

red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of color could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, 5 drops of the mixture were added to 100 cc. of distilled water, when 0.1 cc. of 0.01 normal hydrochloric acid solution or 0.01 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other coloring-matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

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## THE ESTIMATION OF CARBONIC ACID IN WATER.

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THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

### CONDITION IN WHICH CARBONIC ACID EXISTS IN NATURAL WATERS.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of

these bases are, relatively speaking, but sparingly soluble in water. If, however, more than enough carbon dioxide be present to unite with the oxides of calcium and magnesium to form the compounds  $\text{CaCO}_3$  and  $\text{MgCO}_3$ , the solubility of these salts is much increased. It is generally assumed, that when there is present one extra molecule of carbon dioxide for each molecule of calcium carbonate or of magnesium carbonate, compounds of the character of sodium bicarbonate exist, although such salts have never been isolated. These salts are presumed to have the composition represented by the formulas  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ , respectively.

The gas carbon dioxide ( $\text{CO}_2$ ) is quite soluble in water and therefore may exist in natural waters in amounts greater than is required to form the bicarbonates of the alkaline earth bases which may be present. It is usually considered that carbon dioxide thus dissolved in the water exists as a true acid having the formula  $\text{H}_2\text{CO}_3$ .

From the above it is evident that there are three conditions in which carbon dioxide may be present in natural waters. If the carbon dioxide is not combined with any base, it is spoken of as "free carbonic acid;" if it is combined indirectly with the base as in the form of the bicarbonates, it is termed "half bound carbonic acid;" and if directly united to the bases as in calcium and magnesium carbonates, it is called "fixed carbonic acid." The sum of the amounts of the carbonic acid found in these three forms is usually spoken of as the "total carbonic acid." The carbonic acid that is expelled on heating aqueous solutions containing either "free" or "half-bound carbonic acid" or both is sometimes spoken of as "volatile carbonic acid."

Natural waters carry varying amounts of carbonic acid, depending on the character of the geological formations with which they have come in contact. Ground waters having probably been under greater pressure usually contain more carbonic acid than surface waters. Moreover ground waters which become exposed to the air lose the larger proportion of their free carbonic acid and may even part with some of their half-bound and fixed carbonic acid. The loss of the latter results, of course, from a precipitation of carbonates (calcium carbonate principally), as a result of the loss of some of the half-bound carbonic acid.

It was found that the ordinary distilled water of the laboratory

might contain from 6 to 10 parts per million of free carbonic acid. It was necessary to boil off 10 to 15 per cent. of the original volume of such a water in order to free it completely from the gas. A water thus freed from carbonic acid absorbs, when exposed to the air, more or less carbon dioxide depending on the amount present and on the temperature and pressure. Two samples of distilled water free from carbonic acid were exposed in beakers to the air of the laboratory in which the temperature was approximately 16° C.

	A. Free carbonic acid. Parts per million.	B. Free carbonic acid. Parts per million.
Original water.....	0	0
After twenty-four hours.....	2.2	2.2
After forty-eight hours.....	15.0	13.2
After seventy-two hours.....	0.9	0.9

The great variation in the amounts obtained was probably due to the differing quantities of carbonic acid present in the atmosphere of the laboratory on the particular day the samples were examined. On the second day a carbonic acid generator was being used in the laboratory and considerable gas was also being burned.

Waters containing large amounts of calcium bicarbonate and free carbonic acid, not only lose their free but also a portion of their half-bound carbonic acid, when exposed to the air for any length of time. The excess of calcium carbonate (CaCO<sub>3</sub>) is thereby precipitated and the solution grows weaker in lime, until a state of equilibrium is reached.

The following experiments illustrate the action of a strong solution of calcium bicarbonate (Ca(HCO<sub>3</sub>)<sub>2</sub>), when exposed to the air of the laboratory.

	A. Carbonic acid in solution. Free. Half-bound. Fixed. Parts per million.			B. Carbonic acid in solution. Free. Half-bound. Fixed. Parts per million.		
	Original water.....	52.8	109.4	109.4	52.8	109.4
After twenty-four hours	7.9	....	....	7.0	....	....
After forty-eight hours.	1.3	....	....	1.1	....	....
After seventy-two hours	0	80.7	84.5	0	80.7	84.5

Magnesium bicarbonate is much more soluble in water than calcium bicarbonate, but strong solutions show the same tendency to give up their half-bound carbonic acid as do strong solutions of calcium bicarbonate. This occurs, however, without any precipitation of magnesium carbonate (MgCO<sub>3</sub>) because the latter itself is quite soluble in water.

A strong solution of magnesium bicarbonate lost all of its free and 12 per cent. of its half-bound carbonic acid in less than three days when exposed to the air of the laboratory. This solution, therefore, contained 12 per cent. of its total magnesium carbonate in the form of normal magnesium carbonate ( $\text{MgCO}_3$ ). On the other hand the calcium bicarbonate solution, as shown above, contains only 4 per cent. of its total calcium carbonate in the form of the normal carbonate ( $\text{CaCO}_3$ ). This illustrates the difference in degree of the affinity of solutions of these two salts for carbon dioxide.

However solutions of calcium and magnesium carbonate which contain no half-bound or free carbonic acid or only very limited amounts of the former, tend to absorb the gas from the air, and thus form the bicarbonates of these bases. Calcium carbonate solutions in time become acid (*i. e.*, contain free carbonic acid), but the acidity is always very slight and the state of equilibrium seems to be reached when the lime is all in the form of the bicarbonate. On the contrary weak solutions of magnesium carbonate, while they absorb carbon dioxide from the air to form magnesium bicarbonate, only very slowly approach the condition where all the magnesium exists as bicarbonate; in fact the tendency seems to be for the solution to remain as a mixture of these two compounds. That these facts have a bearing on certain classes of natural waters will be shown later.

PRINCIPLES ON WHICH METHODS FOR THE ESTIMATION OF  
CARBONIC ACID ARE BASED WITH A DISCUSSION OF  
THE ERRORS AFFECTING THEIR ACCURACY.

A comparison of the three most commonly employed volumetric methods for the determination of carbonic acid in water, has been made by the writers, with the purpose of discovering, if possible, the sources of error which affected each of them, and also to learn which gave results closest to amounts actually known to be present in solution.

The oldest and best known of the three methods was suggested by Pettenkofer.<sup>1</sup> Trillich<sup>2</sup> modified this method in order to avoid certain difficulties arising in the original method, and as this modification is quite radical, the process as carried out by him

<sup>1</sup> *N. Rep. Pharm.*, 10, 1.

<sup>2</sup> *Ztschr. angew. Chem.*, June 15, 1889, p. 357.

can be considered practically as a new method. Seyler<sup>1</sup> advocates what he terms the Lunge-Trillich method, which in principle differs materially from that of Pettenkofer's or Trillich's modification of Pettenkofer's method.

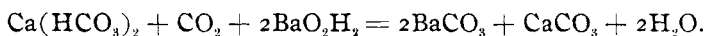
These three methods were those which were investigated and compared. In order to avoid confusion the three will be designated in this paper as Pettenkofer's, Trillich's, and Seyler's methods respectively.

#### PETTENKOFER'S AND TRILLICH'S METHODS.

The estimation of the carbonic acid in natural waters consists in determining the amount of half-bound and free carbonic acid which may be present. The estimation of the fixed carbonic acid is generally regarded as a separate determination, and is not commonly included in the statement of the results.

The principle upon which Pettenkofer based his determination depends on the action which the barium or calcium hydroxide has upon free and half-bound carbonic acid, whereby insoluble calcium and barium carbonates are formed which precipitate out of solution. Either calcium or barium hydroxide may be used, the reactions involved being of similar character.

As an excess of the precipitant is used, the portion unacted upon is determined volumetrically with a standard acid solution, and the amount of the barium or calcium hydroxide which has reacted with the free and half-bound carbonic acid can thus be determined by difference. The reaction is as follows:

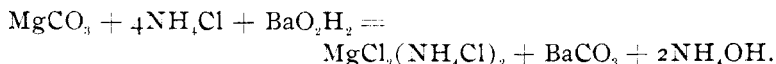


As the calcium carbonate present has been held in solution by the assistance of the half-bound molecule of carbon dioxide, it also precipitates upon the latter's removal by the barium hydroxide.

In so far as that portion of the half-bound carbonic acid, which may be present in a natural water, is combined with the magnesium carbonate to form the bicarbonate, the reaction between it and the calcium or barium hydroxide is the same as shown by the above reaction. But magnesium carbonate ( $\text{MgCO}_3$ ) instead of precipitating out as such, reacts with the calcium or barium hydroxide and forms magnesium hydroxide, which latter, being insoluble, precipitates. The presence, therefore, of magnesium carbonate or in fact any magnesium salt causes the calcium or

<sup>1</sup> *Chem. News*, 70, 104 (1894); and *Analyst*, 22, 312 (1897).

barium hydroxide to be used up. Pettenkofer avoids the precipitation of the magnesium by the introduction of ammonium chloride, which, by forming a soluble salt of ammonium and magnesium chloride, prevents any loss of calcium or barium hydroxide. The reaction is as follows :



An equivalent amount of ammonium hydroxide being formed, no change in the caustic alkalinity of the sample results.

Trillich's modification of Pettenkofer's method consists in not attempting to prevent the reaction between the magnesium salts and the caustic alkali by the addition of ammonium chloride, but in allowing the precipitation to take place. From a direct gravimetric determination of the amount of the magnesium present in another portion of the sample, he is enabled to apply the proper correction to the result obtained volumetrically. Since 40 parts of magnesium oxide (MgO) would react with as much barium or calcium hydroxide as 44 parts of carbon dioxide, the correction is obtained by multiplying each part of magnesium oxide (MgO) present by 1.1 and subtracting the product from the apparent amount of carbonic acid found by the volumetric determination. Trillich's method, therefore, only differs from the original Pettenkofer method in providing another way to overcome the difficulty arising from the presence of magnesium salts.

In order to differentiate between the free, half-bound, and fixed carbonic acid, Trillich uses that portion of his solution which contains the precipitated carbonates and titrates it with hydrochloric acid and cochineal. From this he obtains the "total carbonic acid." By subtracting the "free and half-bound carbonic acid" from this, he obtains the "fixed carbonic acid;" and by finding the difference between the "free and half-bound acid" and the "fixed" (equivalent to the half-bound), he estimates the "free carbonic acid."

It is apparent that by this means the various forms of carbonic acid may be determined in Pettenkofer's method, although the writers are not aware that originally any such differentiation was attempted. Moreover it would seem more simple to use a method which would not involve the objectionable titration of the suspended carbonates and magnesium hydroxide. This can be done by determining the fixed carbonic acid by direct titration of a

separate sample of the water by Hehner's method, and from this all the data given can easily be deduced. In our examination of these methods we have not attempted to carry out Trillich's titration of the portion of the sample containing the precipitated carbonates.

In Pettenkofer's method and in Trillich's as well, oxalic acid is used to titrate the excess of the barium or calcium hydroxide added to the water under examination. If barium hydroxide is used Trillich recommends that to each 9 grams of the barium hydroxide, 0.5 gram of barium chloride be added in order to convert the hydroxides of sodium and potassium, which are common impurities of barium hydroxide, into chlorides. The reason for this and for the addition of barium or calcium chloride in the original Pettenkofer method, is more fully stated by Fresenius<sup>1</sup> as follows :

"If ..... a water contains an alkali carbonate or any other alkali salt whose acid would be precipitated by lime or baryta, a neutral solution of calcium or barium chloride must be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of magnesium carbonate in the carbonic acid water ; this inconvenience consists in the fact that oxalate of an alkali or of magnesium enters into double decomposition with calcium carbonate (which is seldom entirely absent from the fluid to be analyzed), forming calcium oxalate and carbonate of the alkali or of magnesium, which latter will of course again take up oxalic acid."

The details of the Pettenkofer process consist in taking 100 cc. of the water to be analyzed, placing it in a bottle, adding 3 cc. of barium chloride, 2 cc. of a saturated solution of ammonium chloride and 45 cc. of barium hydroxide solution. After allowing the mixture to stand about twelve hours closely stoppered, an aliquot portion of the clear supernatant liquid is pipetted off and titrated with oxalic acid. In our experiments an approximately 0.02 normal solution of sulphuric acid was used. The barium hydroxide solution was approximately 0.05 normal and the indicator employed was rosolic acid.

The Trillich method differs from the above in using 5 cc. of barium chloride in place of 3 cc., omitting the ammonium chloride and using phenolphthalein as the indicator. In titrating the

<sup>1</sup> "Quantitative Chemical Analysis," p. 405 (English edition, 1889).

suspended carbonates for the determination of the total carbonic acid, Trillich employs hydrochloric acid and cochineal as the indicator, as previously stated.

In carrying out these methods the following precautions have been found necessary in order to obtain uniform and consistent results.

1. The barium hydroxide solution (9 grams  $\text{BaO}_2\text{H}_2\cdot 8\text{H}_2\text{O}$  and 0.5 gram  $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$  per liter) should be carefully filtered and kept in a bottle whose outlet to the air is provided with a U-tube containing fused calcium chloride and stick potash. A siphon tube conveniently conveys the liquid to the measuring burette. Solutions thus protected will keep for a long time without serious deterioration. A solution thus guarded from the atmospheric carbon dioxide was found at the end of fifty days to be 0.6 per cent. weaker than when first tested.

2. If oxalic acid is used, it should be frequently tested as it deteriorates rapidly. A solution containing 2.8636 grams per liter (1 cc. = 1 mg.  $\text{CO}_2$ ) was found at the end of forty-five days to be 6.7 per cent. weaker and one fifty days old was 8.7 per cent. weaker.

3. Dry or well drained, ground glass-stoppered bottles with their stoppers well vaselined should be used for holding the samples. On account of the strong tendency which barium hydroxide solutions exposed to the air, show in the absorption of atmospheric carbon dioxide, the most erratic results will be obtained if the bottle stoppers are not tight-fitting.

4. Samples of water to be analyzed should properly, if at all high in free and half-bound carbonic acid, be introduced into the bottle by means of a siphon or tube, similar to the methods used in taking samples for determining dissolved oxygen.

5. After the introduction of the sample into the bottle, the other reagents should be added, the barium hydroxide solution, however, always being the last to be introduced. The barium hydroxide should be introduced by means of a long delivery tip on the burette, the lower end of which dips below the surface of the sample in the bottle. The barium hydroxide should be run in as quickly as possible and the bottle immediately stoppered and shaken.

6. The bottle should then be set aside to stand at least twelve hours and under no condition should the stopper be removed until



the clear supernatant liquid is pipetted off for immediate titration.

7. The removal of the 25 or 50 cc. of the liquid to be titrated should take place without stirring up the precipitate in the bottom of the bottle. This is extremely important and its neglect, even when only a slight amount of sediment is withdrawn, will lead to irregular and unreliable results.

8. The receptacle in which the titration takes place should be a narrow mouthed fairly long-necked flask, preferably of about 250 cc. capacity. The titration should take place immediately upon the withdrawal of the portion from the bottle and the acid should be run in quickly.

9. If the delivery of the acid can be quickly effected the larger portion should be delivered into the flask holding the barium hydroxide as soon as possible without any unnecessary shaking of the flask. The titration can then be cautiously completed. If, however, the burette delivers the acid slowly it is better to run into the empty flask the larger portion of the acid and then add the portion of the sample to be titrated. This avoids undue exposure of the caustic alkali to the air and consequently any carbonating of the barium hydroxide.

10. The standardization of the barium hydroxide solution by the acid should be carried out in a manner similar to the method employed in the titration of the sample. In standardizing the barium hydroxide solution in order to obtain its value in terms of the acid, it is necessary in the Pettenkofer method, that the titration should take place in the presence of ammonium chloride, if rosolic acid or any indicator which is at all affected by this salt, is used. Otherwise the value of the alkali in terms of the acid will be erroneous and the differences, though slight, will lead to considerable error.

In spite of the above precautions an error due to manipulation may arise on account of the extreme sensitiveness of barium hydroxide to atmospheric carbon dioxide. An average of twenty experiments made with the utmost caution, with boiled distilled water and barium hydroxide in well-ground glass-stoppered bottles, thoroughly vaselined, showed a loss of barium hydroxide equivalent to 1.5 parts per million of carbonic acid, with a range of from 1 to 3 parts per million.

Reinitzer<sup>1</sup> found in a solution of lime-water containing 1173.8

<sup>1</sup> *Ztschr. angew. Chem.*, September 15, 1894.

parts per million of calcium oxide, carbon dioxide equivalent to (a) 8.7 parts and (b) 9.3 parts, respectively. The results were obtained by acidulation of the solution, expulsion of the carbon dioxide by heating, absorption and weighing of the gas in caustic potash. He states "we may assume the same conditions hold good with baryta water."

The writers have found carbonic acid in calcium hydroxide solutions to range from 0 to 6 or 7 parts per million, although on an average the quantity was less than 3 parts per million. In the case of barium hydroxide solutions we have never found over 1 part per million of carbonic acid and the average appears to be less than 0.5 part per million. The error arising, therefore, from dissolved carbonates in barium hydroxide solutions, in the absence of other salts which may effect their solution, we are inclined to believe may be usually disregarded as a source of error.

The presence of suspended carbonates in the portion of the sample being titrated, however, is a source of error which must be carefully avoided. This arises from the direct solution of these salts in the titrating acid; and this is true whether oxalic acid is used or sulphuric acid, which latter was employed by the writers. This is shown by the following experiments.

TABLE SHOWING SOLUBILITY OF SUSPENDED CARBONATES BY TITRATING ACID.

<i>I. Acid Added to Alkali.</i>			
Sol. used.	Containing no suspended carbonates.	Containing suspended carbonates.	Remarks.
cc.	N 50 sulphuric acid.	N 50 sulphuric acid.	
10	3.9	5.0	End-point indefinite with suspended carbonates.
Sol. used.	N 20 (approx.) oxalic acid.	N 20 (approx.) oxalic acid.	
cc.	cc.	cc.	
10	2.2	2.7	End-point indefinite with suspended carbonates.

On another sample the following results were obtained :

<i>I. Acid Added to Alkali.</i>			
Sol. used.	Containing no suspended carbonates.	Containing suspended carbonates.	Remarks.
cc.	N 50 sulphuric acid.	N 50 sulphuric acid.	
10	5.0	7.0	End-point indefinite with suspended carbonates.
<i>II. Alkali Added to Acid.</i>			
10	5.0	7.0	End-point indefinite with suspended carbonates.

It will thus be seen that the presence of suspended carbonates is quite inadmissible if accurate results are to be expected.

In both Pettenkofer's and Trillich's methods, the chief disturbing element is magnesium. Its salts must either be kept in solution as in Pettenkofer's method by the use of ammonium chloride, or allowed to precipitate out and be corrected for as in Trillich's method. As the errors arising from the presence of magnesium salts are probably due to two different causes in the two methods, they will be discussed separately.

The erratic results often obtained with Pettenkofer's method are generally acknowledged. Tiemann<sup>1</sup> admits that duplicate results may vary from 5 to 10 parts per million, and that the results are still more uncertain in the presence of magnesium salts. Thinking that ammonium chloride might be instrumental in holding carbonates in solution, some experiments were made to learn what effect it did have. The following experiments show the results obtained with a water which contained 59.2 parts per million of free and half-bound carbonic acid, but which contained no magnesium salts.

TABLE SHOWING EFFECT OF AMMONIUM CHLORIDE IN HOLDING CARBONATES IN SOLUTION.

No.	Sol. (approx. N 20) barium hydroxide. cc.	Saturated solution ammonium chloride. cc.	Carbonic acid (CO <sub>2</sub> ) obtained. Parts per million.
1	10	0	57.4
2	45	0	60.0
3	10	2	0.0 <sup>2</sup>
4	20	2	0.0 <sup>3</sup>
5	30	2	45.0
6	45	2	56.6

It will be noticed that as the concentration of the barium hydroxide solution increases, the ammonium chloride is less able to hold the carbonates in solution. Even with 45 cc. of barium hydroxide solution, the amount is still less than with the same amount of alkali where no ammonium chloride is present. It is apparent from these experiments that carbonates may be held in solution where the concentration of the barium hydroxide solution is not great enough; and such a condition might easily arise in a water containing low amounts of magnesium but considerable

<sup>1</sup> "Chem. Analyses des Wassers," Tiemann.

<sup>2</sup> In the third experiment no loss of barium hydroxide resulted and 38.4 parts per million of fixed carbonic acid were indicated in addition.

<sup>3</sup> No loss of barium resulted in the fourth experiment and 1.9 parts per million of fixed carbonic acid were found in addition.

carbonic acid, which latter would use up a large proportion of the barium hydroxide added.

In order to see whether ammonium chloride was able to hold in solution all of the magnesium which might be present, the following experiments were made :

TABLE SHOWING EFFECTIVENESS OF AMMONIUM CHLORIDE IN HOLDING-MAGNESIUM SALTS IN SOLUTION.

*Solution of magnesium sulphate. Total volume of solution equal to 150 cc.*

Barium hydroxide sol. (approx. N 20). cc.	Saturated solution ammonium chloride. cc.	Magnesium oxide added. Parts per million.	Magnesium oxide precipitated. Parts per million.
45	0.5	27	2.0
45	0.5	27	1.4
45	0.5	91	9.4
45	2.0	27	0
45	2.0	27	0
45	2.0	91	0

*Solution of magnesium carbonate.<sup>1</sup>*

45	2.0	15	0
45	2.0	15	0
45	2.0	15	0

It is evident that 0.5 cc. of a saturated solution of ammonium chloride is not sufficient to hold in solution all the magnesium oxide that was added. Two cc. are, however, able to hold in solution at least 90 parts per million of the oxide without any of it precipitating.

In Trillich's method the magnesium salts are allowed to precipitate as magnesium hydroxide, and are then corrected for as previously stated. It is quite evident, therefore, that unless the precipitation is complete an error is introduced into the correction. The following experiments show that this precipitation is not complete under certain conditions.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE BY BARIUM HYDROXIDE.

*Solution of magnesium carbonate containing 15 parts per million of magnesium oxide. Total volume of solution equal to 100 cc.*

Barium hydroxide solution. cc.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million.
45	13.7	1.3
45	13.7	1.3
45	12.0	3.0
45	13.7	1.3
45	12.0	3.0
45	12.0	3.0
45	12.0	3.0
Average,	12.6	2.4

<sup>1</sup> Total volume of magnesium carbonate solution is equal to 100 cc.

From the above it will be seen that on an average 2.4 parts per million of magnesium oxide, equivalent to 2.6 parts per million of carbonic acid, were not precipitated in a solution containing 45 cc. of an approximately 0.05 normal solution of barium hydroxide in a total volume of 100 cc. From a large number of experiments made with a standard magnesium sulphate solution, it has been found that the same is true of this salt, *i. e.*, that the magnesium is but partially precipitated under certain conditions.

A large excess of barium hydroxide is necessary in order to effect practically complete precipitation, and unless this excess is maintained as the quantity of magnesium increases the quantity of magnesium which remains unacted upon will also increase.

This is well shown by the following table where constantly increasing amounts of magnesium were introduced into the solution.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE WITH CONTINUALLY INCREASING AMOUNTS OF MAGNESIUM SULPHATE.

*Solution of magnesium sulphate. Total volume of solution equal to 100 cc.*

Barium hydroxide solution. cc.	Magnesium oxide added. Parts per million.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million.
45	9.0	10	0
45	27.0	24	3.0
45	54.0	50	4.0
45	91.0	76	15.0

It will be noted that in the first sample, slightly more than the amount of magnesium oxide actually present appears to be precipitated. This seems to be characteristic of results obtained on samples in which the magnesium is in small amount while the barium hydroxide is in large excess. It is due to the fact that the loss of barium hydroxide by carbonating is always greater in such cases. The error from this cause, which may be called the "error of manipulation" and the error due to non-precipitation of magnesium hydroxide, act in opposite directions, the former tending to increase the apparent precipitation and the latter to decrease it. It is probable, therefore, that the quantity of magnesium oxide not precipitated may be greater than is indicated above.

How seriously this error may affect results is shown by the following table. A standard solution was prepared and was found to contain by Trillich's method, when no magnesium salts were present, 46.2 parts per million of free and half-bound carbonic

acid. This result was the average of ten closely agreeing determinations on this solution; and the figures for the carbonic acid found, when magnesium was present, should be compared with it.

TABLE SHOWING EFFECT OF NON-PRECIPIATION OF MAGNESIUM HYDROXIDE IN DETERMINATIONS OF CARBONIC ACID BY TRILLICH'S METHOD.

MgO added : equiv. to CO <sub>2</sub> . Parts per million.	Ba <sub>2</sub> OH <sub>2</sub> solu- tion. No.20(approx.). Parts per cc.	CO <sub>2</sub> found by titration. Uncorr. Parts per million.	Theoretical correction for MgO. Parts per million.	CO <sub>2</sub> cor- rection for MgO. Parts per million.	MgO equiv. to parts per million CO <sub>2</sub> . Ppt'd. Parts per million.	Not ppt'd. Parts per million.
10	10	49.5	10	39.5	3.3	6.7
10	10	50.6	10	40.6	4.4	5.6
10	10	49.4	10	39.4	3.2	6.8
10	10	49.4	10	39.4	3.2	6.8
10	10	49.4	10	39.4	3.2	6.8
20	15	59.2	20	39.2	13.0	7.0
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
30	15	64.6	30	34.6	18.4	11.6
30	15	63.4	30	33.4	17.2	12.8
30	15	64.6	30	34.6	18.4	11.6
50	20	83.0	50	33.0	36.8	13.2
50	20	81.6	50	31.6	35.4	14.6
50	20	83.0	50	33.0	36.8	13.2

*Note.*—Amount of magnesium oxide actually present is equal to 10/11 of amounts given as “MgO equivalent to parts per million of CO<sub>2</sub>.”

The results given above of course exaggerate the error because of the small amount of barium hydroxide and the large amounts of magnesium. They serve to show, however, the error which might arise from this source.

The errors affecting the accuracy of Pettenkofer's and Trillich's methods may be briefly summed up as follows:

1. The error due to the carbonating of the barium hydroxide as a result of manipulation. This is common to both methods and tends to make results higher than they should be. With careful work it can be kept very low and ought not to exceed 1 or 2 parts per million.

2. In Pettenkofer's method the solution of the carbonates by ammonium chloride, which tends to lower the results, seems to be the source of greatest error. The magnitude of this error appears to be governed by the concentration of the barium hydroxide solution and the amount of ammonium chloride present.

3. In the Trillich method the non-precipitation of the magnesium salts, as magnesium hydroxide, tends to lower the results. The excess of barium hydroxide over and above that necessary for the reaction, appears to be fully as necessary here as in Pettenkofer's method. It is probably best to have at least an excess of from 30 to 35 cc. of 0.05 normal barium hydroxide solution for waters containing as much as 60 parts per million of magnesium oxide. The magnitude of this error may vary (even when the prescribed amount of 45 cc. of an approximately 0.05 normal barium hydroxide solution is added to each 100 cc. of water), from 2 to 5 parts per million. This amount may be exceeded with an insufficient excess of barium hydroxide.

Since the error due to unavoidable carbonating of the barium hydroxide in the course of manipulation, increases the results, and all errors arising from solubility of carbonates or non-precipitation of magnesium hydroxide lowers them, these errors tend to neutralize each other. But if the error of manipulation is kept at a minimum, the lowering of the results due to other causes, exceeds the increase, and in consequence too low results are obtained.

#### LUNGE-TRILLICH OR SEYLER METHOD.

This method depends on the action of phenolphthalein as an indicator in the presence of free carbonic acid and of carbonates and bicarbonates of the alkaline earth bases; and on the assumption that in the bicarbonates of these bases there is one molecule of half-bound carbon dioxide for each molecule of fixed carbon dioxide.

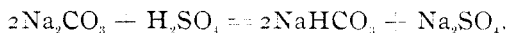
Leeds<sup>1</sup> in this country and Trillich in Europe proposed, at about the same time, the determination of the free carbonic acid in water by titrating the sample with a solution of sodium carbonate, using phenolphthalein as the indicator. The sodium carbonate reacts with the free carbonic acid to form sodium bicarbonate. As soon as the free acid is neutralized, any further addition of sodium carbonate produces a pink color. This affords a direct means for estimating the free carbonic acid without involving the half-bound. With waters which are acid to phenolphthalein, the determination of the fixed carbonic acid by Hehner's method gives at once the half-bound carbonic acid according to

<sup>1</sup> This Journal, 13, 98 (1891).

the assumption stated in the preceding paragraph. With waters which are alkaline to phenolphthalein, by the determination of this "phenolphthalein alkalinity" and the "total alkalinity" obtained with lacmoid as the indicator, the amount of half-bound carbonic acid can easily be estimated. In the latter case of course free carbonic acid is absent.

Seyler, who has made a study of this method, considers it one which gives accurate results, and one which is free from many of the difficulties involved in Pettenkofer's and Trillich's methods. The chief criticism of the method seems to have been as to the correctness of the assumption for quantitative purposes, that, when a water was acid or neutral to phenolphthalein, there was present for each molecule of fixed carbonic acid, one molecule of half-bound carbonic acid; and to the claim that when the water was alkaline to phenolphthalein, only one-half the carbonic acid in the form of the normal carbonates was determined by titrating with acid to the discharge of the color produced by this indicator.

If to 10 cc. of a cold 0.02 normal solution of sodium carbonate, phenolphthalein be added, and then a 0.02 normal solution of sulphuric acid, it will be found that only 5 cc. of the latter are required to discharge the color. The reaction is as follows:



The pink color produced by the phenolphthalein in the sodium carbonate solution is destroyed when one-half the latter becomes saturated with the carbonic acid liberated by the mineral acid; and this occurs when one-half the base has been neutralized. It is therefore evident that bicarbonates of the fixed alkalies are neutral to phenolphthalein.

The assumption that carbonates of the alkaline earth bases react in an analogous manner, is, so far as we can ascertain, correct, as the following experiments will show.

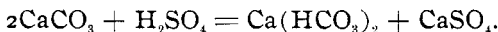
A calcium bicarbonate solution was boiled down to about one-third or one-fourth of its original volume and allowed to cool out of contact with the air. The precipitated calcium carbonate settled out, only such remaining in solution as was soluble without the presence of any free or half-bound carbonic acid. Several portions of the supernatant liquid were withdrawn and titrated with acid, using phenolphthalein as the indicator. The total alkalinity of the solution was also determined with the indicator lacmoid.



## ACTION OF PHENOLPHTHALEIN AS AN INDICATOR IN A SOLUTION OF CALCIUM CARBONATE.

No.	Calcium carbonate solution, cc.	Sulphuric acid.	Sulphuric acid.
		N 50 (approx.). A. <sup>1</sup> cc.	N 50 (approx.). B. <sup>2</sup> cc.
1	100	1.65	3.15
2	100	1.65	3.25
3	100	1.50	3.10
	Average,	1.60	3.17

A solution of magnesium carbonate acted similarly, 1.65 cc. of acid being required to discharge the pink color formed with phenolphthalein, and 3.4 cc. to obtain the end-point with lacmoid. The reaction involved in these two cases is doubtless analogous to the one which takes place in sodium carbonate solutions; *viz.*,



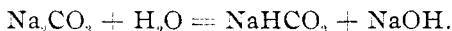
It was found that these solutions of calcium and magnesium carbonate were very sensitive to the absorption of carbon dioxide from the air, even on a very short exposure; and also that it was extremely difficult to free them from the last traces of the half-bound carbonic acid. Only by violent and prolonged boiling and cooling out of contact with the air, could this be accomplished. A calcium carbonate solution, which after boiling was cooled in air free from carbon dioxide, required for 100 cc., 1.5 cc. of acid with phenolphthalein as the indicator, and 3.1 cc. with lacmoid. A portion of the same liquid cooled in a beaker, required 0.95 cc. of acid with phenolphthalein and 3.2 cc. with lacmoid. Magnesium carbonate solutions absorbed carbon dioxide more slowly, as has been previously pointed out.

Hot solutions of calcium carbonate and of magnesium carbonate do not react to phenolphthalein in the same manner as do these cold solutions, since in the former the bicarbonates formed by the liberation of the carbonic acid from the normal carbonates, are immediately decomposed by the heat with evolution of carbon dioxide. It is therefore possible to determine the whole of the carbonates of the alkaline earth bases even with phenolphthalein as the indicator, provided the solution is kept boiling. The same is true of the carbonates of sodium and potassium. But phenolphthalein is by no means a good indicator for this purpose and the results are much more accurately obtained with lacmoid or one of a similar character.

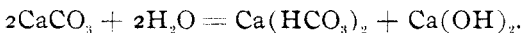
<sup>1</sup> To discharge pink color with phenolphthalein.

<sup>2</sup> To obtain end-point with lacmoid.

It has been considered probable that sodium carbonate in solution undergoes hydrolysis in the following manner.



As the sodium bicarbonate thus formed supplies no hydrogen ions, and the sodium hydroxide is dissociated producing a large number of hydroxyl ions, the solution is therefore quite strongly alkaline. To phenolphthalein it exhibits the alkalinity characteristic of caustic alkaline solutions. It may be that a similar hydrolysis takes place in the case of calcium carbonate and magnesium carbonate solutions.



If this does occur it readily explains why calcium and magnesium carbonate solutions are alkaline to phenolphthalein and why they show the same evidence of the presence of hydroxyl ions as in the case of sodium carbonate solutions.

The essential details of the Seyler process are as follows :

The free carbonic acid is determined by placing 100 cc. of the sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added a solution of sodium carbonate (0.05 or 0.02 normal solution may be used), stirring carefully and thoroughly until a faint permanent pink color is obtained.

The following precautions have been found desirable if accurate results are to be expected.

1. The titration can conveniently take place in a short Nessler cylinder. The writers used a tube approximately 18 cm. long by 3 cm. in diameter, graduated for 50 and 100 cc. The stirring rod used was bent at its lower end into the form of a circle and then turned so as to stand at right angles to the rod. A comparison cylinder containing the same amount of water as there was in the titrating cylinder, was found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly and the strong pink color formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed. When the color remains permanent the titration is complete. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate and with water which has been thoroughly boiled and cooled out of

contact with the air. The exposure of this solution to the air should be avoided as much as possible as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 cc. for the titration, especially if 0.02 normal sodium carbonate solutions are used. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of carbonic acid. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner. Seyler uses methyl orange as the indicator for this titration, but the writers employed lacmoid. The accuracy of this process<sup>1</sup> is well-known and need not be here discussed.

In the absence of free carbonic acid in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound carbonic acid does not equal the fixed; or in other words a portion of the carbonates of the bases exist in solution without the assistance of any half-bound carbonic acid. In such a case the half-bound acid is obtained by first determining the fixed carbonic acid by means of lacmoid. From this is deducted an amount of carbonic acid equal to twice the quantity indicated by the acid required to discharge the pink color produced by phenolphthalein. The difference is the amount of half-bound carbonic acid which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined and then followed by the titration with lacmoid; or they may be made on separate samples.

The principles on which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties and can be easily and quickly carried out. Approximately 0.02 normal solutions of sulphuric acid were used by the writers and the same strength of sodium carbonate solution. Seyler has prepared a series of formulas for calculating the results, which simplifies the work somewhat. If results are obtained with 100 cc. of the sample

<sup>1</sup> J. W. Ellms: This Journal, 21, 359.

and the reagents employed are 0.02 normal the following formulas express the results in parts per million.

I. For waters acid or neutral to phenolphthalein :

Free carbonic acid	4.4 $p$
Fixed or half-bound carbonic acid	4.4 $m$
Volatile carbonic acid	4.4 ( $m - p$ )
Total " "	= 4.4 ( $2m - p$ )

$p$  = cc. 0.02 normal sodium carbonate solution required to produce a pink color with phenolphthalein in 100 cc. of the water ; and

$m$  = cc. 0.02 normal sulphuric acid solution required to obtain the end-point with methyl orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein :

Fixed carbonic acid	4.4 $m$
Half-bound or volatile carbonic acid	= 4.4 ( $m - 2p'$ )
Total carbonic acid	4.4 ( $2m - 2p'$ )

$m$  = cc. 0.02 normal sulphuric acid solution required to obtain end-point with methyl orange or lacmoid in 100 cc. of the sample.

$p'$  = cc. 0.02 normal sulphuric acid required to discharge the pink color produced by phenolphthalein in 100 cc. of the sample.

There is a third case in which free carbonic acid might exist in a solution containing free mineral acid and for which Seyler has given a method with its corresponding formulas for calculating the results. But such a condition would seldom be found in natural waters and need not here be described.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free carbonic acid. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of carbonic acid, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method and which in good work ought not to exceed 1 to 2 parts per million.

## COMPARISON OF THE THREE METHODS ON WATERS CONTAINING KNOWN AND UNKNOWN AMOUNTS OF CARBONIC ACID.

The comparison of the results obtained with known solutions of carbonic acid indicate the relative and actual accuracy of these three methods. Solutions containing known amounts of free and half-bound carbonic acid were prepared by neutralizing partially or wholly measured quantities of a 0.02 normal solution of sodium carbonate with a 0.02 normal solution of sulphuric acid. Solutions of calcium and magnesium salts were introduced in order that these bases might be present and thus produce an artificial water having approximately the same composition as natural waters.

The first table shows the amount of free carbonic acid obtained in a solution known to contain 44 parts per million. This solution contained no calcium or magnesium salts. The term "Trillich method" has been used in the column headings of the following tables in the sense in which it was defined in the first portion of this paper. Strictly speaking, in the absence of magnesium salts where the use of ammonium chloride is unnecessary, the columns could have been headed "Pettenkofer method;" but to avoid confusion the definitions first given have been adhered to.

TABLE SHOWING FREE CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 44 PARTS PER MILLION.

No.	Trillich method. Parts per million.	Seyler method. Parts per million.
1	41.7	44.2
2	43.7	44.7
3	42.2	44.2
4	40.8	43.8
5	42.7	44.0
6	41.7	43.6
7	40.8	44.4
Average,	42.0	44.0

When free and half-bound carbonic acid were present together in known amounts the following results were obtained :

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 8 PARTS FREE AND 40 PARTS HALF-BOUND CARBONIC ACID. (FREE AND HALF-BOUND ACID EQUALS 48 PARTS PER MILLION.)

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method.		
		Free acid. Parts per million.	Half-bound acid. Parts per million.	Free and half-bound acid. Parts per million.
1	47.0	7.0	40.8	47.8
2	46.1	6.2	41.3	47.5
3	46.1	6.6	41.3	47.9
4	47.0	7.0	41.3	48.3
5	47.0	7.9	41.3	49.2
6	45.0	7.9	41.3	49.2
7	45.4	7.5	41.3	48.8
8	46.1	7.9	40.8	48.7
9	46.1	7.0	41.3	48.3
10	46.1	7.9	41.3	49.2
Average,	46.2	7.3	41.2	48.5

The following table shows the results obtained with these methods, when the solution contained double the amount of free and half-bound carbonic acid as was present in the solution from which the figures in the preceding table were obtained.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 16 PARTS FREE AND 80 PARTS HALF-BOUND CARBONIC ACID. (FREE AND HALF-BOUND ACID EQUALS 96 PARTS PER MILLION.)

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method.		
		Free acid. Parts per million.	Half-bound acid. Parts per million.	Free and half-bound acid. Parts per million.
1	92.2	15.8	78.2	94.0
2	91.0	14.5	81.1	95.6
3	91.0	14.1	81.1	95.2
4	90.5	14.5	80.2	95.2
5	90.5	15.0	80.2	94.7
Average,	91.0	14.8	80.1	94.9

No attempt has been made in our work with Pettenkofer's and Trillich's methods to differentiate by titration (according to Trillich's method), the free carbonic acid from the half-bound. Assuming, however, that the half-bound acid in the above solution is, as shown by the average, 80.1 parts per million, then the free carbonic acid by Pettenkofer's or Trillich's method would be 91 parts minus 80.1 parts or 10.9 parts per million.

In the following table are shown comparisons made with solutions containing known amounts of free and half-bound carbonic acid, and which also contained varying but known amounts of magnesium salts.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN SOLUTIONS KNOWN TO CONTAIN 4.9 PARTS FREE AND 41.6 PARTS PER MILLION OF HALF-BOUND CARBONIC ACID, AND WITH VARYING AMOUNTS OF MAGNESIUM SULPHATE. (FREE AND HALF-BOUND ACID EQUALS 46.5 PARTS PER MILLION.)

No.	Magnesium sulphate present equivalent to carbonic acid. Parts per million.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
				Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	10	44.6	43.9	4.6	48.2	45.8
2	10	43.1	43.9	...	....	....
3	10	43.1	44.4	...	....	....
4	20	41.5	45.6	4.3	41.2	45.5
5	20	44.6	44.2	4.0	41.9	45.9
6	40	44.6	43.3	4.0	42.6	46.6
7	40	43.1	40.4	4.6	41.2	45.8
8	40	46.0	40.4	...	....	....
Average,		43.8	43.2	4.3	41.6	45.9

Assuming as in the preceding tables that the half-bound carbonic acid is on an average 41.6 parts per million in the above solution, then the Pettenkofer results indicate 2.2 parts per million of free carbonic acid and the Trillich results 1.6 parts per million.

Comparisons were also made on natural waters containing unknown amounts of free and half-bound carbonic acid. The first table given below shows the results obtained on a sample of Ohio river water by the three different methods. This sample of water contained by a gravimetric determination 10 parts per million of magnesium oxide equivalent to a correction to be applied to the Trillich figures of 11 parts per million.

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN OHIO RIVER WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	14.9	15.4	0.6	16.2	16.8
2	14.9	16.8	0.4	16.4	16.8

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
3	13.4	16.1	0.4	16.2	16.6
4	14.4	16.8	0.4	16.6	17.0
5	14.4	16.8	0.6	16.6	17.2
6	14.4	16.1	0.6	16.2	16.8
7	13.4	16.8	0.4	16.4	16.8
8	14.9	15.4	0.4	16.6	17.0
9	13.2	16.8	0.4	16.6	17.0
Average,	14.2	16.3	0.4	16.4	16.8

The following well water was also examined and is given as an illustration of a water highly charged with carbonic acid and containing a large quantity of mineral salts, especially those of magnesium. A gravimetric determination of the calcium and magnesium, and also of the sulphuric acid, gave the following results.

## WELL WATER.

	Parts per million.
Lime (CaO) .....	378
Magnesia (MgO) .....	128
Sulphuric acid (SO <sub>3</sub> ) .....	351

The free and half-bound carbonic acid were determined by the three volumetric methods and the results obtained are shown in the following table:

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN A WELL WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method.		
			Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free and half-bound carbonic acid. Parts per million.
1	241	242.4	63.4	176.4	239.8
2	241	236.5	66.9	176.4	243.3
3	241	236.5	68.6	176.4	245.0
4	241	246.3	65.1	177.4	242.5
5	238	242.4	68.6	176.4	245.0
Average,	240.4	240.8	66.5	176.6	243.1

As would be expected the variation in the above results is in some cases considerable, but the greatest difference is less than 10 parts per million and the greatest variation from the mean of all the results is less than 5 parts per million.



The results of the above analysis were all obtained on waters which when cold reacted neutral or acid to phenolphthalein. There is one other class of waters, which when cold react alkaline to phenolphthalein, and which in consequence require a modification of Seyler's method as previously described. The number of waters belonging to this class does not seem to be at all large, and the writers have never examined but one water which showed this feature. Seyler states that pure sea water is alkaline to phenolphthalein. He gives the following analysis :

	Parts per million.
Free carbonic acid . . . . .	0
Half-bound carbonic acid . . . . .	44.0
Fixed carbonic acid . . . . .	51.7
	95.7
Total carbonic acid . . . . .	95.7

He also states that he has found well waters which upon standing exposed to the air for some time, reacted alkaline to phenolphthalein, and that such waters contained considerable magnesium carbonate.

The writers have found that at certain times the Mississippi river water is alkaline to phenolphthalein. How long such periods last or at what seasons of the year they occur, we have not had the opportunity to determine. It is quite probable that the so-called "alkali waters" of the Western plains would react alkaline to phenolphthalein as they contain carbonates of sodium. It has been noted that water which has stood in the iron pipes of the laboratory for some time, will, when first drawn, react alkaline to phenolphthalein. This is due probably to the free carbonic acid and bicarbonates in the water reacting with the iron of the pipe to form carbonate of iron, and thus leaving in solution small amounts of normal calcium and magnesium carbonates.

The water examined by us, which reacted alkaline to phenolphthalein, was a mixed sample of Mississippi river water. The samples were taken during the month of September, 1900, opposite Quincy, Illinois. When examined it was found to give a strong pink color with phenolphthalein. Its average approximate composition was as follows :

	Parts per million.
Lime (CaO) . . . . .	35.6 equivalent to 63.5 parts CaCO <sub>3</sub> .
Magnesia (MgO) . . . . .	16.0 " " 33.6 " MgCO <sub>3</sub> .
Sulphuric acid (SO <sub>3</sub> ) . . . . .	7.2
Chlorine (Cl) . . . . .	6.3
Fixed carbonic acid (CO <sub>2</sub> ) . . . . .	39.8 " " 90.4 " when expressed in the form of calcium carbonate.

From a consideration of these results it is more than probable that the magnesium was present partly as normal magnesium carbonate ( $MgCO_3$ ), and the calcium as calcium bicarbonate. Only a limited quantity of the sample was available for experimental purposes. The following table shows the average of the results obtained in determining the carbonic acid by the three volumetric methods.

CARBONIC ACID OBTAINED IN A SAMPLE OF MISSISSIPPI RIVER WATER.

Pettenkofer method.		Trillich method.		Seyler method.	
Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
0	0	0	34.6	0	35.4

Seven different portions of this water treated according to Pettenkofer's method showed that in no instance was any barium hydroxide used up, and that on an average only 60 parts per million (expressed in terms of  $CaCO_3$ ) of carbonates were precipitated out, which still left in solution about 30 parts per million. The reason for this is not clear, but it is probable that the ammonium chloride used was one factor which was instrumental in holding a portion of the carbonates in solution. Whether the dissolved organic matter, which was in considerable amount, was another cause of such unusual results, we are unable to state.

An artificial water prepared so as to contain approximately the same amounts of calcium and magnesium carbonates as were present in the Mississippi river sample, gave the following results:

No.	Pettenkofer method.		Trillich method.		Seyler method.	
	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
1	0	27.9	0	31.6	0	31.7
2	0	29.4	0	31.6	0	32.2
Average,	0	28.6	0	31.6	0	31.9

This water contained 11 parts per million of magnesium oxide, equivalent to a correction in the Trillich method of 12 parts per million.

The tendency here is for Pettenkofer's method to give low results, but the carbonates are not affected to the extent that they were in the river water.

## CONCLUSIONS.

From a consideration of the data obtained in this investigation, it appears that the Lunge-Trillich or Seyler method is the most accurate of the three volumetric methods. The "free and half-bound carbonic acid" as determined on known amounts by this method is on an average less than 1 per cent. too low and shows a possible range of less than  $\pm 3$  per cent. The accuracy of the determination of the "free carbonic acid" is somewhat less, and although the percentage error for low amounts is rather high, the variation from the actual amount is not more than 2 to 3 parts per million. These results are always too low and introduce into the determination of the "volatile carbonic acid" the larger proportion of the error.

Trillich's modification of Pettenkofer's method is less accurate than the Seyler method but more accurate than the Pettenkofer. Results obtained with either Pettenkofer's or Trillich's method are almost always too low. They probably give figures which are on an average between 5 and 10 per cent. too low. While Trillich's method gives more uniform results than Pettenkofer's the figures appear to be about 5 per cent. too low, and they may be as much as 10 or 12 per cent. too low.

Pettenkofer's method is inclined to give still lower results and although those obtained seemed to be only from 1 to 2 per cent. lower than those obtained with Trillich's method, yet it appears somewhat unreliable and one in which under some conditions extremely erratic results are likely to occur. With very low amounts of carbonic acid the percentage error in both Pettenkofer's and Trillich's methods are much greater than those stated above, although it may only represent an actual difference of from 3 to 4 parts per million.

For ease and rapidity of manipulation, for avoidance of difficulties arising from the presence of magnesium salts, and for its greater accuracy, the Lunge-Trillich or Seyler method is, in the opinion of the writers, to be preferred to either of the other two volumetric methods.