mg. may be determined. In case the amount of sodium present is very small (1 mg. or less) the volume of the solution should be 1 or 2 cc.; otherwise a volume of 5 cc. is used.

Not less than 100 cc. of reagent should be used when the probable amount of sodium is 10 mg. or less. For larger amounts the number of cubic centimeters of reagent should be ten times the number of milligrams of sodium present. An excess of reagent in any case does no harm. It is sometimes necessary to filter the reagent before use if the original filtration was not entirely effective.

A thermostatic control is unnecessary for regulating the temperature at 20°, since a variation of a degree either way does no harm. Indeed, it is only necessary to fill a large vessel with water brought to 19 or 20° and then pay no further attention to temperature control. There is no advantage in working at a lower temperature. The stirring or shaking should be vigorous, since gentle agitation leads to incomplete precipitation.

During filtration the solution should be stirred continually to prevent the crystalline precipitate from adhering to the sides of the flask. The alcohol is preferably delivered from a graduated wash bottle having a fine tip. The first portions should be used to remove the adhering precipitate from the sides of the flask with the aid of a rubber-tipped rod. The end of the washing process is indicated by the wash liquid going through colorless. Ordinarily 20 to 30 cc. of the alcohol is required. A phenomenon that attends the washing of these precipitates should be mentioned because of its deceptive appearance. There frequently appears in the filtrate a precipitate closely resembling that of the triple acetate, which makes it look as though the latter were running through the filter. This precipitation is due to salts thrown out of the concentrated solution by the alcohol.

It is preferable to dry the precipitate at 105° and in no case should the temperature be allowed to rise above 110°, since decomposition begins at a slightly higher temperature.

By reason of the small factor and the slight uncertainty involved in the washing correction, there is no advantage in weighing the precipitate closer than the third decimal place. The use of a washing correction may be eliminated by washing with 95% alcohol saturated with the triple acetate.

Experimental Basis of the Procedure

Causes of the Failure of Previous Investigators.—Preliminary experiments showed that variations of a few degrees in the temperature of the solution had such an effect on the solubility of the precipitate that concordant results could not be obtained without at least a rough temperature control, and, secondly, that above 20° the sodium was not completely precipitated. Since 20° is about the average temperature of a laboratory, low results would be obtained on warm days. The early investigators, evidently unaware of these points, did not control the temperature of their experiments and consequently obtained discordant results, which, as a rule, were too low.

Composition and Properties of the Precipitate.—Streng[3] stated that the triple acetate contained nine moelcules of crystal water, while Miholic[4] found only six. Blanchetière[5] on the other hand assumed, without experimental basis, that the precipitate dried at 110° was anhydrous and contained 1.65% of sodium. Our analyses soon showed that this assumption was wrong and that about six molecules of water were retained at 110°. This is in accord with the composition of the analogous and isomorphic sodium uranyl zinc acetate, as found by Barber and Kolthoff. Table I shows the composition of the precipitate formed at 20°.

TABLE I

SHOWING THE COMPOSITION OF A REPRESENTATIVE SAMPLE FROM A MIXTURE OF TWENTY-FIVE PRECIPITATES, ALL OF WHICH HAD BEEN DRIED AT 110°

No.	Uranyl UO_2, %	Magnesium, %	Sodium, %	Acetate radical, %	Water
1	53.77	1.65	1.58	35.79	..
2	53.67	1.65	1.53	35.42	..
3	53.64	1.63	1.58	...	..
4	53.74	1.61	..	...	..
Av.	53.71	1.63	1.56	35.60	7.50
Calcd. compn.[a]	53.79	1.61	1.53	35.26	7.78

[a] The calculated composition is based on the formula, $Mg(C_2H_3O_2)_2 \cdot NaC_2H_3O_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6^1/_2H_2O$.

The values for uranium in the above table were obtained by precipitating the element as ammonium uranate, dissolving and reprecipitating and finally igniting and weighing as U_3O_8. The magnesium was determined by evaporating the filtrate from the uranium precipitate with an excess of sulfuric acid and igniting the mixed sulfates of magnesium and sodium. The magnesium was then determined as the phosphate and after calculating it as sulfate it was subtracted from the mixed sulfates to get the amount of sodium. The acetate radical was obtained by distillation with phosphoric acid and titration of the acetic acid in the distillate with carbonate-free sodium hydroxide. Water was found by difference since the temperature necessary to drive it off caused the decomposition of the material.

These analytical results, it is seen, agree very well with the assumption that the triple acetate has 6.5 molecules of water (see Table I) and contains 1.53% of sodium. This is further confirmed by the numerous analyses made of samples containing known amounts of sodium.

The results in Table I, however, are from a composite sample and since Miholic[4] and Chamot and Bedient[6] have stated that the triple acetates of uranium are of variable composition, it is necessary to offer analyses of a number of individual precipitates. Determinations of uranium and magnesium alone were made since any serious variation in composition would be apparent in these values.

The results of Table II show that the composition of the precipitate is

[6] E. M. Chamot and H. A. Bedient, *Mikrochemie*, **6**, 13 (1928).

not variable if the conditions of its formation are kept constant as described in the procedure above.

TABLE II

ANALYSES OF SEVERAL INDIVIDUAL PRECIPITATES

Weight of precipitate, g.	0.3212	0.6585	0.9686	1.3002	1.6351	
Uranyl (UO_2), %	53.71	53.60	53.67	53.77	53.57	Av. 53.66
Magnesium, %	1.62	1.58	1.63	1.60	1.64	Av. 1.61

Experiments to determine the proper temperature for drying the precipitate showed that it could be heated for thirty to forty-five minutes at 110° without loss, but a higher temperature or a longer period of heating resulted in decomposition. (Barber and Kolthoff,[1] who also experimented with this precipitate, report that it lost only 0.3% after drying for twenty hours at 110°.) Attempts to ignite the substance to a form suitable for weighing met with failure.

The solubility of the precipitate in 95% alcohol—the most satisfactory washing liquid—was found to be 0.001 g. for each 5 cc. of alcohol used. Since 25 to 35 cc. of alcohol is sufficient for the washing of even a large precipitate, it is seen that this solubility is almost negligible when calculated in terms of sodium. For example, the use of 35 cc. of alcohol corresponds to only 0.0001 g. of sodium.

Effect of Volume of Solution on Completeness of Precipitation.—In the early quantitative work[4] with this method 0.1 *N* sodium chloride solutions were used, that is, the concentration was kept constant but the volume of the solution varied. Since under practical analytical conditions the opposite is more likely to be true and since, further, a too high dilution of the solution for analysis also dilutes the reagent, the point was studied by making a series of precipitations with varying volumes of sodium chloride solution, all, however, containing the same amount of sodium. The results showed that the volume of the sodium salt[7] solution should not be more than 5 cc. unless between 25 and 50 mg. of sodium were to be precipitated, in which case the volume might be 10 cc., though even in this case 5 cc. would be better.

Amount of Reagent for Complete Precipitation.—Since the reagent is dilute, large volumes must be used for precipitation. The experimental results on this point are presented in Table III.

The above data indicate the importance of having a sufficiently large volume of reagent present to precipitate all of the sodium as triple acetate. The results show that a large volume is required to precipitate the higher amounts of sodium, so much so in fact that the determination of over fifty milligrams of the element renders the method inconvenient and expensive on this account. For practical purposes it would appear that the

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[7] In these experiments as well as in all subsequent ones the sodium chloride used was purified by several precipitations with hydrogen chloride.

TABLE III

SHOWING THE EFFECT OF VARYING THE VOLUME OF REAGENT

Reagent, cc.	Sodium soln., cc.	Sodium present, g.	Sodium found, g.	Diff., g.
5	2	0.0010	0.0008	−0.0002
10	2	.0010	.0010	.0000
25	2	.0010	.0010	.0000
50	2	.0010	.0011	+.0001
10	2	.0050	.0037	−.0013
25	2	.0050	.0048	−.0002
50	2	.0050	.0050	.0000
75	2	.0050	.0050	.0000
50	5	.0100	.0095	−.0005
75	5	.0100	.0097	−.0003
100	5	.0100	.0097	−.0003
125	5	.0100	.0101	+.0001
75	5	.0200	.0197	−.0003
100	5	.0200	.0198	−.0002
125	5	.0200	.0197	−.0003
150	5	.0200	.0199	+.0001
200	5	.0500	.0486	−.0014
250	5	.0500	.0488	−.0012
300	5	.0500	.0498	−.0002
350	5	.0500	.0496	−.0004
500	5	.1000	.0986	−.0014
600	5	.1000	.0994	−.0006

method is restricted to the determination of small amounts of sodium, which is fortunately the usual case in practice. The uncommonly large volume of reagent required for the complete precipitation of larger amounts of sodium explains in part the failure of previous workers to obtain other than very poor results when working with amounts of sodium in excess of a few milligrams.

Effect of Agitation on Completeness of Precipitation.—As might be expected from the complex nature of the triple acetate, its rate of formation is slow. The solutions should, therefore, stand for twenty-four hours or longer before filtering, or they should be stirred or shaken. The latter is obviously the more sensible procedure in these days of motor-driven laboratory equipment.

A series of experiments was made in which sets of 10-mg. portions of sodium as the chloride in 5 cc. of solution were treated with 125 cc. of the reagent. Without agitation, precipitation was far from complete on three hours' standing and even one hour of "gentle" shaking failed to give quantitative results. Thirty minutes of rapid shaking or stirring (motor-driven apparatus) in a flask, however, gave complete precipitation. These experiments disclose still another reason why previous workers had failed to get good results. They all recommend "gentle" stirring or "occasional agitation."

Test of the Procedure with Known Amounts of Sodium Chloride.—The results in Table IV were obtained by following the procedure given above.

TABLE IV

A TEST OF THE PROCEDURE WITH KNOWN AMOUNTS OF PURE SODIUM CHLORIDE

Corr. wt. ppt., g.	Sodium found, g.	Sodium present, g.	Diff., g.	Corr. wt. ppt., g.	Sodium found, g.	Sodium present, g.	Diff., g.
0.034	0.0005	0.0005	0.0000	0.966	0.0148	0.0150	−0.0002
.033	.0005	.0005	.0000	1.636	.0250	.0250	.0000
.129	.0020	.0020	.0000	1.660	.0253	.0250	.0003
.129	.0020	.0020	.0000	3.215	.0492	.0500	−.0008
.491	.0075	.0075	.0000	3.261	.0499	.0500	−.0001
.489	.0075	.0075	.0000	3.255	.0498	.0500	−.0002
.969	.0148	.0150	−.0002	3.243	.0496	.0500	−.0004

The results of Table IV show that as much as 50 mg. of sodium can be precipitated successfully. Even the worst case, the fourth from the bottom, would give a satisfactory analytical result on the basis of a one-gram sample (see also Table VII).

Influence of Other Ions.—The results in Table V below were obtained by adding the specified amount of reagent to 5-cc. portions of solution con-

TABLE V

EXPERIMENTS ON PRECIPITATING SODIUM IN THE PRESENCE OF OTHER MEMBERS OF THE ALKALI GROUP

Element	Wt. of other element, g.	Reagent, cc.	Sodium present, g.	Sodium found, g.	Diff., g.
K	0.1500	200	0.0200	0.0199	−0.0001
	.2000	200	.0200	.0203	+.0003
	.2500	200	.0200	.0202	+.0002
	.3000	200	.0200	.0218	+.0018
K	.1000	100	.0100	.0101	+.0001
	.1500	100	.0100	.0101	+.0001
	.2000	100	.0100	.0101	+.0001
	.2500	100	.0100	.0103	+.0003
	.3000	100	.0100	.0123	+.0023
	.4000	100	.0100	.0247	+.0147
K	.1000	50	.0050	.0050	.0000
	.2000	50	.0050	.0087	+.0037
	.3000	50	.0050	.0134	+.0084
	.4000	50	.0050	.0194	+.0144
NH_4	.3000	200	.0200	.0200	.0000
	.4000	200	.0200	.0201	+.0001
NH_4	.2000	100	.0100	.0101	+.0001
	.3000	100	.0100	.0100	.0000
	.4000	100	.0100	.0101	+.0001
Li	.0010	100	.0100	.0101	+.0001
	.0030	100	.0100	.0103	+.0003
	.0050	100	.0100	.0107	+.0007
	.0075	100	.0100	.0112	+.0012
	.0100	100	.0100	.0118	+.0018

taining the sodium and another element. The salts (chlorides) of the added elements had been purified until the flame test showed only traces of sodium.

An inspection of these results shows that the ammonium ion is practically without effect on the precipitation. The results for potassium show that under the conditions used no more than 0.25 g. should be present if 100 cc. or more of reagent is employed. With smaller amounts of sodium calling for only 50 cc. of reagent, not more than 0.1 g. is allowable. In such a case, however, more reagent can be used if much potassium is present. The separation from lithium is not good if more than one or two milligrams of that element is present.

The separation from the alkaline earths is presented in Table VI. The experiments were performed as described above for Table V. All of the alkaline earth salts (chlorides) were purified until only spectroscopic traces of sodium remained.

TABLE VI

EXPERIMENTS ON PRECIPITATING SODIUM IN THE PRESENCE OF THE ALKALINE EARTHS AND FERRIC IRON

Element present	Wt. of other element, g.	Reagent, cc.	Sodium present, g.	Sodium found, g.	Diff., g.
Ca	0.3000	100	0.0100	0.0100	0.0000
	.4000	100	.0100	.0101	+.0001
Mg	.3000	100	.0100	.0100	.0000
	.4000	100	.0100	.0101	+.0001
Sr	.3000	100	.0100	.0102	+.0002
	.4000	100	.0100	.0100	.0000
Ba	.3000	100	.0100	.0105	+.0005
	.4000	100	.0100	.0105	+.0005
Fe	.3000	100	.0100	.0101	+.0001
	.4000	100	.0100	.0100	.0000

It is seen that the presence of alkaline earths has no effect on the separation. The high results in the presence of barium were found to be due to traces of sulfate ion in the reagent, which precipitated barium sulfate.

No quantitative experiments were carried out in which sodium was precipitated in the presence of cations other than those recorded above, but this would hardly be necessary because these ions can be removed easily from the solution. Phosphoric acid would obviously interfere and should be removed before attempting to precipitate the sodium.

A Practical Analytical Test.—An important test of a new method is, of course, that of using it in the analysis of some commercial materials the composition of which has been obtained by other methods in competent hands. That test was applied to this method by using it in the determination of sodium in several samples obtained from the U. S. Bureau of Standards. These were Standard Samples No. 88, a Dolomite; No. 70, a Feldspar; and No. 80, a Lime–Soda Glass.

The dolomite was analyzed by treating a one-gram sample with hydrochloric acid and decomposing the insoluble residue by two evaporations with hydrofluoric and sulfuric acids. The two portions were united and evaporated to dryness. The residue was dissolved in hot water, evaporated to 50 cc. and the sodium precipitated as described in the procedure above. A half-gram sample of the feldspar was decomposed by the J. Lawrence Smith method, which was followed up to and including the extraction of the sintered mass with water. This water extract was then acidified with hydrochloric acid and evaporated to dryness. The residue was next dissolved in 5 cc. of water and the sodium precipitated.[8] The lime–soda glass was decomposed with hydrofluoric and sulfuric acids, 0.3000-g. to 0.0400-g. samples being used. The sulfates so obtained were extracted with water and the sodium was precipitated in the solution. The results of these determinations are given in Table VII.

TABLE VII

ANALYSES OF BUREAU OF STANDARDS SAMPLES BY THE DIRECT METHOD FOR SODIUM

No.	Sample	Method of solution	Na_2O, (B. of S.), %	Na_2O by new method, %	
88	Dolomite	Dec. with HCl, H_2F_2 and H_2SO_4	0.08	0.09	0.09
70	Feldspar	J. Lawrence Smith method	2.38	2.32	2.33
80	Glass	Dec. with H_2F_2 and H_2SO_4	16.65	16.79	16.61

The values in Table VII compare favorably with the Bureau's results and were obtained in far less time than the standard methods require.

The Colorimetric Estimation of Sodium

The triple acetate precipitate is readily soluble in water and, since the resulting solution is colored yellow by the uranium compound present, a colorimetric method of measurement naturally suggests itself. The usual preliminary experiments were performed in order to learn the maximum amounts that could be measured in this way, the observational errors involved and the effect of temperature changes on the depth of color of the uranium solution. The results are embodied in the procedure and notes below.

Procedure for Colorimetric Measurement.—The precipitation is made in the manner given under the gravimetric method except that the volume of sodium solution should be only one or two cubic centimeters. The precipitate is collected in an unweighed Gooch crucible and washed with four successive portions of 95% alcohol. Air is then drawn through the crucible for five minutes to remove most of the alcohol, after which the precipitate is dissolved through the crucible into a colorimeter tube with warm water (60 to 70°), using it in 2- to 3-cc. portions. The solution is then cooled to room temperature and diluted to some definite volume,

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[8] It is worth noting that the very large amount of calcium in this solution did not interfere with the precipitation.

between 15 and 25 cc., depending upon the volume of water used in dissolving the precipitate. The depth of color of this solution is next compared with that of a standard solution that has been prepared in the same way.

About 5 mg. of sodium is the maximum amount that can be determined colorimetrically because the amount of uranium compound associated with more than this gives too deep a yellow color for satisfactory comparison. The wash alcohol must be removed in order to avoid cloudy solutions. Good results are obtained only if a colorimeter is employed. Color-comparison tubes alone are not so satisfactory.

It is very important that the solution under analysis and the standard solution be at the same temperature, since the depth of color is strongly affected by the temperature.

The best results are obtained when the solutions show a fairly deep straw color in the colorimeter. At least five readings should be taken with each pair of tubes and the results averaged.

A standard solution of approximately the same concentration as the one under examination should be used. These standard solutions should be prepared by precipitating the sodium from measured portions of standard sodium chloride solution. A convenient strength is 2.542 g. of sodium chloride per liter. One cubic centimeter of this solution contains 1 mg. of sodium.

A peculiar advantage of the colorimetric procedure is that suspended matter need not be removed from the original sodium salt solution. It will be retained in the crucible when the precipitate is dissolved through.

TABLE VIII

EXPERIMENTS ON THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF SODIUM

Sodium present in standards, g.	Depths of standard solns., mm.	Depths of sample solns., mm.	Sodium in sample, g.	Sodium found, g.	Diff. or errors, g.
0.0005	29	25	0.0005	0.0006	+0.0001
	24	22		.0005	.0000
	23	26		.0004	−.0001
.0010	19	43	.0005	.0004	−.0001
	16	38		.0004	−.0001
	20	42		.0005	.0000
.0020	28	22	.0025	.0025	.0000
	25	20		.0025	.0000
	37	31		.0024	−.0001
.0030	26	30	.0025	.0026	+.0001
	30	37		.0024	−.0001
	23	29		.0024	−.0001
.0040	35	30	.0050	.0046	−.0004
	42	35		.0048	−.0002
	28	24		.0047	−.0003
.0060	44	55	.0050	.0048	−.0002
	42	50		.0050	.0000
	36	41		.0052	+.0002

Some typical results obtained by the colorimetric method are given in Table VIII.

The results of Table VIII are seen to be entirely satisfactory except in the instance in which an attempt was made to compare the depths of color of a tube containing 5 mg. of sodium with a standard tube containing 4 mg. More experience with the method will undoubtedly remove such discrepancies.

Summary

1. A method for the direct determination of sodium by precipitating it as magnesium sodium uranyl acetate has been presented.

2. Both gravimetric and colorimetric measurements have been used.

Columbus, Ohio

[Contribution from the Kent Chemical Laboratory of the University of Chicago]

EMULSIONS: STABILITY, AREA PER MOLECULE IN THE INTERFACIAL FILM, DISTRIBUTION OF SIZES AND THE ORIENTED WEDGE THEORY[1]

By William D. Harkins and Norvil Beeman

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1. Introduction

When this work was begun no accurate determination had been made of the distribution of sizes of the droplets in emulsions. If such determinations could be made they would give a basis for a decision with respect to three of the most important fundamental problems of this branch of colloid science. These are: (1) the number of molecules of the emulsifying agent per unit area of the oil–water interface, (2) the stability of emulsions and the effect of aging and (3) the oriented wedge theory of emulsions.

While the requirements of the last two problems might be met by large-scale methods, the demands of the first problem seemed to necessitate the use of a fine-scale, or microscopic method, since with large-scale methods there is considerable uncertainty in the theory which is used to translate the scattering of light or the speed of sedimentation into the sizes of the drops.

2. Experimental Methods

1. Apparatus

1. **Microscopic Equipment.**—An image of the highly diluted emulsion was projected on a screen by the use of a microscope fitted with a 61x, 3-mm. apochromatic oil immersion objective, 1.40 N.A.; an aplanatic condenser 12-mm., 1.40 N.A.; and a 25x, compensating ocular.

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[1] A preliminary version of this article was received August 31, 1925.