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THE ELECTRO-TITRAMETRIC METHOD AND ITS APPLICATION TO GENERAL ANALYTICAL CHEMISTRY.

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Received June 23, 1914.

Since the time of the first use of the empirical normal solutions of Gay-Lussac and the introduction of present normal solution of Ure, volumetric analysis has never received such a strong impulse as that through the application of physical chemistry. This is especially true for the volumetric determinations of acids and bases, in so far as the nature of neutralization is now clearly understood. Our knowledge of the role which indicators may play in neutralization has been increased in recent years very markedly by the introduction of the dissociation theory. We do not consider that this is the place to go into a discussion of indicators, but it will suffice to say here that with the knowledge of the necessary facts, especially of dissociation constants, we may occasionally predict whether an indicator is applicable in a special case or not.

In spite of the fact that in recent times the theoretical knowledge of the color indicators has been considerably increased, and here and there practical applications drawn from those principles have been made, there are still, as every analytical chemist knows, many embarrassing and unmanageable difficulties to contend with.

We can only touch upon a few of those difficulties. For instance, the personal equation which can cause an error of 1 cc. in a 0.01 *N* solution, and further the difficulty encountered with a liquid which possesses a color that may interfere with the recognition of the indicator, and those complications which may arise in the case of very dilute solutions. These are only a few of the reasons why the application of indicators in the general analytical field of chemistry is rather limited. It is therefore not unexpected that attempts have been made to overcome these difficulties by the introduction of another type of indicators which are dependent on and indicative of the physico-chemical changes in the solution.

W. Böttger[1] some years ago, in the case of colored or turbid solutions in which the change of color of an indicator would be more or less masked, recommended the use of the electrometer. It must be said, however, that determinations with this instrument are more laborious and that such measurements are less familiar to chemists than the determination of conductivity. It is the merit of Küster[2] and his associates to have shown that such titrations, which cause great difficulty and uncertainty, could be made with a high degree of accuracy if, instead of depending on the change of color, use was made of the change of physical-chemical property (electrical conductivity) of the liquid by the process of neutralization. We may conclude from their work that the point of neutrality between strong acids and bases can be determined much more exactly by conductivity methods than by the use of indicators. Also, if weak acids were used, as for example tartaric and acetic acids, which, as iswell known, have caused so many difficulties by the ordinary titration method, sharp and good results were obtained by the use of the conductivity method. The point of neutralization of red wine by means of the conductivity determination was much more definite than if determined by titration with litmus. The attempt was also made by them to titrate four quinine derivatives by the electro-conductivity method with good success. Further, Duboux and Dutoit[3] have used this conductivity titration in many of their special researches in wine analysis. From their interesting work, which treats especially the organic acids in wine, we may say that the conductivity titration has proved here also to be a very successful and helpful aid in chemical analysis.

The preparation of exact ammonium citrate solution, which previously gave rise to difficulties, has been solved by the application of the above mentioned method by Hall and Bell,[4] who showed by this method an exactly neutral solution of ammonium citrate was easily prepared.

In our analysis of soil solutions,[5] we had already used the method of titration by conductivity in determining the acid and basic binding capacity of such solutions. We feel that it would be superfluous here to go into

[1] W. Böttger, *Z. physik. Chem.*, 24, 253–301 (1897).

[2] F. W. Küster, M. Grüters, and W. Geibel, *Z. anorg. Chem.*, 42, 225–34 (1904).

[3] P. Dutoit and M. Duboux, *J. suisse de Chim. et pharm.*, 1908, p. 690.

[4] *J. Ind. Eng. Chem.*, 3, 559 (1911).

[5] F. H. Hesselink van Suchtelen and A. Itano, *52nd Ann. Rept. Mich. Board of Agr.*, p. 149 (1913).

the fundamental principles underlying this method of analysis, since they may be considered to be the common property of the analytical and biological chemists; and there is no lack of excellent manuals dealing with the practical phases of measurements of electrical conductivity. We will, therefore, confine ourselves to a brief summary of results and call attention to precautions necessary in carrying out our technique.

It must be said that in the execution of such conductivity titrations, certain precautions have to be followed. These will be treated very briefly because such rules can be deduced easily from the theoretical basis of the applied method and from hydrolysis.

It is quite evident that in most of our experiments a determination of the cell constants did not need to be considered, because it was only necessary to have the relative bridge readings. An exception, however, was made in the case of physiological liquids, such as urine and milk, because such determinations of specific conductance may be of special clinical value.

Because of the fact that electrical resistance varies greatly with temperature, greatest care must be taken that the solutions are not subjected to changes of temperature at the time of titration. In our case, the conductivity cup (filled with vertical electrodes) stood deep in a large 75-liter water bath, and throughout the time of titration the cup remained in the liquid. The cup was agitated by gentle shaking in order to facilitate rapid intermixture.

To relieve the operator of the tedium and strain of acute listening through the telephone receiver, we have substituted in many of our experiments, especially where dilute solutions were employed or a high degree of accuracy was required, an alternating current galvanometer which permitted far sharper determinations to be made. The use of such a galvanometer is advisable, but not essential.

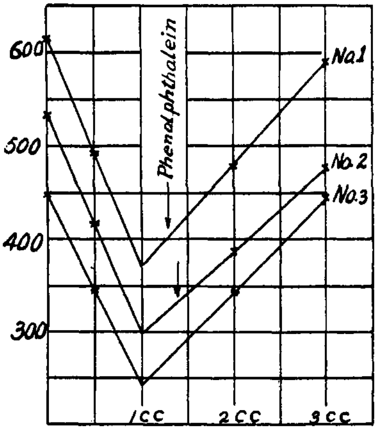
To those familiar with this field of work, this short introduction does not claim to disclose any new point of view, nor, for those not so well versed in these subjects in question, do we attempt an exhaustive presentation of the fundamental supporting theory.

We will now proceed to consider the individual curves, and there, as the case may arise, enlarge upon certain features necessary to an understanding of the subject. We deem it advisable to start with the most simple case in our analysis, namely, the titration of acids and bases, because they may be considered as the basis of our work.

In the preceding paragraphs we have discussed some of the typical features and peculiarities of this special conductivity titration. Let us turn now to a comparison of the accuracy of this method with that of a color indicator. We see at once that the values for neutrality, as obtained by means of phenolphthalein, are all without exception more alkaline than those determined from the conductivity titrations.

The question now arises, "Which method gives the neutral point with greater accuracy?" In deciding this question, use was made of the indicator table so thoroughly worked out by Sörensen. It was easily demonstrated that by the use of an appropriate indicator with a sharp color change at the neutral point, results were obtained which agreed with the conductivity titration. Besides this, it is a well-known fact that the neutral point of phenolphthalein is decidedly alkaline.

It must be noted here that of the above curves, only one (No. 1) was made by an experimenter who was familiar with conductivity titrations. The others were all worked out by men performing the experiment for the first time. This fact leads to an important feature of the conductivity titration; namely, that the influence of the subjective factor which necessarily enters into every chemical analysis is here minimal. This fact will be borne out by a consideration of the above curve.

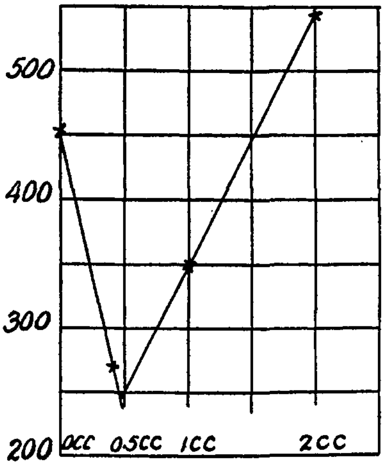


Neutralization of strong acid by strong base.
In cup 10 cc. 0.001 N H_2SO_4.
Titrated with 0.01 N NaOH.

	Readings.		
	No. I.	No. II.	No. III.
0	615.0	533.7	447.5
0.5	492.5	417.6	345.0
2.0	447.5	387.5	342.0
3.0	590.0	477.0	443.0

Theoretically, 0.1 cc.
Found, 0.1 cc.

Fig. 1.



Neutralization of 5 cc. 0.001 N H_2SO_4. with 0.01 N NaOH.

	Readings.
0 cc.	457.5
0.4 cc.	267.5
1.0 cc.	350.0
2.0 cc.	544.7

Theoretically, 0.5 cc.
Found, 0.5 cc.

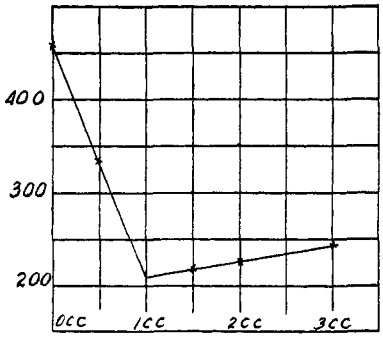
Fig. 2.

It should be added that many of these curves were made without the use of a galvanometer. It is evident that the use of this instrument will still further minimize the influence of the personal equation. The significance of this elimination is emphasized, on the contrary, by a glance at the varying results obtained by different experimenters using phenolphthalein—an indicator noted for the sharpness of its color change.

As may be seen from the graphs, it is an *a priori* fact in conductivity titrations that they are not characterized, as are the color indicator titrations, by a total dependence on one single point at which the color changes. The conductivity titration, on the contrary, is typified by lines, each line being fixed and determined by a series of points, the number of which is under the control of the experimenter. We consider this to be an important advantage over the color indicator method, for many interesting deductions can be drawn from such curves.

In regard to the point of inflection, we may say that it is sharply defined and determinable with exceeding precision. As an illustration of this, the following graph may serve. In this case 0.001 N 5 cc. H_2SO_4 were titrated with 0.01 N NaOH. Even in this concentration, the result was satisfactory.

In the following experiment the electro-titrametric method was employed for the titration of a weak acid (lactic acid) with

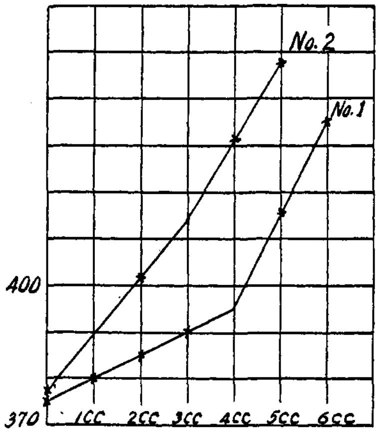


Neutralization of a weak acid (lactic acid) by 0.1 N NaOH.
In cup 5 cc. 0.1 N NaOH (and phenolphthalein).
Titrated with 0.5 N $C_3H_6O_3$.

	Readings.
0	457.5
0.5	335.5
1.5	220.0
2.0	227.5
3.0	245.0

Theoretically, 1 cc.
Found, 1 cc.
Turning point phenolphthalein, 1.07.

Fig. 3.



Determination of malic, tartaric and succinic acids.

In cup 5 cc. 0.1 N tartaric
5 cc. 0.1 N succinic
10 cc. 0.1 N malic
and 40 cc. 95% alcohol.
0.2 cc. 28% NH_4OH.

Titrated with 0.5 N barium acetate.

Readings No. 1.		Readings No. 2.	
0 cc.	375	0 cc.	377.5
1 cc.	380	2 cc.	401.5
2 cc.	385	4 cc.	432.9
3 cc.	390	5 cc.	448.0
5 cc.	415		
6 cc.	435		

Total acids.

Total acids—succinic, as No. 1 plus 1 cc. 36% acetic acid.

Fig. 4.

a strong base (NaOH)—a titration which had hitherto been attended with many difficulties.

The amount of lactic acid was determined by the formation of its zinc salt, and, in accordance with this, a normal solution was prepared (theoretical inflection point, 1 cc.; found, 1 cc.). Here again, as in the experiments described in the foregoing, the electro-titrametric method proved to be of especial value, because of the high degree of precision with which the neutralization point was obtained. It is to be noted here that the titration in this case was performed in the reverse of the usual manner; *i. e.*, the NaOH was placed in the conductivity cup and the acid was added to it from the buret. The reason for this procedure is at once evident and requires no comment.

The graph (Fig. 4) is an illustration of the determination of various organic acids (malic, tartaric and succinic). It is interesting to note that in the case where no acetic acid was added (No. 1), the result was in perfect accordance with the total amount of acids present. In the determination, however, when an addition of acetic acid had taken place (No. 2) only tartaric acid and malic acid showed their presence.

Up to now, we have considered simply the determination of neutralization points. This naturally is the most ordinary kind of determination to make first, but in no way marks the limitation of the sphere of usefulness of the method. We feel confident that the electro-titrametric method will find a constantly widening field of application, and this will naturally be a source of personal gratification to us, should it prove to be the case. The experiments which we have performed are necessarily limited in number and kind, being confined to the determination of those elements and radicals known to be of particular importance in general and biological chemical analysis.

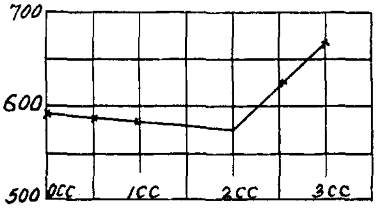
At this juncture we wish to emphasize two points that strongly commend this method, namely, accuracy and ease of performance. The elements and radicals included in our determinations were, Cl, Ag, SO_4, Ba, U, PO_4, NO_3, K, Ca, Fe″.

In the first determinations of those elements and radicals, we aimed to test the method as to its application and limitations, and we used, therefore, chemicals of highest purity (Kahlbaum), even going so far as to check their purity by standard methods of analysis.

The first of these experiments was a determination of Cl in KCl by means of $AgNO_3$. Fig. 5 shows the sharpness and precision which characterizes the determination. The value obtained by the conductivity titrations coincided exactly with the theoretical value (theoretical, 35.46 mg. Cl; found, 35.46 mg. Cl).

The next analysis was the determination of SO_4 in K_2SO_4. In the cup was 10 cc. $N/10$ K_2SO_4. This was titrated with $N/3$ $Ba(NO_3)_2$.

At this point, attention should be called to the fact that, in order to obtain the highest degree of precision, we introduced, in many instances into the cup, a very small portion of the salts yielding the precipitation to be expected. It will be seen that in addition to what has been said already, the analysis of K_2SO_4 by the electro-titrametric method does away with the laborious processes of precipitation, incineration, and weighing, and avoids the many opportunities for error engendered by these operations.

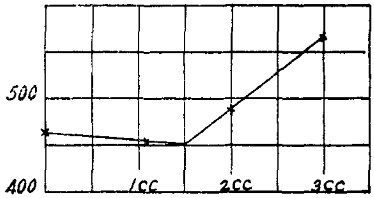


Determination of Cl.
In cup 10 cc. 0.1 *N* KCl.
Titrated with 0.5 *N* $AgNO_3$.

	Readings.
0 cc.	592
0.5 cc.	586.5
0.955 cc.	582.3
2.000 cc.	576
2.55 cc.	629.5
3.00 cc.	668.3

Theoretically, 2 cc. = 35.46 mg. Cl.
Found, 2 cc. = 35.46 mg. Cl.

Fig. 5.



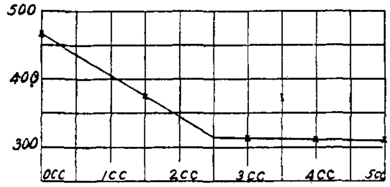
Determination of SO_4.
In cup 5 cc. 0.1 *N* K_2SO_4.
Titrated with *N*/3 $Ba(NO_3)_2$.

	Readings.
0 cc.	463.0
1.06 cc.	452.1
2.005 cc.	485.0
2.986 cc.	567.8

Theoretically, 1.52 cc. *N*/3 $Ba(NO_3)_2$ = 240.175 mg. SO_4.
Found, 1.58 cc. = 240.175 mg. SO_4.

Fig. 6.

The next determination was that of PO_4 in $(NH_4)_2HPO_4$, the titration being formed with uranium nitrate as reagent. A glance at Fig. 7 shows that the analytical result agrees exactly with the amount introduced.

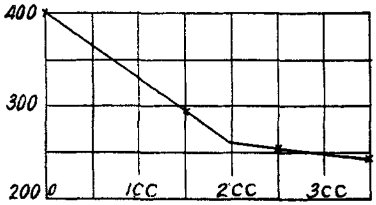


Determination of PO_4.
In cup 10 cc. 0.1 *N* $(NH_4)_2HPO_4$.
Titrated with 0.25 *N* $UO_2(CH_3COO)_2$.

	Readings.
0 cc.	466.5
1.5 cc.	375
3.0 cc.	311
4.0 cc.	310
5.0 cc.	310

Theoretically, 2.5 cc. contains 31.68 mg. PO_4.
Found, 2.5 cc. contain 31.68 mg. PO_4.

Fig. 7.



Determination of NO_3.
In cup 5 cc. 0.1 *N* $NaNO_3$.
Titrated with 0.25 *N* $C_{20}H_{16}N_4$ (addition of 1 drop 1 : 1 H_2SO_4).

	Readings.
0 cc.	401
1.5 cc.	297.5
2.5 cc.	257.5
3.5 cc.	245.0

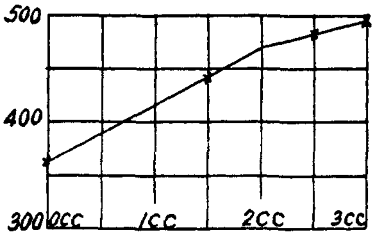
Theoretically, 2 cc. = 31.005 mg. NO
Found, 2 cc. = 31.005 mg. NO_3.

Fig. 8.

This analysis in particular is noteworthy because of the fact that in using the ordinary indicators (cochineal or potassium ferrocyanide) the turning points are not very definite; and, in general, leave much to be desired.

Another electro-titrametric determination was that of NO_3 in a solution of $NaNO_3$ (a salt which may be looked upon as chemically pure Chili saltpeter), containing also free H_2SO_4. This solution was titrated with a 0.25 *N* solution of nitron in acetic acid. In this experiment, where the theoretical amount of nitrate present was 31.005 mg., the electro-titrametric method again showed perfect coincidence. A differential determination of nitrates and nitrites is possible by the use of hydrazine sulfate.

In the experiments now to be described, determinations were made of several cations. The first was that of K in KCl (Sylvin). The reagent used here was sodium cobalt nitrite. The result obtained was once more in exact accord with the theoretical calculation: actually present, 39.10 mg.; determined by the conductivity titration, 39.10 mg.

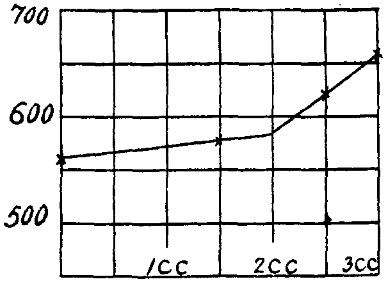


Determination of K.
In cup 10 cc. 0.1 *N* KCl.
Titrated with 0.5 *N* $Na_3CO(NO_2)_6$.

	Readings.
0 cc.	362.5
1.5 cc.	442
2.5 cc.	482
3.0 cc.	495.5

Theoretically, 2 cc. = 39.10 mg. K.
Found, 2 cc. = 39.10 mg. K.

Fig. 9.



Determination of Ca.
In cup 10 cc. 0.1 *N* $CaCl_2$.
Titrated with 0.5 *N* $H_2C_2O_4$.

	Readings.
0 cc.	562.5
1.5 cc.	578.0
2.5 cc.	623.5
3.0 cc.	657.5

Theoretically, 2 cc. = 20.035 mg. Ca.
Found, 2 cc. = 20.035 mg. Ca.

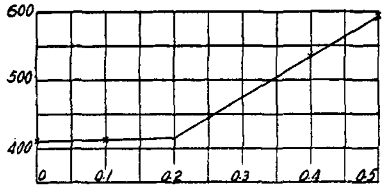
Fig. 10.

In this case the precipitation requires 3–4 minutes for completion. The conductivity reading then becomes constant. Although the conductivity curve in this instance permits of reasonably high accuracy, it is nevertheless not as sharp as in the other determinations which preceded, or in those which follow it. We have, however, good grounds for the belief that by the use of another cobalt nitrite a sharper graph would result; in any case the reagent must be used fresh.

The next determination of a cation was that of Ca in $CaCl_2$. The reagent used was 0.5 N oxalic acid. As before, the result of the analysis checked with the theoretical amount present.

The next experiment was the determination of the Fe″ content of $FeCl_2$. The titration was performed with 0.5 N Na_2S. One can hardly fail to be struck here with the extraordinary sensitivity of the electro-titrametric method so notably illustrated by the results of this experiment. Thus, 2.792 mg. Fe″ was dissolved in the conductivity cup. A glance at the graph shows that by the analysis exactly this amount was found to be present.

Up to now we have considered exclusively the analysis of elements and radicals in a solution containing only the pure salt. It is hardly necessary to say that by the application of such reliable and specific reagents as we used, the accuracy of the results would not be affected by the presence of foreign substances. Many experiments have convinced us of the applicability of the electro-titrametric method in the case of a solution of a mixture of salts. We invariably found that the presence of salts other than the one in question did not cause variation or inaccuracy of results. For this reason we feel it unnecessary to go any further into this question, resting content with the statement that intelligent choice of the reagents used will,

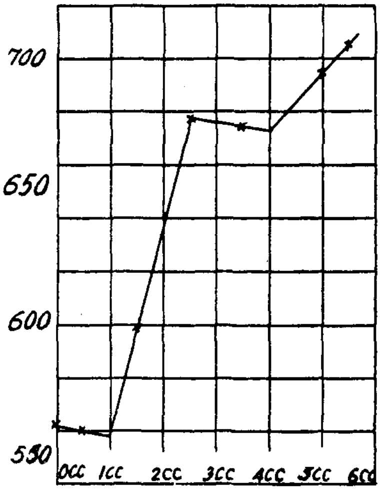


Determination of Fe″.
In cup 1 cc. 0.1 N $FeCl_2$.
Titrated with 0.5 N Na_2S.

	Readings.
0 cc.	410
0.1 cc.	410.7
0.4 cc.	535
0.5 cc.	594

Theoretically, 0.2 cc. = 2.792 mg. Fe″.
Found, 0.2 cc. = 2.792 mg. Fe″.

Fig. 11.



Determination of Cl and SO_4 in the same solution.
In cup 5 cc. 0.1 N NaCl; 5 cc. 0.1 N K_2SO_4.
Titrated with (A) 0.5 N $AgNO_3$; (B) $N/3$ $Ba(NO_3)_2$.

Readings.

A.		B.	
0 cc.	563.0	0 cc.	678.0
0.5 cc.	560.5	1.0 cc.	675.0
1.5 cc.	598.5	2.5 cc.	694.5
2.5 cc.	678.0	3.0 cc.	706.0

A:

Theoretically, 1 cc. = 35.46 mg. Cl.
Found, 1 cc. = 35.46 mg. Cl.

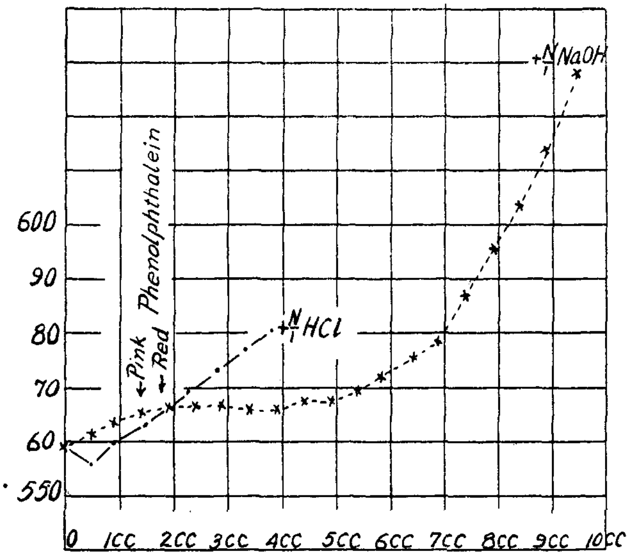
B:

Theoretically, 1.51 cc. = 96.09 mg. SO_4.
Found, 1.5 cc. = 96.09 mg. SO_4.

Fig. 12.

in the case of a mixture of substances in solution, prevent the possibility of even the slightest disturbance. A single illustration of this may be seen in Fig. 12, representing the determination of four different substances, Ag, Cl, Ba, SO_4, in a solution containing a mixture of K_2SO_4 and NaCl. The graph speaks for itself in language that is unmistakable.

Previously, we dealt with the determination of acids, bases, salts, and mixtures of salts. At this point we take occasion to state that this method, which was so successful for the above mentioned substances, was also of great value in the analysis of liquids of biological constitution. We have purposely concentrated the largest part of our attention upon the analysis of the working basis of the method in its wider applications. Therefore, we reserve, for later publication, the analysis of biological liquids. We may, however, remark that by means of our method of analysis of the



Determination of the acid and basic binding capacity (HCl. NaOH) of urine (sp. cond. $260.5^{10^{-4}}$).
In cup 50 cc. urine.
Titrated with (A) N HCl; (B) N NaOH.

Readings. Acid binding (A).		Readings. Base binding (B).			
0	555.0	0	559.0	4.9	567.5
0.5	556.5	0.5	561.5	5.4	569.5
0.9	560.0	0.9	564.0	5.9	572.0
1.5	563.5	1.4	565.5	6.4	575.5
2.3	569.5	1.9	566.5	6.9	581.0
2.8	573.5	2.4	567.0	7.4	587.0
3.3	577.0	2.9	567.0	7.9	595.5
3.8	580.7	3.4	566.0	8.4	603.5
		3.9	566.0	8.9	614.0
		4.4	567.5	9.4	628.0

Fig. 13.

chlorine and phosphate in such liquids (for example, urine) no difficulties were presented, the results being in perfect accord with those obtained by the other methods. The advantages of the electro-titrametric method in these latter instances are, the possibility of an exact analysis of a few cubic centimeters, and at the same time an extremely high degree of precision.

It is necessary here to call attention to the fact that in the determination of SO_4 in such liquids certain complications were encountered, which impressed us with the fact that we had to deal with a liquid of different composition from the synthetical solution. Observing certain precautions, as for example, degree of acidity, kind of reagent, etc., we were in some instances able to obtain results which closely agreed with those of gravimetric determinations.

The last curve is an illustration of the acid- and base-binding capacity of a physiological liquid, in this case urine. The previous statement in regard to the use of indicator is especially true in this case. It should not be overlooked, however, that the direction of the curve in such cases is probably not entirely due to the above stated phenomena, because other factors, such as changing viscosity, may affect the total result. It is interesting to note that in this connection successive precipitations were observed after the addition of certain amounts of the reagent.

It is the belief of the writers that such curves may prove to be in some cases a more instructive demonstration of the complex properties of such liquids and that more deductions might be drawn from such curves than those from a turning point of an indicator.

As the nature of this publication is preliminary, the authors wish to reserve the right to develop this field more completely in the near future.

AMHERST, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

A RAPID LABORATORY METHOD OF MEASURING THE PARTIAL VAPOR PRESSURES OF LIQUID MIXTURES.

BY M. A. ROSANOFF, C. W. BACON AND R. H. WHITE.[1]

Received July 2, 1914.

Section I.—Introductory Remarks.

It is scarcely necessary to point out that the partial pressures of volatile mixtures are not measured as such. What is really determined, is the composition of the vapor which is in equilibrium with the liquid mixture. The partial pressures are then assumed to be proportional to the molar percentages of the components in the vapor, and their absolute values become known if the total pressures have been determined manometrically.

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[1] I gladly acknowledge my indebtedness to my research assistant, Dr. John F. W. Schulze, for valuable help in preparing this paper for publication. M. A. R.