TABLE I—COMPARISON OF METHODS USED

Method number	METHOD USED	Digested 5 hrs. after clear				Digested 3 hrs. after clear			
		No. of detns.	Max.	Min.	Av.	No. of detns.	Max.	Min.	Av.
1	Kjeldahl (modified) Official: 50 cc. H ₂ SO ₄ + 0.7 g. Hg + KMnO ₄	4	8.38	8.34	8.36	5	8.30	8.22	8.26
2	Kjeldahl (modified) Official: 30 cc. H ₂ SO ₄ + 0.7 g. Hg + 20 cc. H ₂ SO ₄ (added later) + KMnO ₄ ..	5	8.45	8.38	8.41	2	8.34	8.32	8.33
3	Kjeldahl-Gunning-Arnold, modified by using KMnO ₄ and excess H ₂ SO ₄ : 50 cc. H ₂ SO ₄ + 0.7 g. Hg + 10 g. K ₂ SO ₄ + KMnO ₄	5	8.10	7.95	8.04	2	8.15	8.14	8.14
4	Kjeldahl-Gunning-Arnold, modified by using KMnO ₄ and excess H ₂ SO ₄ : 30 cc. H ₂ SO ₄ + 0.7 g. Hg + 10 g. K ₂ SO ₄ + 20 cc. H ₂ SO ₄ (added later) + KMnO ₄	5	8.29	8.20	8.26	..			
5	Kjeldahl-Gunning-Arnold, modified by using excess H ₂ SO ₄ (no KMnO ₄): 30 cc. H ₂ SO ₄ + 0.7 g. Hg + 10 g. K ₂ SO ₄ + 20 cc. H ₂ SO ₄ (added later).	5	8.28	8.19	8.22	..			
6	Kjeldahl-Jodlbauer (Official Kjeldahl to include nitrates): 50 cc. H ₂ SO ₄ + 0.7 g. Hg + 2 g. salicylic acid + 2 g. Zn dust + KMnO ₄	8	8.29	8.18	8.23	..			
7	Kjeldahl-Gunning-Jodlbauer: 50 cc. H ₂ SO ₄ + 0.7 g. Hg + 2 g. salicylic acid + 2 g. Zn dust + 10 g. K ₂ SO ₄ + KMnO ₄	5	8.28	8.16	8.24	..			
8	Dyer's modification of Kjeldahl-Gunning-Jodlbauer: 50 cc. H ₂ SO ₄ + 0.7 g. Hg + 2 g. salicylic acid + 2 g. Zn dust + 10 g. K ₂ SO ₄ + 1 g. sucrose + KMnO ₄	6	8.33	8.21	8.27	3	8.28	8.27	8.27
9	Gunning-Copper sulfate (modified by using KMnO ₄): 50 cc. H ₂ SO ₄ + 0.2 g. CuSO ₄ + 10 g. K ₂ SO ₄ + KMnO ₄	5	8.41	8.04	8.23	5	8.30	8.20	8.24
10	Gunning-Copper sulfate: 50 cc. H ₂ SO ₄ + 0.2 g. CuSO ₄ + 10 g. K ₂ SO ₄	5	8.26	8.25	8.25	..			
11	Official Gunning: 50 cc. H ₂ SO ₄ + 10 g. K ₂ SO ₄	6	8.27	8.09	8.17	..			
12	Vanadium-Gunning: 50 cc. H ₂ SO ₄ + 10 g. K ₂ SO ₄ + 0.2 g. V ₂ O ₅ (a).....	..				6	8.12	7.96	8.06

(a) Experiment Station Record, 32, 310.

TABLE II—PERCENTAGE NITROGEN IN CASEIN AND PIGS BY DIFFERENT TREATMENTS

DETERMINATION:		NITROGEN IN CASEIN								NITROGEN IN LOT II PIGS								NITROGEN IN LOT II PIGS							
METHOD:		Kjeldahl-Gunning-Arnold								Kjeldahl-Gunning-Arnold								Gunning-Copper Sulfate							
NUMBER		TOTAL HEATING				Hours heating				TOTAL HEATING				Hours heating				TOTAL HEATING				Hours heating			
		15	30	45	60	1	3	5	15	30	45	60	1	3	5	15	30	45	60	1	3	5			
1	A	13.23	13.89	14.20	14.46	14.56	14.64	14.39	7.32	8.06	8.06	7.91	8.18	8.32	Lost	7.33	7.63	7.70	7.94	8.13	8.20	8.44			
	B	13.36	13.87				14.62	14.49	7.25	8.05	7.97	7.88	8.17	8.34	8.46			7.77			8.26	8.37			
2	C	13.39	13.96	14.24	14.44	14.53	14.57	14.41	7.59	7.71	8.16	8.13	8.20	8.37	8.43	7.34	7.64	7.77	7.92	8.11	8.27	8.37			
	D	13.49	Lost				14.67	14.54	7.58	7.73	8.15	8.12	8.23	8.37	8.46			7.77			8.30	8.38			
AVER.		13.37	13.91	14.22	14.45	14.55	14.62	14.46	7.44	7.89	8.09	8.01	8.20	8.35	8.45	7.34	7.64	7.75	7.93	8.12	8.26	8.39			
Dry basis aver.		14.41	15.00	15.33	15.58	15.68	15.77	15.60																	

(a) 35 minutes were required until clear.

(b) 70 minutes were required until clear.

bumping, the usual frothing resulting from the use of zinc is obviated, and at the same time the distillation of mercury is eliminated. We experienced no further contamination of the condensers or receivers after making this change.

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METHODS FOR THE DETERMINATION OF CARBON DIOXIDE AND A NEW FORM OF ABSORPTION TOWER ADAPTED TO THE TITRIMETRIC METHOD¹

By E. TRUOG

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A large number of different methods and forms of apparatus have been recommended for the determination of carbon dioxide. This is largely due to the fact that the determination is made for a large variety of purposes and under numerous different conditions. In the chemical analyses of soils and in the investigation of soil phenomena, the writer has had numerous occasions to determine carbon dioxide. In such work carbon dioxide is usually determined by one of the three following methods: gas-volumetric, gravimetric, and titrimetric. In order to secure sufficiently accurate results for most purposes with the gas-volumetric method, rather elaborate apparatus is usually required, and hence the method is not used as generally as the others.

¹ Publication authorized by the Director of the Wisconsin Experiment Station.

THE GRAVIMETRIC METHOD

The gravimetric method, in which the carbon dioxide is absorbed in a KOH bulb or other absorbing tubes, gives very accurate results when the large number of precautions are strictly observed. These precautions and the disadvantages of the gravimetric method have been very completely set forth by J. R. Cain.¹ A precaution often ignored, but of great importance, is in the use of drying reagents of the same hygroscopicity at both ends of the CO₂ absorption bulb. The air must be dried to exactly the same degree, both when it enters and leaves the absorption bulb, or there will be an error due to loss or gain of water. In the writer's experience errors from this source may amount to as much as two milligrams. In the case of rapid aspirations of large volumes of gas so much absorbing and drying apparatus is needed that errors in weighing become serious.

THE ALKALI TITRIMETRIC METHOD

Owing to disadvantages of the gravimetric method, various titrimetric methods have come into use. Of these methods the absorption of the carbon dioxide in a sodium or potassium hydroxide solution and determination of the carbonates by double titration with phenolphthalein and methyl orange has been the most widely used. This method for the absorption and determination of free carbon dioxide was first used by Brown and Escombe.² These investigators apparently

¹ *Technological Paper*, 33, Bur. Standards; also *THIS JOURNAL*, 6 (1914), 465.

² *Phil. Trans.*, (B) 193 (1900), 289.

used the method very carefully, as several important precautions were given as follows: Pure sodium hydroxide free from iron and aluminum should be used. The volume should be kept low and in titration, loss of carbon dioxide locally should be prevented by thorough shaking. Contamination by carbon dioxide from the air should also be prevented by proper protection. They recognized the need of standard end points as a control and used vessels of the same shape, containing the same amounts of solution and indicators for the two end points, as were used in the regular analyses. In their check experiments in which varying known amounts of carbon dioxide were determined, the differences between the actual amounts present and those found range from 0.05 cc. to nearly 0.20 cc. of 0.1 *N* solution. This causes an error of 0.2 to 0.8 mg. of CO₂. These investigators, however, make no mention of the amount of indicator used or of the effect of carbon dioxide on the methyl orange end point. Later investigators have shown that these are considerations that need to be taken into account.

Küster¹ made an extended study of this double titration for carbon dioxide. He found that pure sodium bicarbonate reacts alkaline to phenolphthalein, even when present in small amounts. A rise of temperature makes the reaction more marked. An addition of sodium chloride depresses the reaction. He concludes that phenolphthalein is not suitable as an indicator for the accurate determination of alkali carbonates.

Noll² after an extended investigation comes to the conclusion that the correct results can be obtained only by use of phenolphthalein in the proper amount. The amount of phenolphthalein to be used is to be regulated by the amount of carbonates present. He also states that it is permissible to have only a small amount of carbonates present.

Auerbach³ in studying the determination of carbonates in water states that the titration should only be made in case of small amounts of carbonates and with very dilute amounts of phenolphthalein, otherwise it is necessary to make a correction. He used 5 drops of a phenolphthalein solution which contained one gram in 500 cc. He used a dilution of about 300 cc., and states that higher concentrations of indicator require larger amounts of carbon dioxide to dispel the color, while higher concentrations of bicarbonate prevent to a certain extent the formation of the color.

The writer has investigated this double titration method to a certain extent. A solution of sodium carbonate was prepared as follows: Kahlbaum's sodium bicarbonate which gave no test for chlorides or sulfates was used. A 17 g. sample of this was placed in a platinum dish and heated at 300° C. to constant weight in an electric furnace. The sodium carbonate was dissolved in 2000 cc. of CO₂ free water giving an approximately 0.1 *N* solution. Measured portions of this solution were titrated against sulfuric acid solution

of slightly less than 0.1 *N* strength. All measuring instruments used in this work had been carefully calibrated. The phenolphthalein solution used contained one gram in 100 cc. of alcohol. The methyl orange solution contained one gram in 1000 cc. of water. In the titrations of Table I two drops of phenolphthalein and one drop of methyl orange were used. The titrations were made in Erlenmeyer flasks, and the solutions were always diluted with such amounts of CO₂-free water as to make the final volume after titration close to 200 cc.

Standard end points for each titration were also used. The one for the phenolphthalein end point consisted of an Erlenmeyer flask similar to the one used in the regular titration, and to which was added 200 cc. of water and two drops of phenolphthalein. Since carbon dioxide has a very appreciable effect on methyl orange, it is necessary to vary this end point according to the amount of carbonates that are titrated. Carbon dioxide in amounts equal to those liberated in the titrations were added to 200 cc. of water containing one drop of methyl orange. The end points for each case were then made by adding 0.1 *N* sulfuric acid to 200 cc. of water until the color of the methyl orange indicated just a little stronger acidity than the corresponding one with carbonic acid. The end points with carbonic acid are not permanent because of escape of carbon dioxide, and hence it is necessary to make them with a non-volatile acid in which case they remain constant for several days.

In making the titration with phenolphthalein, the tip of the burette, which had been lengthened, was allowed to dip below the surface of the solution in the flask until near the end point, when it was raised. This procedure eliminates, largely, the possibility of escape of carbon dioxide due to local concentration of the mineral acid at the surface. This may also be accomplished by thoroughly shaking the flask and adding the acid very slowly. Such a procedure, however, may introduce other errors, since the vigorous shaking increases the opportunity for absorption of carbon dioxide during the first part of the titration; and may introduce an error in the opposite direction during the last part of the titration. An error due to the latter cause is apparently possible on considering the following: To 25 cc. of approximately 0.1 *N* Na₂CO₃ solution, diluted with water to 175 cc., were added two drops of phenolphthalein and then 0.1 *N* H₂SO₄ till the pink color was dispelled. The flask containing this solution was now placed in a Camp shaker and shaken for five minutes, when the solution was again distinctly colored. It took 0.3 cc. more of 0.1 *N* acid to change this color to the same shade as the blank which was not shaken. This is evidently due to loss of carbon dioxide. By simply letting the solution stand the same phenomenon will take place after several hours. After several days the solutions will become strongly colored. Table I gives a few of the results which have been obtained by following the procedure outlined.

If the method is to give correct results, then the titration with phenolphthalein should be just one-half

¹ *Z. anorg. Chem.*, **13** (1897), 127.

² *Z. angew. Chem.*, **25** (1912), 998.

³ *Ibid.*, **25** (1912), 1722.

of the total on continuing to the methyl orange end point. From Table I it is evident that the method has given very good results when not over 25 cc. of 0.1 N Na_2CO_3 , equivalent to approximately 50 mg. of CO_2 , was present. If larger amounts of carbonates are present, then the end point with phenolphthalein comes

TABLE I—DOUBLE TITRATION OF SODIUM CARBONATE WITH H_2SO_4

All solutions approximately 0.1 N and all figures represent cc.

Na_2CO_3 taken	Phenolphthalein		Methyl orange	
	Calculated	Consumed	Calculated	Consumed
10	5.53	5.48	11.06	11.05
10	5.53	5.50	11.06	11.10
25	13.81	13.76	27.62	27.68
25	13.81	13.75	27.62	27.55
50	27.62	27.20	55.24	55.15
50	27.62	27.15	55.24	55.00
75	41.43	40.91	82.86	82.76

too soon when only two drops of indicator are present. In two other trials not given above it was found as follows:

When 50 cc. of Na_2CO_3 were taken, it required four drops of phenolphthalein to bring the end point at the proper place. Similarly with 0.5 cc. of phenolphthalein and 50 cc. of Na_2CO_3 an excess of 1.10 cc. of acid was used.

Thus, if too little phenolphthalein is used in proportion to the amount of CO_2 present, then the end point comes too soon; and if the reverse condition obtains, then the true end point is overstepped. That such is the case can also be shown in the following simple manner: To 50 cc. of 0.1 N Na_2CO_3 diluted to about 100 cc. are added two drops of phenolphthalein and then acid till the color disappears. If more phenolphthalein is now added, the color will again appear, and the intensity will depend upon the amount of phenolphthalein added as well as the temperature and the amount of shaking and length of time the solution stands.

The results just given are in full accord with those of the investigators already cited. In order to obtain correct results it is absolutely necessary to regulate the amount of phenolphthalein used according to the amount of carbonates present. If precautions are not taken in regard to the use of phenolphthalein and to the effect of CO_2 on the methyl orange end point, then two errors enter into the determination; but since they are in opposite directions when only small amounts of phenolphthalein are used, they compensate to a certain degree. It is possible that because of this compensation, Brown and Escombe¹ were able to get as good results as they did, apparently without regard to these precautions. The evidence is conclusive that in order to be assured of correct results with the double titration method for carbonates, several precautions need to be carefully observed. To observe all these precautions causes considerable inconvenience.

It should also be noted that the end points, especially with phenolphthalein, are not at all sharp or positive, and thus it is possible to make the titration only under the best conditions of light. Even under such conditions many persons find it absolutely impossible to discern the true end points because of the gradual color change. The method thus leaves much to be desired.

¹ *Loc. cit.*

Bowser¹ recommends the use of KOH instead of $NaOH$ for the absorption of the CO_2 and states that it is more satisfactory. The writer has found that this gives a slightly better end point with phenolphthalein than when $NaOH$ is used, but the improvement is not sufficient to make the method satisfactory. Bowser also recommends the addition of 10 to 15 cc. of ethyl alcohol to further improve the end point. When solutions of Na_2CO_3 and K_2CO_3 to which phenolphthalein has been added are brought to the colorless point with acid and then allowed to stand, the resultant solution of $NaHCO_3$ regains its color much more rapidly than the solution of $KHCO_3$. This is undoubtedly due to the greater dissociation or breaking up of the $NaHCO_3$ and loss of CO_2 by dissipation to the air. The action of the alcohol probably consists in retarding this dissociation and preventing the loss of CO_2 to the air because of its greater solubility in alcohol than in water. The writer has found no advantage in the use of the alcohol and, as is well known, it decreases greatly the sharpness of the methyl orange end point.

THE BARIUM HYDROXIDE TITRIMETRIC METHOD

In search of a better method the writer was led to try the method of absorption in a measured excess of $Ba(OH)_2$ in which the carbon dioxide is precipitated as $BaCO_3$ which is practically neutral to phenolphthalein. The excess of $Ba(OH)_2$ is then easily determined by titration, and thus by difference the amount of CO_2 is quickly determined. The principle of the method is essentially that of the C. Winkler titration method for carbon dioxide and carbonates. This method has the advantage of a good end point. The presence of the precipitate of $BaCO_3$ in the solution in which the titration is made may appear objectionable, but the experimental data show that the presence of the precipitate has absolutely no harmful effects. The precipitate, being pure white, aids rather than hinders the eye in detecting the end point. Küster² gives considerable data which show conclusively that carbonates can be determined with great accuracy by this method.

The writer has tested the method as follows: Measured quantities of standard $Ba(OH)_2$ were treated with excess of CO_2 , and then boiled to expel the excess and change all bicarbonate to normal carbonate. Measured quantities of $Ba(OH)_2$ and four drops of phenolphthalein were added to these samples. Standard acid was then added till the color disappeared. The results showed that $Ba(OH)_2$ could be determined in the presence of $BaCO_3$ very accurately. The experimental results never varied from the calculated by more than one drop of 0.15 N acid and the end point was always good.

J. R. Cain³ recommends the absorption of the CO_2 in $Ba(OH)_2$ and after filtering off and washing the $BaCO_3$, titrates it with standard acid. For very small amounts of CO_2 this is undoubtedly a very good method, and Cain has outlined a procedure for filtering and washing that has given excellent results. When larger

¹ THIS JOURNAL, 4, pp. 203, also 265.

² Z. angew. Chem., 13 (1897), 127.

³ *Loc. cit.*

amounts of CO_2 are to be determined, then the washing of the precipitate becomes more troublesome, and there is nothing to be gained by this procedure over that of titrating the excess of $\text{Ba}(\text{OH})_2$.

A serious objection to the method of titrating the excess of $\text{Ba}(\text{OH})_2$ has been that of securing complete absorption in the case of rapid aspirations carrying considerable amounts of CO_2 . The ordinary form of absorption towers with glass beads, as are used with alkali hydroxides, are not adapted for use with $\text{Ba}(\text{OH})_2$ since in this case a precipitate is formed which prevents complete washing. When the aspiration is slow, and small amounts of CO_2 are to be absorbed, Meyer bulb tubes are a satisfactory form of absorption apparatus. Brady¹ has described an arrangement adapted for such purposes.

A NEW FORM OF ABSORPTION TOWER

In an attempt to secure an absorption apparatus for use with $\text{Ba}(\text{OH})_2$ that would be satisfactory for both slow and rapid aspirations, carrying either small or large amounts of CO_2 , the writer has devised the absorption tower shown in Fig. 1. This apparatus consists of a 500 cc. suction flask (A), a glass tube

FIG. 1.—ABSORPTION TOWER ADAPTED TO THE USE OF BARIUM HYDROXIDE FOR THE ABSORPTION AND TITRIMETRIC DETERMINATION OF CARBON DIOXIDE

water are quickly poured into the funnel and the soda-lime tube is replaced. This water is now allowed to run into the tower, thus washing the funnel free of $\text{Ba}(\text{OH})_2$. The suction draws the absorbing solution up into the tower. The apparatus is now ready for the absorption of CO_2 . When the absorption is complete, the suction is closed off with a pinch-cock or stop-cock and the stop-cock of (E) is gradually opened

allowing CO_2 -free air to enter, when the absorbing solution settles into the flask. The flask is next disconnected from the source of CO_2 and after the solution has settled into the flask, the stop-cock of (E) is closed. The air in (E) is now free from CO_2 and ready for the next determination. The stopper at the top of the tower is raised and the extending tubes washed off into the tower with a little CO_2 -free water. The tower is raised a few inches from the flask, when the beads slide out. If they stick to the tower, a little gentle tapping at the top suffices to make them drop. The inside of the tower is immediately rinsed with about 100 cc. of CO_2 -free water poured from a beaker. The tower is raised and removed after also washing off the lower end on the outside. Four drops of phenolphthalein are added and the excess of $\text{Ba}(\text{OH})_2$ is immediately titrated.

By following the directions as given, the flask and tower are filled with CO_2 -free air previous to washing. The washing is quickly and easily made, and if the flask is then corked or the titration immediately made, there is scarcely any chance for contamination from the air. The $\text{Ba}(\text{OH})_2$ is delivered directly from a burette into the funnel (E) which contains CO_2 -free air. The soda-lime tube (F) is always replaced as quickly as possible. In the titration the flask is shaken continuously to prevent local action of the acid on the BaCO_3 and possible loss of CO_2 . The glass beads cause no hindrance in the titration. A little BaCO_3 may stick to the sides of the tower, but this need not be completely washed out as it does not enter into the titration. After titration a little strong acid is added to the flask to dissolve the BaCO_3 . The beads are then poured onto a scoop-shaped screen, washed under the tap, rinsed with distilled water and poured back into the tower, which has been replaced in the flask.

Perforated glass beads should be used in preference to the solid spherical kind, as they break up the bubbles more completely and increase the efficiency of the absorption. In the old form of towers, perforated beads could not be used advantageously, since they made complete washing very difficult. This objection is entirely done away in this form of tower. If solid spherical beads are used they should be mixed with some short pieces of glass tubing in order to leave sufficient pore space for the absorbing solution. Alkali hydroxides may be used also with this form of tower and the absorbed CO_2 may then be determined by double titration, or better, by adding an excess of BaCl_2 and then titrating the BaCO_3 after neutralizing the excess of hydroxide. The best plan of all is to use a standard solution of $\text{Ba}(\text{OH})_2$ to absorb the CO_2 . Solutions of $\text{Ba}(\text{OH})_2$ free from carbonates are much more easily prepared than those of the alkalies. By using a sufficiently large tower there is no trouble in getting complete absorption with $\text{Ba}(\text{OH})_2$ even with rapid aspirations. A tower of the height in the figure suffices for most purposes. If the aspiration is extremely rapid the column of beads should be increased to twenty inches in height. The precipitate of BaCO_3 aids in the absorption, by checking the movement of gas bubbles.

¹ THIS JOURNAL, 6 (1914), 843.

REAGENTS

STANDARD HYDROCHLORIC ACID SOLUTION—A 0.4 *N* solution is employed.

BARIUM HYDROXIDE SOLUTION—A 0.4 *N* solution is prepared as follows: Dissolve 80 g. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in 1000 cc. of water, heat to boiling and then filter with a Buchner funnel into a stock bottle which has been freed of CO_2 . A double filter paper is carefully laid on the funnel and drawn down and then the funnel is never allowed to suck dry till the solution has all gone through. In this way a solution free of carbonates is much more quickly and easily prepared than by allowing the precipitate to settle and siphoning over. The burette and appropriate guards are then attached and the proper dilution is made after titrating against the standard acid.

PHENOLPHTHALEIN SOLUTION—One gram of the indicator is dissolved in 100 cc. of ethyl alcohol.

ACCURACY OF METHOD

In order to test the efficiency of the apparatus and technique in preventing the contamination of the $\text{Ba}(\text{OH})_2$ by the CO_2 of the air, measured quantities of the $\text{Ba}(\text{OH})_2$ were placed in the tower in the regular way, and after aspirating CO_2 -free air through the apparatus for some time, the solution was removed in the regular way and titrated. The titrations disclosed no measurable quantities of CO_2 , and hence the contamination is practically entirely prevented. In order to test the efficiency of the absorption with this tower, measured quantities of the $\text{Ba}(\text{OH})_2$ solution were treated with CO_2 and after boiling to expel the excess of CO_2 , the precipitate of BaCO_3 was transferred to an evolution flask and the evolved CO_2 drawn through the absorption tower and determined by titration. The results never varied from the calculated by more than a drop of 0.4 *N* acid, which represents less than 0.5 mg. of CO_2 . The $\text{Ba}(\text{OH})_2$ in the tower will absorb efficiently with rapid aspiration to nearly one-half saturation, which represents about 0.15 g. of CO_2 . With slow aspiration still more may be safely absorbed. The tower is conveniently attached to almost any form of apparatus in which CO_2 is evolved for measurement. For more accurate determinations of small amounts of CO_2 , more dilute solutions of $\text{Ba}(\text{OH})_2$ and HCl should be used.

SUMMARY

I—The gravimetric determination of CO_2 by weighing of absorption apparatus gives accurate results in the case of small amounts of CO_2 , slow aspiration, and due precautions in weighing and drying. In the case of rapid aspirations carrying considerable amounts of CO_2 the gravimetric method is troublesome.

II—The determination of CO_2 by absorption in alkali hydroxide and double titration has many disadvantages. The amount of indicator used needs to be carefully regulated and standard end points should be used. Under the best conditions, the end points are not sharp, making it absolutely unusable by some people. Good results can be obtained in the case of people having a good eye for color by observing the

necessary precautions, but this leads to a great deal of inconvenience.

III—A new form of tower, described above, makes possible the use of $\text{Ba}(\text{OH})_2$ as an absorbing medium for CO_2 under nearly all conditions. It also eliminates practically all contamination of CO_2 from the air, and greatly facilitates the washing. The titration has the advantage of a very good end point. The standard solution of $\text{Ba}(\text{OH})_2$ is easily prepared free of carbonates.

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THE AMINO ACID NITROGEN OF SOIL

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INTRODUCTION

The importance of the amino acids as the chief products of the chemical, and under some conditions, of the biological decomposition of protein material, makes desirable a quantitative knowledge regarding their occurrence in the soil. While there is, no doubt, present in the soil representatives of all the classes of compounds between undecomposed protein and ammonia and nitrates, yet there are no methods which have been applied to the quantitative determination of any of these classes of compounds except ammonia, nitrates, and nitrites, which together make up but a small proportion of the total nitrogen compounds. It would seem, therefore, that a more complete knowledge of the nitrogen of the soil is very important from an academic and a practical standpoint. In this investigation, our attention has been confined to the amino acid nitrogen. Many investigators have found amino acids in soil after subjecting it to hydrolysis, but there has been no quantitative determination of the amino acids as such. In fact, the only investigations showing the presence of amino acids in the soil were made by Shreiner and Shorey, who found histidine, arginine,¹ and lysine,² in a weak alkali extract of soil.³

Except for the work of Chardet, which has not been confirmed, the only proof there is of the presence of amino acids in the soil is the work of Schreiner and Shorey. Until quite recently, there has been no method sufficiently sensitive to permit of the accurate determination of the amino acids in the soil, but the copper method of Kober,⁴ being capable of detecting, with considerable accuracy, one part of amino acid nitrogen in 500,000 parts of solution, has been found very suitable for soil work. By this method 5 to 30 parts of amino acid nitrogen per million parts of soil have been found, so it can easily be seen how the earlier methods would be entirely unsuited. The formol titration method of Soerensen⁵ has been shown

¹ *J. Biol. Chem.*, **8** (1910), 382.

² U. S. Dept. Agric., Bur. of Soils, *Bull.* **88** (1913).

³ Since the experimental part of this paper was completed, Chardet (*Rev. gén. chim.*, **17**, 137) reports the analysis of 4 soils for amino acid nitrogen by the Soerensen method. He found from 49 to 68 per cent of the total nitrogen was amino acid nitrogen. Following his directions, as given, we have been unable to find an appreciable amount of amino acid nitrogen in any of several soils examined.

⁴ *J. Am. Chem. Soc.*, **35** (1913), 1546.

⁵ *Z. physiol. Chem.*, **64** (1910), 120.