The foregoing data are produced graphically in Fig. 4. It will be noted that sodium chloride appears to have some influence on the precipitation of magnesium by calcium hydroxide, but that nevertheless the precipitation is quite complete. In the parallel tests with sodium carbonate, the amount of magnesium held in solution by sodium chloride is less in proportion to the entire amount present than was the case in the preceding experiments with solutions of somewhat greater concentration. In the more dilute solution, only about 6 per cent. of the magnesium present was held in solution, while in the less dilute about 15 per cent. was held in solution by 10 molecules of sodium chloride.

There is no intention to draw any generalizations from the single experiment with calcium hydroxide. Other experiments are in progress in this laboratory which may form the subject of a further communication on similar lines.

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THE DETERMINATION OF CARBONIC ACID IN DRINKING-WATER.

BY FRED B. FORBES AND GILBERT H. PRATT.

Received April 27, 1903.

IN the course of an investigation of the action of the various public water supplies of Massachusetts upon metallic pipes, it became desirable to know the amount of free carbonic acid contained in these waters at different times, as the results of many experiments indicated that this substance was in a large measure responsible for the action of water upon pipes, especially those of lead.[1]

Carbonic acid, as is well known, may exist in natural waters in three forms: Fixed carbonic acid combined directly with the alkaline earth bases, calcium oxide and magnesium oxide, to form normal carbonates, half-combined carbonic acid, and free carbonic acid.

The actual existence of bicarbonates of calcium and magnesium in solution has never been absolutely proven, as these salts have never been isolated; but for all practical purposes these compounds may be assumed to exist, as the behavior of the normal carbonates in solution in the presence of an excess of carbonic acid leads strongly to this conclusion.

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[1] Report of Massachusetts State Board of Health, 1898, 541; 1900, 487.

If more carbonic acid than is necessary to form bicarbonates with the alkaline earth bases is present, it remains dissolved in the water in the free state, and is generally considered as a true acid with the formula H_2CO_3.

When a water containing free and half-bound carbonic acid is heated, the free acid is easily driven off. On boiling, the half-bound acid may also be expelled, though completely with some difficulty, resulting in the precipitation of the normal carbonate with which it was combined.

The method for the determination of carbonic acid originally used in the investigation was the well-known Pettenkofer method,[1] which determines the sum of the free and half-bound. For the separation of the free from the half-bound, a modification devised by Dr. T. M. Drown and which will be described later was employed. It was early seen that in the Pettenkofer method, when carried out as directed in most works on analytical chemistry, there were several sources of considerable error, and some modifications were introduced in order to avoid these errors.

During the course of our work the very excellent paper on "The Estimation of Carbonic Acid in Water" by J. W. Ellms and J. C. Benecker[2] appeared, recommending the Lunge-Trillich or Seyler method,[3] and experiments were made by us with this method, and also with the method of boiling off the carbonic acid directly, and absorbing in potash bulbs. This latter method is not practicable from a water analyst's point of view, as it requires an apparatus too complicated for use in the field, and all determinations of free carbonic acid to be of value must be made at the source of supply, as a water, after being drawn, very soon loses a considerable part of its dissolved carbonic acid. This method has been used, however, as a check on the other two, in experiments upon natural waters whose carbonic acid contents were unknown.

It is the purpose of the following pages to give an account of a series of results obtained with the three methods, and to point out some of the errors in each.

THE PETTENKOFER METHOD.

The usual mode of procedure is given by Sutton[4] as follows: "100 cc. of the water are put into a flask with 3 cc. of a strong

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[1] *N. Rep. Pharm.*, **10**, 1.

[2] This Journal, **23**, 405 (1901).

[3] *Chem. News*, **70**, 104 (1894); *Analyst*, **22**, 312 (1897).

[4] "Volumetric Analysis," 7th edition, 1896, p. 96.

solution of calcium or barium chloride, and 2 cc. of saturated solution of ammonium chloride; 45 cc. of baryta or lime-water, the strength of which is previously ascertained by means of decinormal acid, are then added, the flask well corked and put aside to settle; when the precipitate is fully subsided, take out 50 cc. of the clear liquid with a pipette, and let this be titrated with decinormal acid. The quantity required must be multiplied by 3 for the total baryta or lime-water, there being only 50 cc. taken: the number of cubic centimeters so found must be deducted from the quantity required for the baryta solution added; the remainder multiplied by 0.0022 will give the weight of carbonic acid existing as free and as bicarbonate in the 100 cc. The addition of the barium or calcium chloride, and the ammonium chloride is made to prevent any irregularity which might arise from alkaline carbonates or sulphates or from magnesia."

The reactions which take place between the barium and ammonium chorides and magnesium are fully explained in Fresenius' "Quantitative Analysis,"[1] and will not be repeated here.

There are a great many precautions which must be observed in order to obtain results that are at all reliable. Among the principal of these are the avoidance of exposure to the air of the barium hydroxide solution and of the sample of water at all times especially during the titration, the use of a siphon to introduce the sample of water into the ground glass-stoppered bottle in which the precipitation is made, the addition of ammonium chloride during the standardization of the barium hydroxide solution, if rosolic acid is used as an indicator, and the allowance of a sufficient time for the separation of the carbonates in crystalline form before withdrawing the supernatant liquid for titration.

In carrying out this method according to the above directions, even with a strict observance of all the precautions noted, there are several sources of considerable error that do not seem to be generally recognized. They are due to the fact that working on such a small quantity of water as 100 cc. and employing N/10 acid, very slight errors in the titration of the aliquot portion of 50 cc., in measuring out the sample for titration and in measuring the original sample, make a considerable difference in the final result.

Long practice with the method has convinced us that it is impossible to titrate much closer than 0.05 cc., due principally to the

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[1] Fresenius' "Quantitative Analysis," English edition, 1859, p. 405.

fact that the best indicator that we can use, rosolic acid, is somewhat affected by ammonium salts, and the end-point is a little uncertain. Suppose, for example, that our barium hydroxide is exactly N/10, 45 cc. equaling 45 cc. of our sulphuric acid, that our measurements are correct, and that after carrying out the process according to Sutton's directions we obtain a reading of 14.40 cc. acid for the aliquot portion of 50 cc. which we titrate. A simple calculation shows this to be equivalent to 3.96 parts per 100,000 carbonic acid in the original sample. Suppose that instead of 14.40 cc. our acid reading had been 14.35 cc.; then a similar calculation shows this to be equivalent to 4.29 parts, as against 3.96 in the first case. This is not only an error of 8.3 per cent. on the value 3.96, but is an absolute difference of 0.33 part on any value, due to this one source of error.

In order to lessen the effect of all three of these errors, we have modified the details of the method as follows:

Ground glass-stoppered bottles of 16-ounce capacity, holding approximately 480 cc., are accurately calibrated by weighing completely filled with water. The bottle is filled with the water to be analyzed by means of a siphon, the glass stopper inserted leaving no air bubble, and the neck of the bottle wiped dry. The glass stopper is then carefully removed, and 57 cc. of the water withdrawn by means of an accurately calibrated pipette, in order to make room for the reagents. Three cc. of strong barium chloride solution (8 grams per liter), 2 cc. of saturated ammonium chloride solution, and 50 cc. of standard barium hydroxide are then introduced, the bottle quickly stoppered, well shaken, and set aside to settle.

There is now in the bottle an air space of only 2 cc., which is left to avoid the possibility of loss of liquid when the stopper is inserted. After the precipitated carbonates have completely settled out, several portions of 100 cc. are siphoned off and titrated with N/50 sulphuric acid, which is prepared from our N/10 acid, against which the barium hydroxide is standardized, by carefully diluting with water freed from carbonic acid by boiling. The barium hydroxide that we use is approximately N/15, and is carefully preserved out of contact with the air, the bottle in which it is kept being fitted with an arrangement whereby the air is drawn through soda-lime before entering either the bottle or the burette. The figure obtained by averaging several results of titration of portions of 100 cc. is taken as the true value.

The use of this large quantity of water and the titration of 100-cc. portions reduce considerably the errors due to the difficulty of obtaining the exact end-point, and those due to inaccuracies of measurement.

The decrease in the concentration of the barium hydroxide solution, due to the increase in the volume of our sample, renders it necessary, in some cases, to allow a longer time than is usually given for the complete precipitation of the carbonates. Standard solutions of free or of combined carbonic acid seem to settle out well on standing over night (that is, twelve to sixteen hours), but some natural waters require longer. We have generally found that samples made up in the afternoon of one day and titrated in the morning of the second day after, have stood a sufficiently long time.

The following table shows one of many series of results obtained by our method with standard solutions of sodium carbonate half neutralized with sulphuric acid.

CARBONIC ACID. (Parts per 100,000.)

Taken.	Found.	Average.	Error. Per cent.
1.10	0.99	1.05	4.5
1.10	1.05		
1.10	1.06		
1.10	1.08		
2.20	1.98	2.14	2.7
2.20	2.15		
2.20	2.23		
2.20	2.20		
3.30	3.12	3.17	4.0
3.30	3.21		
4.40	4.21	4.22	4.0
4.40	4.15		
4.40	4.23		
4.40	4.28		

These samples all stood twenty-four hours before titrating, and the carbonic acid was all in the half-combined state. A great many experiments were also performed in which the sodium carbonate was completely neutralized by sulphuric acid, thus giving all the carbonic acid in the free state. These results were invariably lower than the results on half-bound, due undoubtedly to loss of free carbonic acid during manipulation.

In order to see if more complete precipitation could be obtained by allowing the samples to stand a longer time, the following series of determinations was made:

CARBONIC ACID. (Parts per 100,000.)

Time stood. Hours.	Taken.	Found.
18	2.20	2.25
66	2.20	2.16
113	2.20	2.07
	Average,	2.16

It is seen that the shortest period of the three gave complete precipitation, thus showing that the cause of low results in our first table was not because of insufficient time allowed for the carbonates to separate out.

The following table shows a series of determinations of carbonic acid in natural waters, and in the same waters after the addition of known amounts of carbonic acid (as half-bound).[1]

(Parts per 100,000.)

Water No.	CO_2 added.	Total found.	Mean.	Parts added found.
1	0.00	1.15	1.21	2.31
	0.00	1.27		
	2.20	3.51	3.52	
	2.20	3.52		
2	0.00	1.43	1.51	2.08
	0.00	1.58		
	2.20	3.61	3.59	
	2.20	3.56		
3	0.00	1.32	1.27	2.27
	0.00	1.21		
	2.20	3.54	3.54	
	2.20	3.54		
			Average,	2.22

SEPARATION OF FREE FROM HALF-BOUND.

In order to separate the free from the half-bound carbonic acid, Dr. T. M. Drown has devised the following apparatus: A piece of glass tubing about 2.5 feet long and ⅝ of an inch in diameter, drawn out at one end to a small aperture, is inserted through a rubber stopper into the mouth of an aspirator bottle having a side tubular. The glass tube is filled with gravel about the size of peas. A strong current of air is drawn down through the gravel by means of an aspirator or pump, while the water is slowly dropped

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[1] Half-bound added instead of free in order to avoid loss of free carbonic acid in making up solutions.

into the tube at the top from a separatory funnel at the rate of about two drops a second. The water collects in the bottle, and when in sufficient quantity is withdrawn, and the half-bound carbonic acid determined by the Pettenkofer method as before. By this means the free carbonic acid is eliminated from the water, while the half-bound is unaffected. If the water is very high in free carbonic acid, it might be necessary to pass it through the column a second time, but for most waters once is sufficient. The loss in volume due to evaporation has been found to be only about 1 per cent., with a vacuum of 2.5 pounds, and may be neglected in most instances. The following table shows a series of results on standard solutions made by wholly or partially neutralizing solutions of sodium carbonate with sulphuric acid.

SEPARATION OF FREE FROM HALF-BOUND CO_2. (Parts per 100,000.)

Taken.		Found.		
Free.	Half-bound.	Half-bound.	Mean.	Remarks.
4.40	2.20	2.22	2.25	Aspirated 2 drops per second.
4.40	2.20	2.27		" 2 " " "
4.40	2.20	2.31	2.30	" 1 drop " "
4.40	2.20	2.28		" 1 " " "
4.40	2.20	2.17	2.18	" twice. 2 drops per second.
4.40	2.20	2.19		" " 2 " " "
1.10	1.67	1.90	1.84	" 2 drops per second.
1.10	1.67	1.77		" 2 " " "
0.00	2.20	2.31	2.31	" 2 " " "
0.00	2.20	2.30		" 2 " " "
1.10	1.10	1.22	1.22	" 2 " " "
1.10	1.10	1.21		" 2 " " "
2.20	1.10	1.05	1.12	" 2 " " "
2.20	1.10	1.19		" 2 " " "
2.20	2.20	2.36	2.34	" 2 " " "
2.20	2.20	2.31		" 2 " " "

Care must be taken to keep the water dropping at a uniformly slow rate, and to keep the current of air drawing steadily through the tube. If the free carbonic acid is not all expelled, then, of course, the half-bound result is high, and the figure for free, being obtained by subtracting the half-bound from the sum, is naturally low. With careful work, however, the method gives very good results, and is more convenient than the modification of the Pettenkofer method introduced by Trillich in order to accomplish the separation of the free from the half-bound.

THE LUNGE-TRILLICH OR SEYLER METHOD.

This method is very completely discussed in the paper by Ellms and Beneker, and is recommended by them as preferable to any other volumetric method for the determination of free and half-bound carbonic acid in natural water. It depends upon the assumption that in the bicarbonates of the alkaline earth bases there is 1 molecule of half-bound carbonic acid for each molecule of fixed, and that these bicarbonates are neutral to phenolphthalein.

When a solution containing free carbonic acid is titrated with sodium carbonate, with phenolphthalein present as an indicator, sodium bicarbonate is formed; this being neutral to phenolphthalein, as soon as all the free carbonic acid is used up, any further addition of sodium carbonate produces a pink color. Thus the free carbonic acid is obtained directly. By a determination of the fixed carbonic acid by Hehner's[1] process, the half-bound is obtained, as we have assumed this to equal the fixed when the water is acid to phenolphthalein.

When the water is alkaline to phenolphthalein, the phenolphthalein alkalinity is first determined, and then the total alkalinity with lacmoid or methyl orange, according to Hehner's process. Twice the phenolphthalein alkalinity subtracted from the total alkalinity gives the half-bound carbonic acid, no free acid being present in this case, and the half-bound being less than the fixed—that is, some of the normal carbonates are held in solution without the aid of any half-bound.

If no free carbonic acid is present, the half-bound may equal the fixed, and the water will be neutral to phenolphthalein. There is another condition in which carbonic acid might occur in a free state which is mentioned by Seyler, but which would occur so rarely in a natural water that it is hardly necessary to consider.

The mode of procedure is as follows: For the determination of the free carbonic acid, 100 cc. of the sample are introduced into a tall glass cylinder (a 100 cc. nitrite tube) by means of a siphon, 5 or 6 drops of a neutral alcohol solution of phenolphthalein of the usual strength added, and N/50 sodium carbonate run in from a burette with careful stirring, until a permanent faint pink color is obtained. If the water is high in free carbonic acid, it is better to take less than 100 cc., and in any case, great care must be exercised in manipulation, especially in not stirring too

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[1] Ellms : This Journal. 21, 359 (1899).

vigorously, in order to avoid loss of carbonic acid; on the other hand, the titration should be quickly completed in order to avoid absorption of carbonic acid from the air, which readily takes place during the end of the reaction. Great care is necessary in the standardization of the solutions and in their preservation, in order to avoid absorption of carbonic acid.

For the determination of the fixed carbonic acid, from which the half-bound is calculated, the well-known method of Hehner is employed. The writers prefer methyl orange as an indicator.

The following table shows the action of sodium carbonate solutions with the two indicators, when titrated with sulphuric acid.

Solution No. 1.			Solution No. 2.		
	cc H_2SO_4.			cc. H_2SO_4.	
cc. Na_2CO_3.	Methyl orange.	Phenolphthalein.	cc. Na_2CO_3.	Methyl orange.	Phenolphthalein.
10	9.75	4.85	10	9.65	4.78
10	9.67	4.90	10	9.62	4.80
10	9.73	4.85	10	9.63	4.80
10	9.70	4.84	..	...	...
10	9.75	4.89	..	...	...
Average,	9.72	4.87		9.63	4.80

With phenolphthalein as an indicator, only half the quantity of acid is required to give an end-point as with methyl orange.

THE DIRECT METHOD.

This method for the determination of carbonic acid consists in boiling off the gas in a suitable apparatus, fitted with a return-flow condenser and drying tubes, and absorbing the carbonic acid in a weighed potash bulb or soda-lime tube. Various modifications of the apparatus have been employed by different workers, but the form that we have found quite satisfactory is constructed as follows: A liter, round-bottomed flask, supported on a lamp-stand, contains the sample of water, and a perforated rubber stopper fits tightly into the neck of this flask. Through one perforation passes a return-flow condenser, while through the other passes a tube bent so as to form a water-seal, and carrying at its upper end a small separatory funnel.

The return-flow condenser is a tube about 24 inches long and 0.5 inch in diameter for 7 inches of the lower end and 5 inches of the upper end, while the main body of the tube is 1 inch in diameter, and is surrounded by a water-jacket. This form of tube is employed in order to give a large condensing surface.

A small delivery tube conducts the carbonic acid gas through a U-tube containing glass beads moistened with sulphuric acid, thence through another U-tube containing fused calcium chloride, thence to the potash bulb. Beyond the potash bulb is a tube containing soda-lime, to remove carbonic acid from any air accidentally drawn back into the bulb during the process.

Before each analysis the apparatus is freed from carbonic acid by boiling water in the flask, and aspirating while cooling, until the bulb weighs constant. When the flame is removed, an aspirator is attached to the last tube, in order to draw through any carbonic acid which may be present, and to equalize the pressure before disconnecting the bulb. All the air which enters the apparatus is drawn through a Liebig bulb containing caustic potash solution and connected with the separatory funnel.

The free and half-bound carbonic acid are thus determined together in this apparatus. In order to differentiate, the fixed may be decomposed by sulphuric acid introduced by means of the separatory funnel after the free and half-bound are expelled, and the carbonic acid evolved absorbed in the weighed bulb as before. From these data, the half-bound acid may be calculated.

The following table shows a few results by this method on standard solutions. In order to avoid loss of carbonic acid, they were prepared by measuring into the flask the required amount of dilute sulphuric acid, then introducing the weighed amount of sodium carbonate wrapped in a bit of paper. Before the reaction could take place, the flask was quickly stoppered.

CARBONIC ACID. (Parts per 100,000.)

Taken.			Found.		
Free.	Half-bound.	Sum.	Free.	Half-bound.	Sum.
3.30	...	...	3.20	...	...
4.40	...	...	4.47	...	...
4.40	...	...	4.40	...	...
4.40	...	...	4.40	...	...
2.93	1.47	4.40	...	...	4.30
3.23	0.59	3.82	...	...	3.60
1.47	1.47	2.94	1.47[1]	1.20	2.67
2.93	1.47	4.40	3.07[1]	1.13	4.20
1.47	1.47	2.94	1.73[1]	1.27	3.00
5.87	2.93	8.80	...	...	8.53
5.87	2.93	8.80	...	3.00	...

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[1] In every case the sum of the free and the half-bound acid is determined first, and then the fixed, from which the half-bound is calculated. The free is thus always obtained by difference, and any error in either the sum or the half-bound affects the free result; in fact, these errors are frequently in the same direction, so that the accuracy of the free result is not as great as that of the other figures.

These results show the method to be capable of giving fairly accurate results, on standard solutions, at least, especially when the carbonic acid is all in the free state. When there is half-bound also present, it is somewhat more difficult to obtain accurate results, the tendency being for them to be low on account of the difficulty of expelling the last traces of half-bound carbonic acid. A source of some trouble in the method when a potash bulb is used is the tendency of the potash solution to go over into the drying tube, due to the strong suction which it is necessary to apply in order to keep the current moving always in the right direction.

In working with natural waters, this method has been applied only to clear and colorless waters containing little organic matter, as according to some writers, in some waters, especially those which are polluted with sewage,[1] decomposition of unstable organic matter at the boiling temperature may liberate free carbonic acid.

COMPARATIVE DETERMINATIONS BY ALL THREE METHODS ON NATURAL WATERS.

In experiments on standard solutions with various methods of determining carbonic acid, the conditions are quite different from those obtained in actual practice, as it is impossible to prepare the standard solutions so that they are similar in composition to natural waters, since the composition of the natural waters in which we are called upon to determine carbonic acid varies greatly. For this reason a series of results obtained by any method, in solutions of carbonic acid in distilled water does not necessarily determine to what degree of accuracy the method may be relied upon in actual practice. This is especially true of the Seyler method, as the titration of solutions of carbonic acid made by partially or completely neutralizing sodium carbonate solutions with sulphuric acid amounts to little more than a restandardization of the solutions. The errors that are found in such results are the errors of standardization and of manipulation in making up the solutions. Also, in both the Pettenkofer and the Seyler methods the principal cause of low results on free carbonic acid is due to the loss which unavoidably occurs before the method can be fairly applied.

The following table shows a series of determinations on natural waters of varying composition:

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[1] Burghardt: *Chem. News*, 1887, p. 121.

CARBONIC ACID. (Parts per 100,000.)

Water No.	Seyler.			Modified Pettenkofer.[1]			Direct boiling.
	Free.	Half-bound.	Sum.	Free.	Half-bound.	Sum.	Sum.
1	1.98	0.57	2.55	...	...	2.60	2.53
2	2.02	0.62	2.64	1.90	0.69	2.59	2.40
3	0.75	0.70	1.45	...	...	1.25	...
4	1.01	0.57	1.58	0.21	0.48	0.69	1.47
5	1.10	1.32	2.42	...	...	1.92	2.67
6	0.79	0.53	1.32	...	...	1.13	1.20
7	0.97	1.10	2.07	1.05	1.19	2.24	...
8	0.70	0.97	1.67	0.84	0.70	1.54	...
9	1.76	1.28	3.04	1.84	1.34	3.18	...
10	0.57	1.23	1.80	0.77	1.07	1.84	...
11	0.26	0.26	0.52	0.13	0.44	0.57	...
12	2.20	0.44	2.64	2.19	0.61	2.80	...
13	0.57	0.26	0.83	0.51	0.33	0.84	...
14	0.75	0.53	1.28	0.32	0.77	1.09	...
15	0.75	1.85	2.60	0.99	1.57	2.56	...
16	0.92	1.45	2.37	0.88	1.18	2.06	...
17	0.84	1.32	2.16	0.93	1.02	1.95	...
18	0.26	0.40	0.66	0.15	0.34	0.49	..
19	0.70	0.31	1.01	0.45	0.28	0.73	...
20	0.04	1.41	1.45	0.11	0.83	0.94	...
21	0.88	1.06	1.94	1.00	0.64	1.64	. .
22	0.97	0.66	1.63	1.18	0.24	1.42	...
23	2.64	0.48	3.12	0.91	0.31	1.22	...
24	0.62	0.70	1.32	0.65	0.20	0.85	...
25	2.29	1.45	3.74	...	...	3.66	...
26	2.86	0.31	3.17	...	...	1.85	...
27	1.94	1.01	2.95	...	...	2.36	...
28	1.94	0.92	2.86	...	...	2.87	...

It is a rather difficult matter to make comparisons of the two principal methods, the Seyler and Pettenkofer, for the following reasons: All the waters were acid to phenolphthalein and so by the Seyler method the free carbonic acid was phenolphthalein and so by the Seyler method the free acid was determined directly, and the half-bound calculated from the fixed, which is determined by Hehner's method. Thus, the free and the half-bound represent actual determinations, while the sum is naturally obtained by adding these two results together. In our modification of the Pettenkofer method, on the other hand, the sum and the half-bound represent actual determinations, while the free is obtained by difference. It is thus seen that the only one of

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[1] Free expelled by aspirating, and the half-bound determined ; this figure subtracted from the sum to give the free.

the three figures which represents an actual determination in both methods is the figure for half-bound; and unfortunately, in one method, the Seyler, this figure is obtained independently of the free, while in our modification of the Pettenkofer method this figure is dependent on the thoroughness with which the free is expelled by aspiration.

A study of the table shows the following facts:

1. In seven out of twenty cases in which complete results were obtained by both methods, no result by either method differs from the corresponding result by the other method by over 0.20 of a part. This is a large percentage difference, to be sure, when the figure is low, but is a small absolute difference when the opportunities for error are considered, and as far as our present knowledge of the significance of carbonic acid in a drinking-water goes, such small differences are not important.

2. Considering only the half-bound results, as these figures are more nearly comparable in both methods, it is seen that in thirteen out of twenty cases, in which the half-bound was determined, the Seyler result is highei than the modified Pettenkofer. This seems to indicate that the method of separation of the free from the half-bound by aspiration in the modified Pettenkofer method can be relied upon for sufficient accuracy.

3. Considering the figures for the sum of the free and half-bound obtained by both methods, it is seen that in twenty instances out of twenty-eight in which the sum was determined, the result by the Seyler method was higher than that by the modified Pettenkofer. In experiments Nos. 1, 2 and 6, the results on the sum of the free and half-bound by three methods vary less than 0.10 part from the average of the three figures.

4. Considering the free results, it is seen that out of twenty determinations, the Seyler method gave higher results in ten, or just half.

From these few comparisons it appears that the Seyler method tends to give higher results than the modified Pettenkofer, and that these higher results are nearer the true value is shown by the results obtained by the boiling method, and also by the experiments on standard solutions.

To know the amount of the carbonic acid that is in the free state is of the most importance to the water analyst, so it is the result on the free acid that really deserves the most attention.

It will be seen from the table that, although half the free results by the modified Pettenkofer method are higher than those by the Seyler, yet there are some results which are erratic. For example, in experiment No. 4, the sum by the Seyler method checks well with the result obtained by the boiling method, and the results on half-bound by both the Seyler and the modified Pettenkofer methods agree well, yet the sum, and hence the free which depends upon it, is much lower in the modified Pettenkofer than in the Seyler. This is only one example among many similar ones which have occurred and which we have not given in our table.

The cause of these erratic results which frequently occur in the Pettenkofer method is not apparent from any of our experiments. It is a well-known fact that magnesium is liable to influence the results somewhat, but whatever might be learned by experiments with standard solutions containing magnesium, our experience has shown that the erratic results frequently obtained by this method with natural waters cannot often be traced directly to this element.

Considering the experiments of other investigators, together with those which we have performed, it seems that there is something to be said in favor of each method. Both methods require the utmost care in manipulation, this being especially true of the Seyler method for the determination of free carbonic acid. The advantages of the Pettenkofer method seem to be the less liability to loss or absorption from the air of free carbonic acid during the determination of the sum or half-bound, while the longer time and more apparatus required to complete the determination constitute a disadvantage. In regard to accuracy, the results are generally somewhat low, especially with waters low in carbonic acid, and frequent erratic results are obtained. The presence of magnesium salts is also a possible source of difficulty.

The Seyler method has the advantage of convenience and quickness of execution, but the determination of the free carbonic acid by titration with phenolphthalein as an indicator is a matter of considerable uncertainty, and under some conditions, of difficulty. Disturbances due to the presence of magnesium salts are avoided in this method, and the determination by Hehner's method of the fixed, from which the half-bound is calculated, is satisfactory. The results by this method are liable to be somwhat low, but not as low as those by the Pettenkofer.

Neither method can be relied upon to give results always within a certain percentage of the true values, and thus neither has a preeminent claim to scientific accuracy; for practical work in water analysis, however, the Seyler method, in the hands of an experienced operator, especially on account of rapidity of completion, has much to commend itself, and it is our purpose to employ it in our regular work.

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TITRATIONS WITH POTASSIUM IODATE.

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As is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation:

$$KI + 3Cl_2 + 3H_2O = KCl + HIO_3 + 5HCl. \qquad (1)$$

On the other hand it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be

$$KI + Cl_2 = KCl + ICl. \qquad (2)$$

In both cases the end of the reaction is shown by the immiscible solvent becoming colorless. If instead of chlorine water we titrate with a solution of potassium iodate, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation

$$5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O, \qquad (3)$$

while if a great excess of hydrochloric acid is present the reaction runs

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O, \qquad (4)$$

the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colorless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behavior is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus,