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Dissolved Oxygen in Water and its Significance

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Dissolved Oxygen in Water and Its Significance

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

H. T. Graber

ENTITLED Dissolved Oxygen in Water

and its significance

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF B. S. in Chemistry,

Arthur W. Palmer,

HEAD OF DEPARTMENT OF Chemistry.

For many years a high standard of purity for drinking waters has been rigidly insisted upon; mainly on account of the pathogenic or disease producing germs contained in a polluted water. We cannot expect to find the effect of impure water always sudden and violent. The results of the continual imbibition of polluted waters are, indeed, often gradual, and may under ordinary observation, yet be found not the less real and appreciable by close inquiry. It is a well authenticated fact that cholera breeds in impure and polluted waters.(2) On the authority of Sir William Lawrence, Bethlem Hospital and the "House of Occupations," of London, containing 700 persons were supplied with water from a deep well sunk upon the premises in 1825. Sir Wm says, "there was not a single case of cholera in the hospital or House of Occupations during the severe epidemics of 1832, '49, & 52; although the immediate surrounding neighborhood suffered severely. Again, on the authority of Surgeon Major

[2] A. C. C. De Renzy, the inmates of Millbank Prison suffered severely from cholera in the epidemics of 1832 and 49 while being supplied by Thames water. In the next cholera epidemic of 1854 the prisoners were again attacked but the disease was at once extinguished by changing the water supply. The change was made, in the midst of the cholera epidemic, to a new artesian well. <u>Six days</u> after the change the disease suddenly stopped, and a marked improvement took place in the health of the prison, and it is a matter of history that in the forty seven years since the change there has been but one death from diarrhoea and dysentery. In fact it is only when such striking and violent effects as these are produced that public attention is arrested, and interest in the water supply is renewed. The not less certain evils are borne with the indifference of the times. Although no sickness may be produced during the life of a man by the habitual use of an impure water, yet there can be no question but that impure water like impure air, effects the physique of individuals and tends to the degeneration of the race.(3) The question of wholesomeness of a

water hinges mainly upon the presence or absence of putrescent matters, as they themselves are the cause of the derangements of the human system. Most serious however, are the consequences when the low forms of organic life which, in all probability, form the specific poison of cholera, typhoid fever, and other diseases gain admission to drinking waters polluted with putrescent matter. A number of observations point to the conclusion that these organisms, or their germs, are not infectious as long as they are surrounded by fresh organic matter, but as soon as fermentation sets in they show their poisonous virulence. Thus it has been shown that the discharge of cholera and typhoid patients are not infectious as long as they are fresh. For this reason the determination of the condition of the organic matter becomes a very important one."[4] But however carefully executed no individual point in the analysis of waters can give such information as regards the fitness or unfitness of a water for drinking purposes, and, as above said, it is also quite evident that the danger, where there is any, lies buried in what the chemists term "organic matter"; and that there are times when this "organic matter"

is in a more than usual dangerous state.

The point of difficulty in the examination of this organic matter is not so much its quantitive examination as its qualatative; for you may have a water rich in organic matter, yet harmless, or a water containing but a minimum of organic matter of the most poisonous character. However our opinion as to the state of the organic matter of water, if it has any, is as far as the chemists have gone, only to be arrived at by the putting together of many analyses, for chemical analysis is incapable, at its present stage, of discriminating between living and dead, fresh or putrescent, organic matter. To briefly show how extensive is the determination of organic matter in a water it must be well to say that it is only after the following determinations have been made that conclusions concerning the nature of the organic matter can be drawn. The determinations are First - Organic carbon, second, Organic nitrogen, 3rd - Organic carbon + nitrogen, 4th Nitrogen as free ammonia, 5th Nitrogen as Albuminoid ammonia, 6th Nitrogen as total ammonia, 7th Oxygen consumed by acid $K_2 Mn_2 O_8$ in 1 hour and 8th Oxygen consumed by $K_2 Mn_2 O_8$ in three hours.

To summarize our results we must take into consideration the quality of the organic matter, that is, we must determine what is produced in the water by its standing under favorable conditions for the growth of vegetable or other life, we must determine the products of decomposition, if easily decomposed organic matter be present, we must determine nitrites as remnants of organic matter, nitrates from the same source, chlorides, indicating contamination from animal matter, total organic matter and ammonia by weighing and other methods and lastly the amount of "dissolved Oxygen" present as indicating the activity of decomposition or destruction.

The most valuable method of examining a water to determine the relative condition of the organic matter present is undoubtedly to be found in the determination of the relative amounts of oxygen present; for if the air dissolved in a water is found to contain less oxygen than its normal amount, it, of course, shows that this element is being consumed by chemical changes going on within the water, or, in other words such a water is not in its normal state and therefore is unfit for general use, for, in judging of the character of a water for domestic uses,

one of the most important points to be determined is whether it is or is not polluted by sewage and other deleterious substances. This contamination exerts an appreciable effect upon all the gaseous bodies held in solution in the water and specially upon the oxygen present.

This oxygen dissolved in water comes chiefly from two sources. Part of it is absorbed from the air, but some of it comes from the oxygen liberated by vegetable growths beneath the surface of the water. This latter oxygen being liberated below the surface of the water is dissolved before it reaches the surface unless the water is already saturated.

We generally consider then that the relative quantity of oxygen present in a water affords a key to its detorioration by organic matter; because it is unlikely that a large quantity of oxygen can be held in solution by a water containing oxidizable matter. Waters which contain their normal proportion of oxygen in relation to their other gaseous constituents would be regarded as free from sewage and decaying matter, a diminution in above said quantity would indicate the presence of easily oxidizible organic matter.

But waters may contain both a large amount of oxygen and also a great quantity of organic matter, for if the water is agitated in contact with air it absorbs the oxygen quite rapidly; and if samples are taken before the organic matter has had ample opportunity to consume the oxygen, analyses will show large amounts of both to be present. It is for this reason that the method soon to be described was made for collecting samples of water in air free compartments, determining the amount of aeration the water possessed at the time of collection and then letting the water stand regular periods of 24, 48, 76, etc. hours before determining if any increase or diminution in the relative amounts of oxygen present has been taken place. Again deep well waters which rarely contain putrescent organic matter, contain little or no dissolved oxygen, but this diminution or lack is due to its oxidizing and destroying the organic matter in its passage through the strata.

In general, concerning this oxygen or air dissolved in a water I may quote passages from various authors. [6] Leffmann and Beam: "The aeration of a water is favorable to the destruction of organic matter, a diminution in the quantity

7 of dissolved oxygen may mean excess of organic matter and microbic life. Diminution is associated with the development of lower vegetable life, causing disagreeable taste and smell". 5 (Dip. Thesis) "If the dissolved oxygen is high it indicates that there is little organic or oxidizable matter present or that the organic matter is but slowly oxidized. If low, it indicates that organic matter has consumed it in the process of decomposition, or that low forms have absorbed it; for bacteria need oxygen for their growth and absorb it from the water;

(8) "But the mere presence of oxygen in contact with the organic matter of the water has little effect in promoting its oxidation, unless living organisms, as bacteria, etc. be present. Hence we see how important this method of aeration becomes.

In general, however, for the interpretation of results obtained from the dissolved oxygen determination, the following observations have been made 1st a water which which does not diminish in its degree of aeration during a given time may or may not contain organic matter, but presumably does not contain growing organisms.

Such organic matter may be deemed not to be considered dangerous. 2nd a water which,

9 by itself, or after the addition of gelatin or other appropriate cultivating medium consumes oxygen from the dissolved air, at lower temperatures, but does not consume any after heating for 3 hours at 140° F, may be regarded as having contained living organisms, but none that could survive 140° F, such water should always be boiled for a long time before using and lastly - a water which, by itself, or after the addition of gelatin or other cultivating medium continues to absorb oxygen from the contained air after heating to 140° F may be taken as containing spores or germs which are harmful.

(9) The determination of the changes in the nitrates and nitrites present is a item of great value for in the presence of decomposable, non stearilized organic matter, and in the absence of sufficient dissolved oxygen for the growth of bacteria, and the nitrates are reduced to nitrites and eventually to free nitrogen, some bacterial ferments even prefering the oxygen in nitrates to that dissolved in the water.

It is a matter of history that about ninety years ago free oxygen in water was estimated by means of nitric oxide, and that by this

method Priestly obtained results which were inaccurate and variable. His coworker, Cavendish obtained almost absolutely the same results for the oxygen of the air as Bunsen and more modern observers who have employed the method of exploding a mixture of hydrogen and oxygen.

The question, of course, arose "how came it to pass that Cavendish could get results correct, whilst other experimenters operating at the same date and using the same method obtained discordant and erroneous results?" The answer is evident. This nitric oxide method answered perfectly when the conditions were right, but when the conditions were not complied with the method fails. Even up to 1872 the estimation of this dissolved oxygen had to be accomplished by means of a very troublesome, complicated and time-taking process, in consequence of which this important feature of water analysis was seriously neglected. In 1872 however, Schützenberger and Chas. Richter described an important process in which they made use of the remarkable reducing power of an acid discovered by Schützenberger in 1869 and called by him hydrosulphurous acid, now popularly known as hydrosulphurous or dithionous acid.

11. By the help of the sodium salt of this acid the estimation of the oxygen dissolved in water became at once easy and rapid. This was the beginning of our present methods and the many variations and improvements soon followed.

In general the methods for this determination of dissolved oxygen may be divided into two great classes. First the Gas-volumitic and secondly - the Titration methods.

To the first class, the gas volumetric, not much need be said for, on account of the numerous and expensive apparatus necessary for a delicate determination, the method is seldom used. Never the less, these methods, when correctly executed are very accurate and sensitive.

The theory in vogue in the methods consists essentially in boiling out the dissolved gases in a measured volume of water, and collecting said gases over Mercury. The CO_2 is then determined by absorption in KOH. The nitrogen remains as an unabsorbable residue while the oxygen is absorbed by[10] potassium pyrogallate $(C_6H_2).OK_3$ and its volume measured or is estimated by explosion with hydrogen.

In 1878 Mohr advanced the theory of the union of the oxygen present in well waters

with FeO and the titration of the ferrous salt with potassium permanganate.

At the same time a notice is given in the "Jahresberichte über der Fortschritte der Chemie" which passes the oxygen, liberated by boiling the water, through an ammoniacal solution of Protoxide of iron, and titrating the excess of ferrous iron, with manganic acid called "chameleon."

In 1885, vol. 51 of the Chemical News gives a method for preparing chromous chloride, made by reducing chromic chloride with zinc. This chromous chloride was a strong oxygen absorber.

The method of P. Schützenberger, found in detail in the Journal of the Chemical Society, Vol. 49: p. 751 is not much used at the present time. It requires a complicated piece of apparatus and its solutions are very unstable. The method depends upon the fact that a solution of sodium hydrosulphite ($NaHS_2O_4$) immediately decolorizes Coupier's soluble aniline blue; while the bisulphite of sodium which differs from the hydrosulphite by containing but one atom more of oxygen, has no effect upon the of the aniline dye. The hydrosulphite in the presence of free oxygen immediately oxidizes to the

Hydrosulphite, hence, if to a water containing dissolved oxygen, we color it with Coupier's blue and then run in our hydrosulphite solution, the water will remain blue until the hydrosulphite has absorbed all the oxygen present in the water and oxidized to the bisulphite. When this point is reached, and no more oxygen is present to oxidise the hydrosulphite to the bisulphite, we will have free hydrosulphite in solution and the blue colour immediately disappears. On account of the great instability of this hydrosulphite solution this method is, as above stated; seldom used although it is claimed that if two samples of the same water are taken and one allowed to flow quietly along the side of a beaker while the other sampled is poured boldly into another beaker, the two waters will show, by this method, a decided difference in the amounts of dissolved oxygen, the sample which was poured violently, of course, containing the greater amount of dissolved oxygen.

But aside from this fact Sir Henry Roscoe and Mr. Josh Lunt found that the results by this method are not concordant for the same water; that results are high if the titration is performed quickly, and are high if the ti-

4tration is performed in a similar vessel. Results are low when the water has been exposed to hydrogen and are less in proportion to the amount of exposure. Differing in this distinguishing feature.

In the Journal of the Chemical Society for 1880, page 185, a method is given by J. C. Thresh in which he replaces the air in the bottle used by coal gas. The method requires a bottle fitted with a four holed stopper. Through two of these openings coal gas is passed into the bottle. A separatory funnel to admit the water and a burette for sodium thiosulphate solution are to be fitted into the two remaining holes. Burette and funnel are filled then 1 c.c. of a solution of sodium nitrate and potassium iodide and one c.c. of dilute sulphuric acid are added by means of pipettes and the stoppers quickly replaced.

Bottle is agitated and allowed to stand fifteen minutes after which a current of coal gas is passed through the bottle. The water to be tested is now allowed to run into the bottle. Thiosulphate solution is now added until the brown color of the iodine is almost destroyed when one c.c. of starch solution

is [illegible] and the titration complete.

(12) In 189[illegible] J. L. [illegible] advanced a method the principle of which is that in the absence of oxygen nitrous acid and hydrogen iodide react to form iodine, water and nitric oxide but that in the presence of free oxygen, the nitric oxide becomes re-oxidized and, serving as a carrier of the oxygen, an amount of iodine is liberated equivalent to the oxygen present, in addition to that resulting from the nitrous acid; hence deducting that liberated by the nitrous acid from the oxygen dissolved in the original solutions used for the whole amount, the difference is that due to the oxygen dissolved in the water.

(13) In 18[illegible]7 Moritz [illegible] modified the above method. He treated the water with strong hydriodic acid in the presence of nitric oxide, then neutralized the acid with potassium bicarbonate and estimated the liberated iodine by means of N/10 arsenious acid.

L. [illegible] gives a method in the J. of the Soc. of the Chemical Industry, vol. [illegible], 18[illegible].

The principle depends upon the oxidation of ferrous-tartrate to ferric tartrate in an alkaline solution and the disappearance of the [illegible]

color due to phenosafranine in the presence of free ferrous tartrate. The [illegible] [illegible] ferrous tartrate to the water under consideration, phenosafranine being used as the indicator; and as soon as the free oxygen disappears the first drop of ferrous salt added decolorized the liquid.

The Levy method is given in Annuaire de l'observatoire de Mont Souris. The basis for the determination in this method is the amount of ferrous hydrate oxidized in suspension to ferric by the dissolved oxygen present in the water.

The apparatus used is a Levy pipette, a special pipette calibrated to contain 107 c.c. and fitted with two stop cocks. At the upper end of the pipette a small cylindrical funnel is attached, while the lower end is drawn out into a very small tube four and one half inches in length.

The reagents necessary for the determination are a solution of ammonium ferrous sulphate containing 20 grms of the crystallized salt to a litre. A 15% solution of KOH, a 50% by volume of H_2SO_4 (con. diluted 1 to 1) and a $K_2Mn_2O_8$ solution of such a strength that each c.c.

of the solution equals one part of oxygen for every million parts of water, when titrating 100 c.c. samples. It is essential in adding the above reagents to the water in the pipette that no air is admitted into the pipette.

The method of procedure is as follows. Fill the pipette with the water to be tested taking care that no air remains in it. Add 2 c.c. of the caustic potash solution to the funnel. Open the lower cock and then carefully open the upper one and allow the KOH. to enter the pipette, closing the cock before air is allowed to enter the pipette. Now rinse out the funnel two or three times with distilled water, and then place exactly 5 c.c. of the ammonium ferrous sulphate solution in the funnel. Put 5 c.c. of the H_2SO_4 (1:1) in the beaker to be used for the analysis, after opening the lower cock, place the tip of the pipette under the surface of the acid in the beaker. This precaution is taken because if any ferrous hydroxide should happen to pass through the pipette, at this stage of the operation, into the outer air it would be changed to ferrous sulphate in which state the oxygen of the air would have little affect upon it.

8 Open the upper cock and allow the ammonium ferrous sulphate to enter using same precautions as before against the entrance of air. Close both cocks and give the pipette a gentle gyratory motion once or twice to insure that all of the water comes in contact with the reagents. Allow to stand until the precipitate settles. In the presence of an alkaline solution the oxygen dissolved in the water oxidizes some ferrous hydrate to ferric hydrate and a mixture of the two settles out. While waiting measure out accurately 107 c.c. of the water, add 5 c.c. of the sulphuric acid, then 2 c.c. of the caustic potash, 5 c.c. of the ammonium ferrous sulphate solution 25 c.c. of distilled water to equal that added to wash out pipette and titrate with the permanganate solution. The amount of oxidation of ferrous salt caused by substances other than dissolved oxygen is determined in this blank as the dissolved oxygen has no effect upon the ammonium ferrous sulphate in an acid solution.

After the pipette has stood about five minutes add 5 c.c. of the H_2SO_4 to the funnel and open the upper cock only. The acid being of greater density than the water flows down

into the water, [illegible] it and dissolving the precipitated ferrous and ferric hydroxides without permitting the entrance of air. When the solution in the pipette is complete, open the lower cock and allow the contents of the pipette to flow into a beaker. Rinse out the pipette with 25 c.c. distilled water. Titrate with permanganate as quickly as possible, especially if water is contaminated with organic matter, and take first indication of change as the end reaction as organic matter exerts a reducing action upon the permanganate.

This latter titration gives us the amount of oxidation due to the dissolved oxygen, and subtracting this from the blank gives us the amount of ferrous salt oxidized to ferric by the dissolved oxygen in the water.

The reactions are as follows.

$(NH_4)_2Fe(SO_4)_2 + 2NaOH = Fe(OH)_2 + (NH_4)_2SO_4 + Na_2SO_4$

in the presence of oxygen

$2Fe(OH)_2 + H_2O + O = 2Fe(OH)_3$

unoxidized $Fe(OH)_2 + H_2SO_4 = FeSO_4 + 2H_2O$

$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + \boxed{8H_2O}$

The description of the last method to be described is found in the Berichte der Deutschen Chemischen Gesellschaft for 1888, S. 2843.

20. This depends upon the facts that oxygen will readily convert manganous hydroxide into manganic hydroxide, and that manganic hydroxide in the presence of potassium iodide and hydrochloric acid will liberate iodine and be reduced to manganous chloride. The liberated iodine is titrated with sodium thiosulphate using a starch indicator.

The only special apparatus necessary is a bottle of known capacity that can be closed air tight. The reagents necessary are an eighth normal solution of sodium hydroxide, a solution of 40 grams of pure manganous chloride in 100 c.c. of water, a starch solution, crystallized potassium iodide, hydrochloric acid of sp. g. 1.20 and an N/100 thiosulphate solution.

The method is as follows, fill the bottle with water to be tested, add 1 c.c. of a sodium hydroxide + KI solution by means of a long pipette calibrated so as to be able to add the solution to the bottom of the bottle and have solution enough above the level of the water in the bottle, to force the 1 c.c. out of the pipette. Now add 1 c.c. of the manganic chloride solution, stopper tightly and mix

thoroughly. The $KOH+KI$ and $MnCl_2$ react to form $MnOH_2$ which in the presence of free oxygen oxidizes $MnO.H_3$. After the precipitate has entirely settled add 5 c.c. of the conc. hydrochloric acid down the side of bottle so as to come in contact with precipitated hy-droxides. Restopper the bottle and shake again, let stand until all the precipitate has dissolved. The manganic hydroxide is changed to manganic chloride which reacts with the KI of the $KOH+KI$ and liberates iodine. The amount of iodine liberated being directly proportional to the amount of manganic chloride present, and therefore also directly proportional to the amount of oxygen dissolved in the water. Now the contents of the bottle are poured into a beaker, bottle is rinsed out with 25 c.c. of distilled water and the iodine titrated with $N/100$ $Na_2S_2O_3$ using starch as an indicator. As this method requires a blank - the directions for the blank follow. To 500 c.c. of distilled water, add one c.c. of sodium hydroxide without KI and one c.c. of the manganous chloride, stir well, filter, and dissolve the precipitate in about 5 c.c. of fuming hydrochloric acid making the solution up to a definite volume by means of distilled water.

This is the manganic chloride solution. Take 2 beakers, in one, place one hundred c.c. of distilled water and in other place 100 c.c. of sample, add one hundred c.c. of the manganic chloride solution to both, allow to stand five minutes. Now add some KI to the beakers and titrate by means of the N/100 $Na_2S_2O_3$ using starch as an indicator. Calculate to a litre the difference between the distilled water and the water under consideration and add this amount to the amount of the thiosulphate used for the determination of oxygen then calculating to parts per million.

The reactions for this method follow.

$2\,MnCl_2 + 4\,NaOH = 2\,Mn(OH)_2 + 4\,NaCl$

$2\,Mn(OH)_2 + H_2O + O = 2\,Mn(OH)_3$

$2\,Mn(OH)_3 + 6\,HCl = 2\,MnCl_3 + 6\,H_2O$

$KI + HCl = HI + KCl$

$2\,MnCl_3 + 2\,HI = 2\,MnCl_2 + HCl + I$

$2\,Na_2S_2O_3 + 2\,I = Na_2S_4O_6 + 2\,NaI$

This method was tried for sewage, but it was unsuccessful. The high "nitrates in the sewage oxidized" the hydroiodic acid liberating iodine according to the equation.

$HI + HNO_2 = I + H_2O + NO$

This liberation of iodine continued and made

it impossible to expel the blue color of the solution, due to the union of the starch and iodine, by means of the sodium thiosulphate.

In order to accomplish the results which I wished to obtain I worked upon sewage because this water contains organic matter in excess and the effect of said organic matter upon the dissolved oxygen can be watched on a large scale. It was first necessary that I should obtain a method which would be unaffected by the high nitrates in the water. To this end I first tried the "Winkler" or Manganous chloride method.

On the 21st of November, 8^{30} A.M. I went to the manhole of the Champaign sewer, between the metal works and old street railway line, and collected two pails of sewage. The temperature of the water was 16 °C. The sewage was taken to the laboratory, transferred to a four gallon jar, mixed, and twelve patent stoppered bottles were filled with it.

The bottles had been previously calibrated by subtracting the weight of the empty bottles from the weight of the bottle filled with H_2O and, assuming that one gram of water occupies a volume of one cubic centimeter at 15 °C, taking

This weight in grams changed to cubic centimeters, as volume. The bottles were filled by means of an [illegible] syringe, a short piece of rubber tubing containing at its centre a large bulb and at either end a valve working in an opposite direction to the valve at the other end. By means of this syringe water was sucked from the jar and forced into the bottles and, as the bottle contained air the sewage probably absorbed some of this gas.

To avoid making a collection of samples containing more oxygen than was originally contained in the water, this first sewage forced into the bottle was completely displaced. In this manner all twelve bottles were filled, the operation being finished at 11 A.M.

Ten of the bottles were now carefully stoppered so as not to have any air bubbles under the corks. To the other two bottles 1 c.c. of a 33% sodium hydroxide solution containing 100 grams of potassium iodide per litre was added and then 1 c.c. of a manganous chloride solution of such strength that (volume for volume of the $NaOH$ and $MnCl_2$ solutions were equivalent.

The solutions were brought together near the bottom of the bottle, where they reacted with one

another away from atmospheric influence.

This was done by means of two long narrow pipettes delivering 1 c.c. and drawn out such that the end reached the bottom of the bottle while the 1 c.c. mark was above the surface of the sewage.

The weight of the solution in the pipette above the water forced the reagents into the bottle and displaced two c.c. of the sewage, a volume equal to the amount of reagents added. Having added the reagents, I immediately corked the bottles, excluding all air bubbles, shook them gently four times and let them stand undisturbed for five minutes. The manganous chloride reacts with the sodium hydrate and produces a white curdy precipitate of Manganous hydrate which, in the presence of free oxygen in the water is oxidized to manganic hydroxide.

After standing five minutes the precipitate had settled completely and five c.c. of fuming HCl was allowed to run down the inside of the bottle, bringing the strong acid in contact with the precipitate. I now replaced the stopper with the proper precautions and shook the bottle until all the MnO_2 and

$Mn\,OH_3$ were dissolved. No oxygen was [illegible] dissolved in the water which I tested. I had free iodine present in the sewage imparting to the solution an amber tint.

The oxidized manganic hydrate is changed upon dissolving to manganic chloride; the potassium iodide in solution reacts with the HCl to form KCl and HI, and the $MnCl_3$ reacts with the HI liberating free iodine according to the equation $MnCl_3 + HI = MnCl_2 + HCl + I$. The contents of the bottle was now poured into a beaker, the bottle being washed with twenty five c.c. of water, 1 c.c. of a freshly prepared starch solution was added and the blue solution titrated to colorless with N/100 $Na_2S_2O_3 + 5H_2O$ solution.

A blank must be run on the water since the method is affected by the presence of nitrites and much organic material because nitrous acid liberates iodine from hydriodic acid ($HI + HNO_2 = I + H_2O + NO$), and organic matter takes up some iodine. In order to correct for this the following method was resorted to. I made a solution of <u>manganic</u> chloride by adding 1 c.c. of the $MnCl_2$ solution used above and 1 c.c. of a 33% NaOH solution

27. to 500 c.c. of distilled water, and stirred, filtered through a small filter, and washed, dissolved the precipitate in conc. HCl, diluted it to 500 c.c. and mixed. To 100 c.c. of the water to be tested and to 100 c.c. of distilled water I added 100 c.c. of the above Mn_2Cl_6 solution, then a crystal of KI and titrated the liberated iodine with N/100 $Na_2S_2O_3$ as per above.

The difference between these titrations of the distilled water and the sewage gives the correction to be added for every 100 c.c. of water used. Now since 1 c.c. of N/100 $Na_2S_2O_3 + 5H_2O$ solution is equivalent to 0.0000798 grams of oxygen or 0.055825 c.c. at 0 °C and 760 m.m. pressure, let V = the contents of the bottle; n the number of c.c. of sodium thiosulphate solution used in the first titration; n_2 the correction to be applied for the same volume of water and we have A, the volume of dissolved oxygen per Litre of water thus:—

$$A = \frac{0.055825\,(n + n_2) \times 1000}{V - 2}$$

for the number of cubic centimeters per litre or

$$A = \frac{0.09975\,(n - n_2) \times 1000}{V - 2}$$

gives the number of miligrams of dissolved oxygen per.

litre of water. By knowing the temperature of the sewage, and comparing it with the table giving the amounts of oxygen in saturated water solutions at various temperatures, the percentage of saturation is obtained by dividing the milligrams found, by the saturated weight at the given temperature.

The nitrites and free ammonia without distillation were also determined, the nitrites by comparing the pink color produced by 1 c.c. each of sulphanilic acid and naphthylamine hydrochloride solutions with standard colors, the free ammonia by the addition of Nessler's solution and comparing the brown color produced with the color produced in a solution of known ammonia content.

Winkler Method

Date of Collection	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen	Percentage Saturation	Nitrites	Free Ammonia
Nov. 21st	11.00 AM. Nov. 21st	16°C	7.889 7.693	78.35 77.39	0.533	14.0
" "	11.00 AM. Nov. 22nd	"	"High nitrites interfered."		2.25	12.0
" "	11.55 A.M. Nov. 23rd	"			3.00	
" "	12.30 AM. Nov. 24th	"			4.00	

This was successful for the Winkler method the first day and the table shows that on that day the water contained 0.5 parts Nitrogen as Nitrites per million parts of water and 14.0 parts nitrogen as free ammonia. On the

next day the blue color returned to the solution as quickly as it was titrated with the sodium thiosulphate and the reason is shown by the table. On this day the nitrites had increased from 0.5 to 2.25 parts and the free ammonia had decreased to 12.0 parts per million. These results indicate that this method cannot be used for sewage or any other water which contains 2.25 or more parts N. as nitrites per million.

At 2 P.M. of this same day Nov. 21, I filled 12 bottles with tap water, letting the water run about a half hour and using the embress syringe with same precautions as before stated. Two bottles were tested immediately and the remainder were set aside to stand periods of 24, 36, 48 & 72 hours; the object being to note the rate of disappearance of the dissolved oxygen in a bottle water.

Winkler Method

Date of Collection of Sample.	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation	Nitrites	Free Ammonia
Nov. 21st	4^{20} P.M. Nov. 21st.	17 °C	1.49 1.72	15.36 17.69	0.0	Not determined
"	12^{30} A.M. Nov. 22nd	"	1.12 1.12	11.57	0.0	" "
"	11^{35} A.M. Nov. 23rd.	"	0.41 0.41	4.26	0.0	" "

The results from analysis show that ordinary tap water as used by the cities of Champaign

and therefore does not contain any nitrites. But does contain a great deal of oxidizable organic matter, for the above table shows that, in both standing only five days the amount of dissolved oxygen diminishes over sixty per cent.

These facts are supported by chemical analysis which shows the water to contain large quantities of iron and organic matter.

The Levy method was next tried for oxygen determination. I dissolved 0.3953 grams of pure potassium permanganate in a litre of water and mixed thoroughly. This solution was of such strength that 1 c.c. required in the titration of 100 c.c. of water represents 1 part of oxygen per 1000,000 parts of water. The $K_2Mn_2O_8$ and all subsequent solutions of it was standardized against iron wire, using a small Erlenmeyer flask fitted with a rubber stopper through which a straight glass tube is passed fitted with an India rubber slit valve, which allows gas or vapor to pass out, but closes to atmospheric pressure when the evolution ceases. Dilute sulphuric acid was the solvent used.

At 2 P.M. Nov. 28th 18[illegible] two large galvanized iron pails were filled with water from the manhole behind the Metal Shops.

31 The temperature of the sewage was 14°C. The water was taken to the laboratory, transferred to a large crock and filtered through cheese cloth.

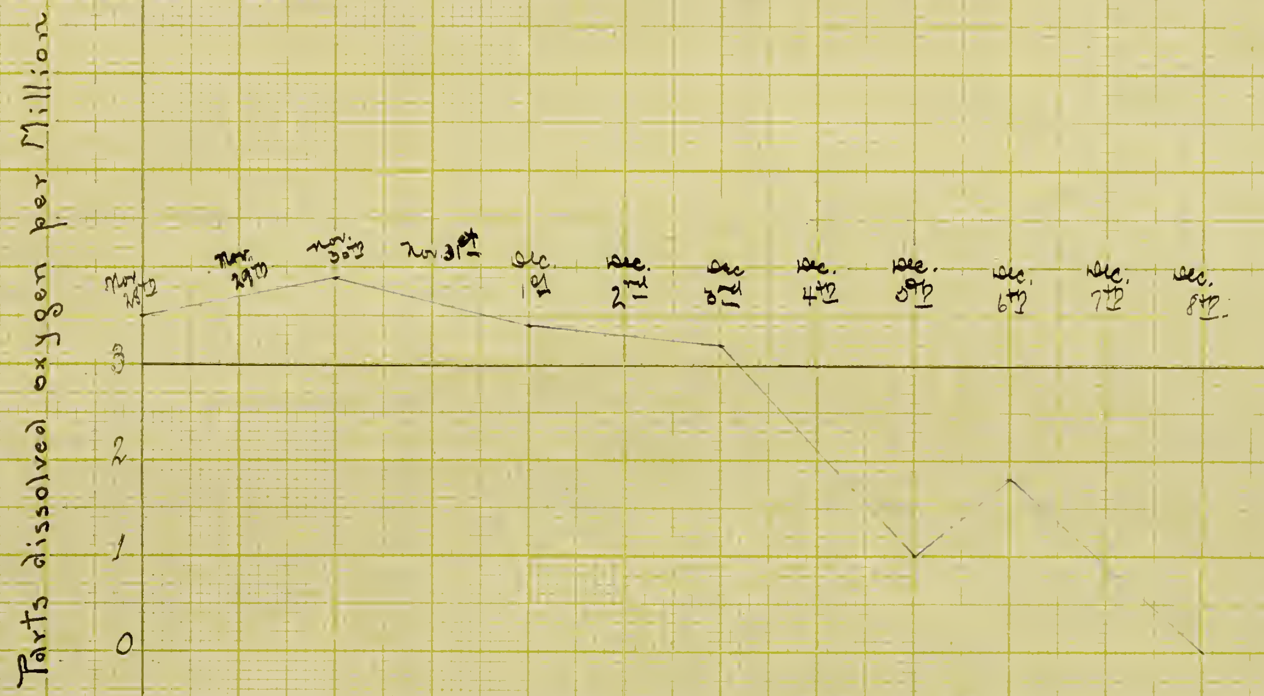
At 2 30 P.M. it was tested. The directions for this method have been given in the introduction. The degree of aeration having been determined, twelve 300 c.c. bottles were filled with the sewage by means of the embryo syringe using the above precautions as to exclusion of air, the displacement of first water entering the bottles, etc.

These bottles were placed in a cool, dark place in my desk and were left to stand periods of 24, 48, 60, 72 etc. hours before determining whether any increase or decrease in aeration had taken place.

Sewage by the Levy Method.

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation	N. as Nitrites	N. as Free Ammonia
Nov. 28th.	Nov 28th. 3 00 P.M.	14°C	3.5 3.5	34.2	- -	--
" "	Nov. 30th. 10 00 A.M.	"	3.9 4.0	37.79	----	----
" "	Dec. 1st. 10 50 A.M.	"	3.4 3.3	33.21 32.31	----	----
" "	Dec. 3rd. 8 25 A.M.	"	3.2 3.1	31.41 30.52	3.0	25.0
" "	Dec. 5th. 10 30 A.M.	"	1.0 1.0	9.65	2.0	25.0

Levy's Method



Sewage –

from Champaign Sewer

Disappearance of dissolved Oxygen in

Date of Collection	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation	N. as Nitrites	N. as Free Ammonia
Nov. 28th.	Dec. 6th.	14°C	1.9	18.33	3.0	30.0
	10⁰⁰ A.M.		1.9			
" "	Dec. 7th.	"	0.0	0.0	2.0	20.0
	9³⁰ A.M.		0.0	0.0		
" "	Dec. 10th.	"	0.0	0.0	2.5	20.0
	9⁰⁰ A.M.		0.0			

At 3 o'clock P.M. on Dec. the third, 1900, I obtained two more pails of sewage from the above said manhole, brought them to the laboratory, temperature of water was 14°C. I filtered the sewage through cheese-cloth and determined the percentage saturation of the water and the amounts of nitrates and free ammonia present.

Then ten bottles were filled* with the sewage, stoppered, and set in a dark place.

I now took about a gallon of the sewage, transferred it to a large two gallon glass bottle, corked and shook vigorously for five minutes, and renewed the oxygen in the bottle by passing into the water a current of dry filtered air. In this way the sewage was repeatedly shaken up with fresh air. Having passed air into the bottle five times, the amount of oxygen dissolved in this lot was determined and a series of ten bottles

were filled from it. These bottles were then set in a dark place and tested at periods of 24, 36, etc. hours.

* In all subsequent places where the filling of bottles is necessary it will be understood that it was done with the impress syringe with all precautions. Results obtained from this saturated and unsaturated sewage are as follows.

Normal Sewage

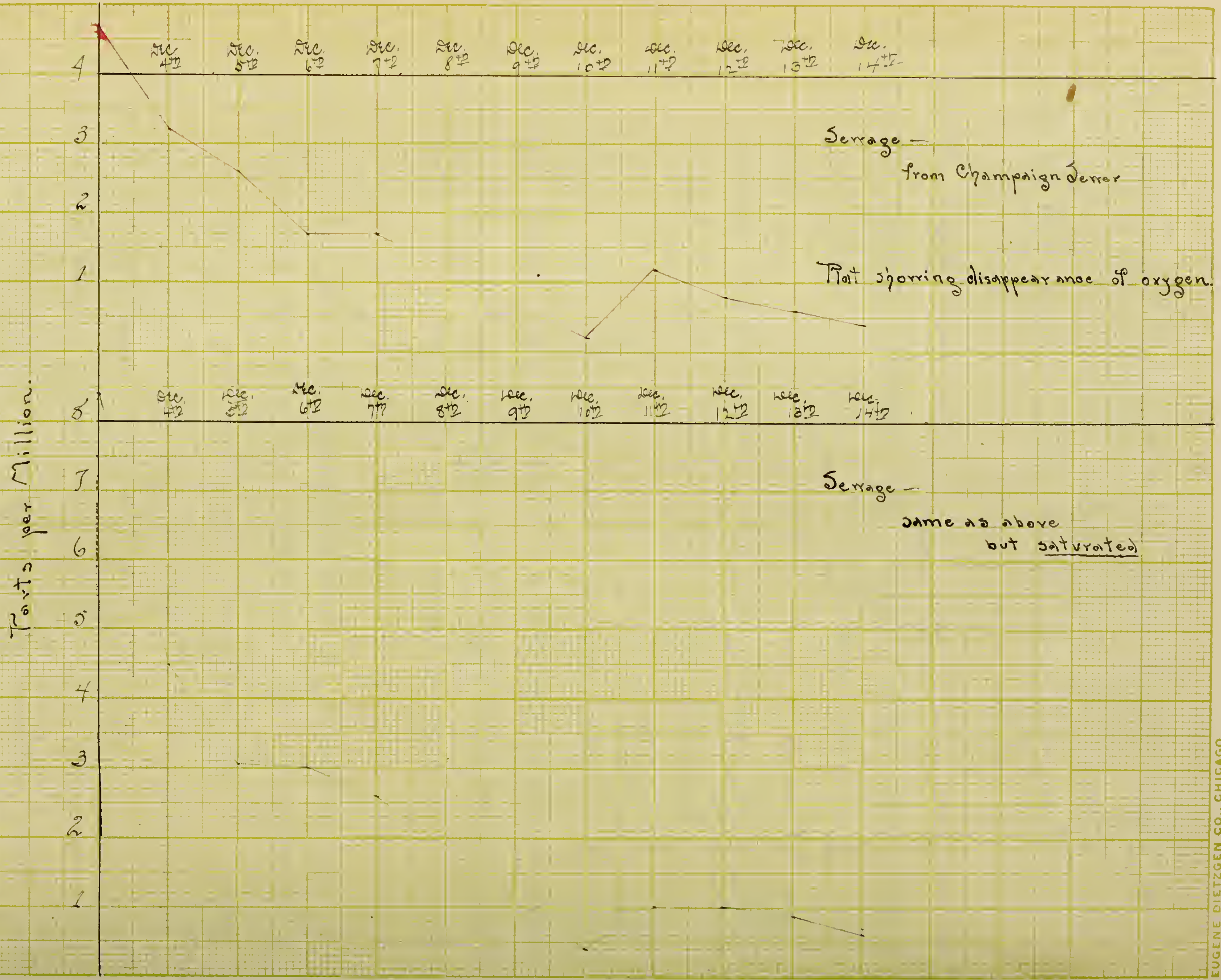
Date of Collection	Date and Hour of Examination	Temperature when Collected	Parts diss. Oxygen per Million	Percentage Saturation	N. as Nitrites	N. as Free Ammonia
Dec. 3rd	Dec 3rd.	14°C	4.74	45.76	3.5	20.0
	3⁵⁰ P.M		4.74			
" "	Dec. 4th.	"	3.25	31.37	7.0	15.0
	9³⁰ A.M.		3.25			
" "	Dec. 5th.	"	2.6	25.09	3.0	30.0
	10⁵⁰ A.M.		2.6			
" "	Dec. 6th.	"	1.67	16.11	3.0	40.0
	10³⁰ A.M.		1.89	18.24		
" "	Dec. 7th.	"	1.78	17.18	2.0	15.0
	10⁰⁰ A.M.		1.78			
" "	Dec. 10th.	"	0.22	2.15	2.0	36.0
	10⁴⁰ A.M.		0.22			
" "	Dec. 11th.	"	1.18	10.8	0.015	40.0
	9³⁰ A.M.		1.18			

Sewage, normal, continued

Date of Collection	Date and hour of Examination	Temperature when Collected	Parts dissolved oxygen per Million	Percentage Saturation	N. as Nitrites	Nitrogen as Free Ammonia
Dec. 3rd	Dec. 12th. 8^{40} A.M.	14°C	0.89 0.89	8.63	0.015	60.0
" "	Dec. 13th 9^{30} A.M.	"	0.67 0.67	6.47	0.025	40.0
" "	Dec. 14th. 10^{30} A.M.	"	0.49 0.49	4.74	0.025	15.0

Sewage partly saturated with air

Dec. 3rd	Dec. 3rd 5^{00} P.M.	14°C	8.46 8.46	81.66	3.5	20.0
" "	Dec. 4th. 8^{30} A.M.	"	4.46 4.46	43.05	6.0	15.0
" "	Dec. 5th. 9^{30} A.M.	"	3.10 3.10	29.92	6.0	35.0
" "	Dec. 6th. 10^{55} A.M.	"	3.0 3.0	28.95	4.0	40.0
" "	Dec. 7th. 10^{30} A.M.	"	2.6 2.6	25.09	4.0	15.0
" "	Dec. 10th. 10^{40} A.M.	"	0.44 0.44	4.31	3.0	41.0
" "	Dec 11th. 9^{40} A.M. 11^{00} A.M.	"	1.18 1.18 1.18 1.18	1.08	3.0	40.0
" "	Dec. 12th. 9^{20} A.M.	"	1.18 1.18	1.08	2.0	40.0
" "	Dec. 13th. 9^{30} A.M.	"	0.89 0.89	0.86	1.5	40.0
" "	Dec. 14th. 10^{30} A.M.	"	0.688 0.786	0.65 0.75	1.0	15.0



Sewage —
from Champaign Sewer

Plat showing disappearance of oxygen.

Sewage —
same as above
but saturated

The first of the three tables shows that the [illegible] method can be used for sewage and other waters high in nitrites and that after standing for nine days the dissolved oxygen in the water had entirely disappeared. By a comparison of the other two tables for the same sample of water, saturated and normal, we see that in both cases there is a constant decrease in the percent of saturation of the sewage, followed by a reduction of the nitrates to free ammonia, with a decrease in said nitrites. It was also shown that in the same length of time the amount of oxygen remaining in the saturated and normal sewage was almost the same, showing the more food as air, [illegible] the organic matter the greater the oxidation.

Following these, some experiments were made upon the disappearance of dissolved oxygen in the Illinois River water.

Monday, December 24th 1900, a series of liter bottles were filled from the Illinois, between the hours of 10 and 11 A.M. The water was taken from the channel, between the second and third piers of the Upper Free bridge at Averyville. A boat was used in its collection, and the water was drawn by means of a long rubber tubing weighted and extending

about fourteen inches below the surface of the water and connected with the [illegible] [illegible].

The temperature of the water was 1°C and after collection it was immediately taken to the Peoria Water works pumping station and tested. The other bottles were then tested at regular periods the following week. This same day another series of bottles were filled with water taken from the channel of the Illinois River, six miles below the city, about fifty yards below the entrance into the river, of the slop pipe of the east distillery.

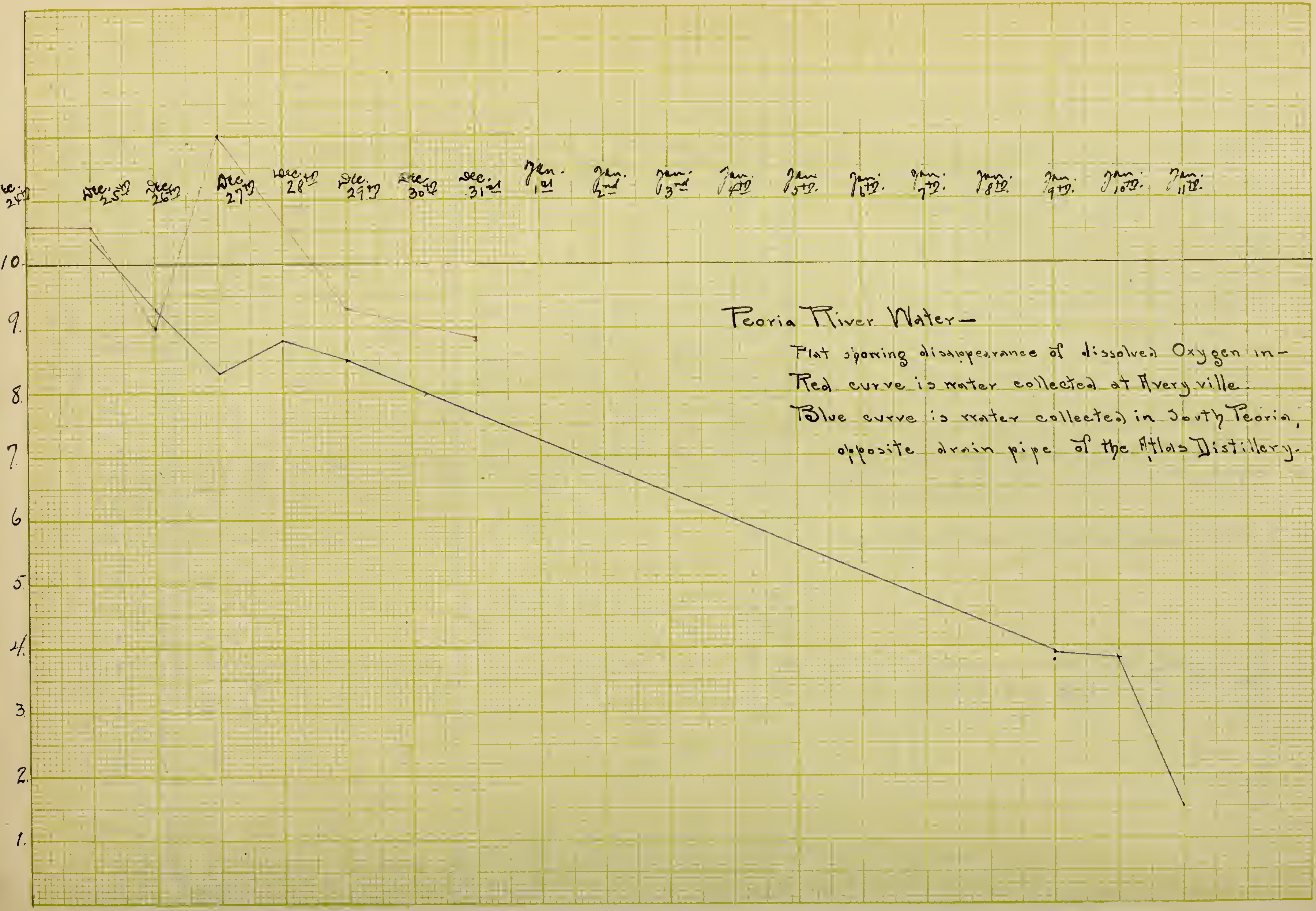
This collection was made between 3 and 4 o'clock in the afternoon but it took so long to reach the pumping station that the darkness made a determination of this collection impossible, so the water stood until the next day before it was possible to experiment upon it. The tabulated results of these two series follow.

Illinois River Water at Averyville

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation	Nitrogen as Nitrites	Free Ammonia
December 24th	Dec. 24th.	1°C	10.6	74.28	0.008	4.0
	11³⁰ A.M.		10.5	7358		
.. ..	Dec. 25th.	..	10.6	74.28	0.008	4.0
	12⁰⁰ A.M.		10.5	73.58		
.. ..	Dec. 26th.	..	9.04	63.34	0.03	5.0
	10³⁰ A.M.		9.04			

Averyville water continued-

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved oxygen per Million	Percentage Saturation	N. as Nitrites	N. as Free Ammonia
Dec. 24th.	Dec. 27th.	1°C	11.02	72.22	0.06	4.0
	10^{30} AM.		11.02			
	12^{0} AM.		11.02			
			11.71	75.05		
" "	Dec. 28th.	"	10.7	75.05	0.08	2.0
	10^{45} AM.		10.4	72.88		
" "	Dec. 29th.	"	9.3	65.17	0.04	4.0
	10^{45} AM.		9.3			
" "	Dec. 31st.	"	8.84	61.91	0.04	0.2
	10^{30} AM.		8.84			
Illinois River Water at South Peoria.						
Dec 24th.	Dec. 24th.	1°C	---	---	----	----
Dec. 24th.	Dec. 25th.	"	10.44	72.88	0.016	6.0
	11 P.M.		10.44			
" "	Dec. 26th.	"	9.4	65.87	0.02	4.0
	11^{00} A.M.		9.4			
" "	Dec. 27th.	"	8.2	57.46	0.065	5.0
	11^{30} AM.		8.3	57.16		
" "	Dec. 28th.	"	8.8	61.94	0.065	1.0
	11^{00} AM.		8.8			
" "	Dec. 29th.	"	8.6	60.27	0.075	4.0
	11^{15} AM.		8.5	59.57		
" "	Dec. 31st.	"	7.7	54.66	0.3	2.0
	11^{15} AM.		7.6	53.95		



Peoria River Water—

Plat showing disappearance of dissolved Oxygen in—
Red curve is water collected at Averyville.
Blue curve is water collected in South Peoria,
opposite drain pipe of the Atlas Distillery.

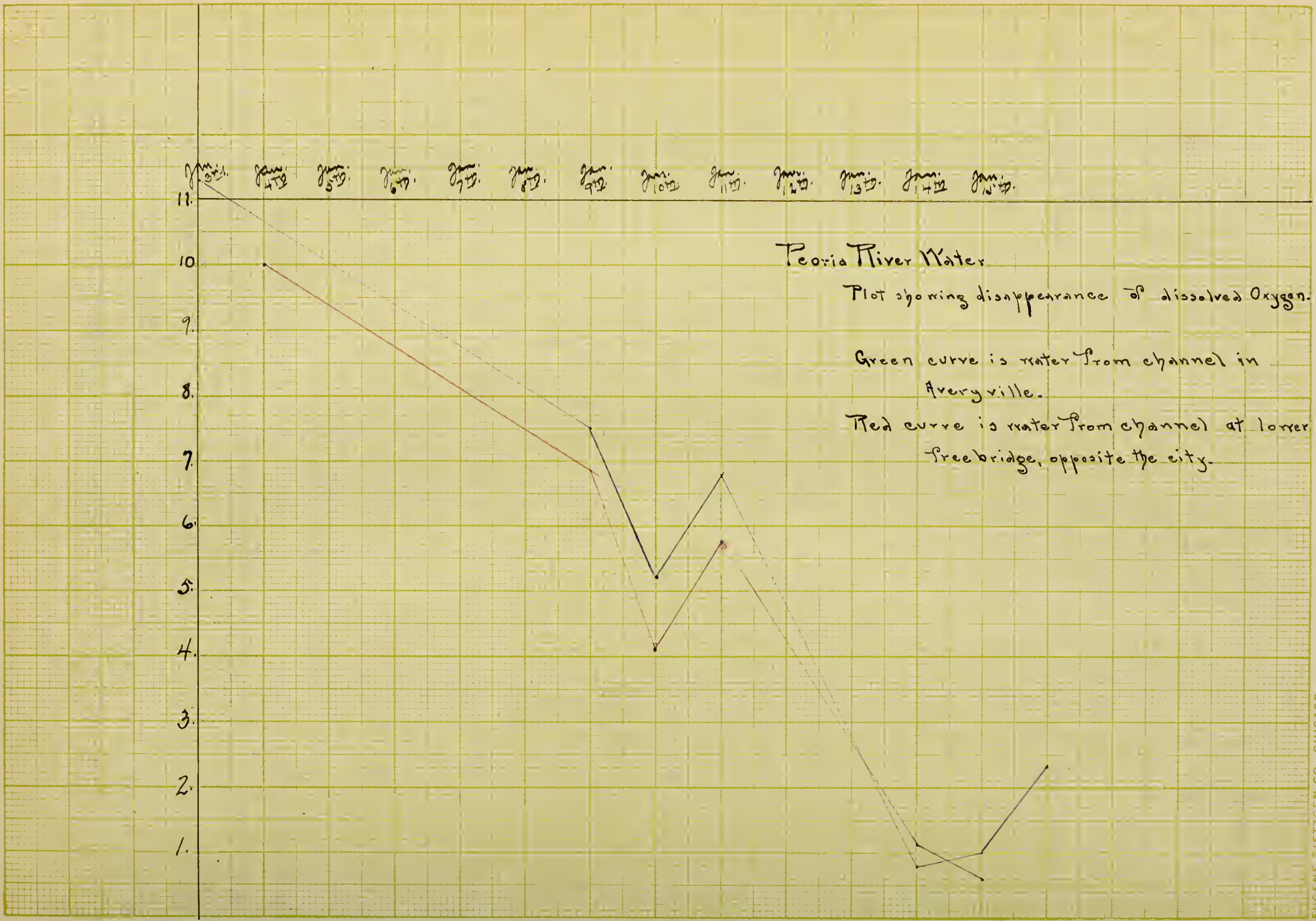
South Peoria water continued

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved oxygen per Million	Percentage Saturation	N. as Nitrites	N. as Free Ammonia
Dec. 24th.	Jan. 9th. 10^{30} AM.	1 °C	3.9 3.9	27.4	0.05	2.0
" "	Jan. 10th. 10^{35} AM.	"	3.8 3.8	26.62	0.05	2.0
" "	Jan. 11th. 9^{00} AM.	"	1.5 1.5	10.51	0.01	3.0

On the 3rd of Jan. [illegible], two more series of twelve bottles each, were collected from the Illinois river, one from the channel at Averyville and the other from the channel between the second and third pier of the lower free bridge, opposite the city of Peoria

Illinois River Water at Averyville

Date of Collection	Date and hour of Examination	Temperature when Collected	Parts dissolved oxygen per Million	Percentage Saturation	Nitrites	Free. NH_3
January 3rd	Jan. 3rd 10^{30} A.M.	1 °C	11.3 11.3	79.18	0.008	4.0
" "	Jan. 9th. 10^{05} AM.	"	7.66 7.47	53.67 52.34	0.35	5.0
" "	Jan. 10th. 4^{00} AM.	"	7.27 7.27	51.04	0.05	3.0
" "	Jan. 11th. 9^{30} A.M.	"	7.0 7.0	49.05	0.125	5.0
" "	Jan 14th. 8^{55} AM.	"	0.8 0.8	6.16	0.2	2.0
" "	Jan. 15th 1^{00} AM.	"	1.0 1.0	7.0	0.2	4.0
" "	Jan. 16th. 8^{50} AM.	"	2.3 2.3	16.11	0.15	4.0



Peoria River Water

Plot showing disappearance of dissolved Oxygen.

Green curve is water from channel in Averyville.

Red curve is water from channel at lower free bridge, opposite the city.

Illinois River Water collected from lower bridge

Date of Collection of Sample.	Date and hour of Examination	Temperature when Collected	Part of dissolved Oxygen	Percentage Saturation	Nitrogen as Nitrites	Nitrogen an Free Ammonia
January 4th.	Jan. 4th.	3° C	10.0	88.41	0.004	1.2
	11⁰⁰ A.M.		10.0			
" "	Jan. 9th.	"	6.9	61.0	0.075	3.0
	11⁵⁵ A.M.		6.9			
" "	Jan. 10th.	"	4.12	37.31	0.4	1.0
	3⁴⁰ P.M.		4.12			
" "	Jan. 11th.	"	5.79	51.79	0.15	1.0
	10¹⁰ A.M.		5.79			
" "	Jan. 14th.	"	1.1	9.72	0.3	2.0
	9⁴⁰ A.M.		1.1			
" "	Jan. 15th.	"	0.6	5.3	0.2	3.0
	9⁴⁰ A.M.		0.6			

A glance at the plot representing the disappearance of the dissolved oxygen in the first two collections shows that the water before it received the city's filth was rather highly saturated, and upon standing for twelve hours did not decrease in its amount of dissolved oxygen and that its

subsequent decrease in aeration was not nearly so sudden as the water collected six miles below the city. The results show that as far as nitrogenous organic matter is concerned, the water before it reaches the city contains less than it does after receiving the city's refuse. The two series run from water collected at Averyville and opposite the city of Peoria also strengthens this view.

The Averyville water is more highly saturated but for five days the decrease of aeration of the two waters runs parallel, then the water collected at the lower bridge takes a sudden drop. From these results alone it is plain to see that the water before it reaches the city is in a much purer condition than it is after it leaves it.

Numerous titrations were also made on the water to see if the percentage of the air dissolved in the water varied from day to day.

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Nitrites	Free NH_3	Percentage Saturation
"Averyville Water"						
December 24th	Dec. 24th	1 °C	10.6	0.008	4.0	74.28
	11^{30} A.M.		10.5		4.0	
January 3rd	Jan. 3rd	"	11.3	0.008		79.18
	12^{10} A.M.		11.2		4.0	
December 29th	Dec. 29th	"	11.8	0.008		88.14
	12^{10} A.M.		11.9			
"Lower Bridge" water January 4th	Jan. 4th 11^{00} A.M.	"	10.0	0.004	1.2	74.07
			10.0			

The above titrations show that the water, both above and opposite the city was fairly well saturated. I next proceeded to determine the disinfectant properties of various elements.

At 9 A.M. Feb. 8th I collected some Champaign sewage from the manhole in the University grounds and saturated it with air in order to be able to watch the effect of sterilization. After passing air into the water and shaking it in a large bottle, I determined its percentage of saturation and made three series of ten bottles each. The series No. 1, I corked without adding any reagent to the sewage. To series No. 2 I added 1 c.c. of a saturated solution of mercuric chloride and to series No. 3, I added one large drop of Chloroform. The bottles were then carefully stoppered and set aside in a cool dark place.

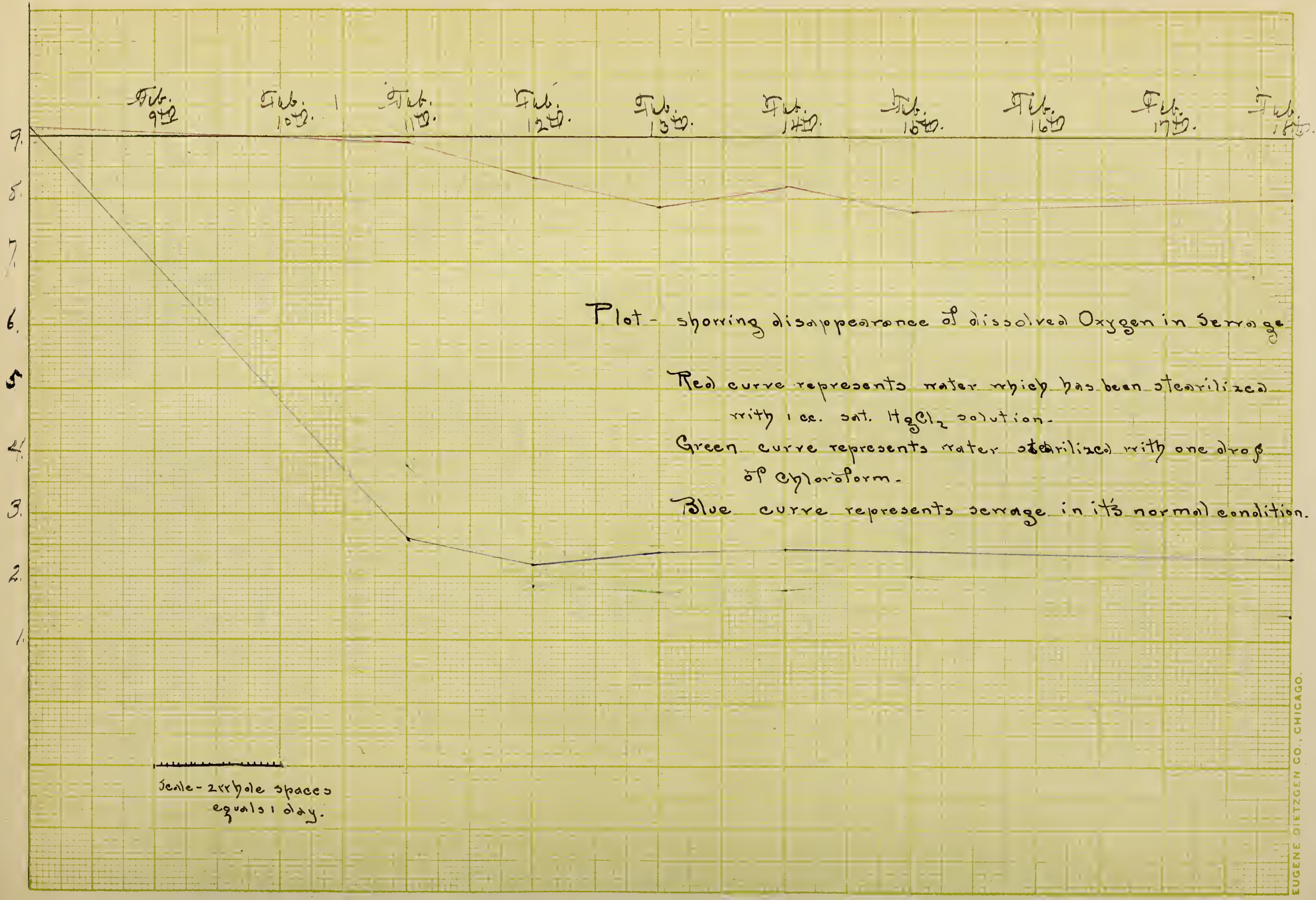
The results follow.

Sewage normal, saturated

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation
Feburary 8th.	Feb. 8th.	7°C	9.13	75.02
	10:20 A.M.		9.13	
" "	Feb. 11th.	"	2.6	21.36
	2:00 P.M.		2.6	
" "	Feb. 12th. 1:45 P.M.	"	2.2.	18.07

Normal saturated Sewage Continued

Date of Collection of Sample	Date and hour of Examination	Temperature Oxygen Collected	Parts dissolved Oxygen per Million	Percentage Saturation
Feburary 8th.	Feb. 13th.	7°C.	2.49	20.53
	1^{45} P.M.		2.49	
" "	Feb. 14th.	"	2.4	19.72
	3^{00} P.M		2.34	18.88
" "	Feb. 15th.	"	2.4	19.72
	1^{45} P.M.		2.5	21.17
" "	Feb. 18th.	"	2.3	18.88
	1^{45} P.M.		2.3	
	Sewage same as above plus mercuric chloride			
Feburary. 8th.	Feburary 8th.	7°C	9.13	75.02
	10^{20} A.M.		9.13	
" "	Feb. 11th.	"	8.9	73.13
	2^{30} P.M.		8.9	
" "	Feb. 12th.	"	8.4	69.02
	2^{30} P.M.		8.2	67.37
" "	Feb. 13th.	"	7.9	65.45
	2^{05} P.M.		7.8	64.8
" "	Feb. 14th.	"	8.2	67.37
	2^{35} P.M.		8.2	
" "	Feb 15th.	"	7.81	64.17
	2^{35} P.M.		7.81	
" "	Feb. 18th.	"	7.9	65.45
	2^{25} P.M.		7.8	65.17



Plot - showing disappearance of dissolved Oxygen in Sewage

Red curve represents water which has been stearilized with 1 cc. sat. $HgCl_2$ solution.

Green curve represents water ~~st~~sterilized with one drop of Chloroform.

Blue curve represents sewage in it's normal condition.

Scale - 2 whole spaces equals 1 day.

Sewage same as above plus chloroform.

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per million	Percentage Saturation
February 8th.	Feb. 8th.	7°C	9.13	75.02
	10.00 AM.		9.13	
" "	Feb. 11th.	"	3.65	29.9
	3.20 P.M.		3.65	
" "	Feb. 12th.	"	1.9	15.62
	2.45 P.M.		1.9	
" "	Feb. 13th.	"	1.79	14.7
	2.45 P.M.		1.79	
" "	Feb. 14th.	"	1.8	14.79
	3.50 P.M.		1.8	
" "	Feb. 15th.	"	2.02	15.69
	3.00 P.M.		2.02	
" "	Feb. 18th	.	1.2	13.96
	3.10 P.M.		1.7	

Another collection of sewage was made from the University manhole and three more series of 10 bottles each were made using mercuric chloride, chloroform and normal sewage as per above.

The tabulated results follow

Sewage normal, saturated.

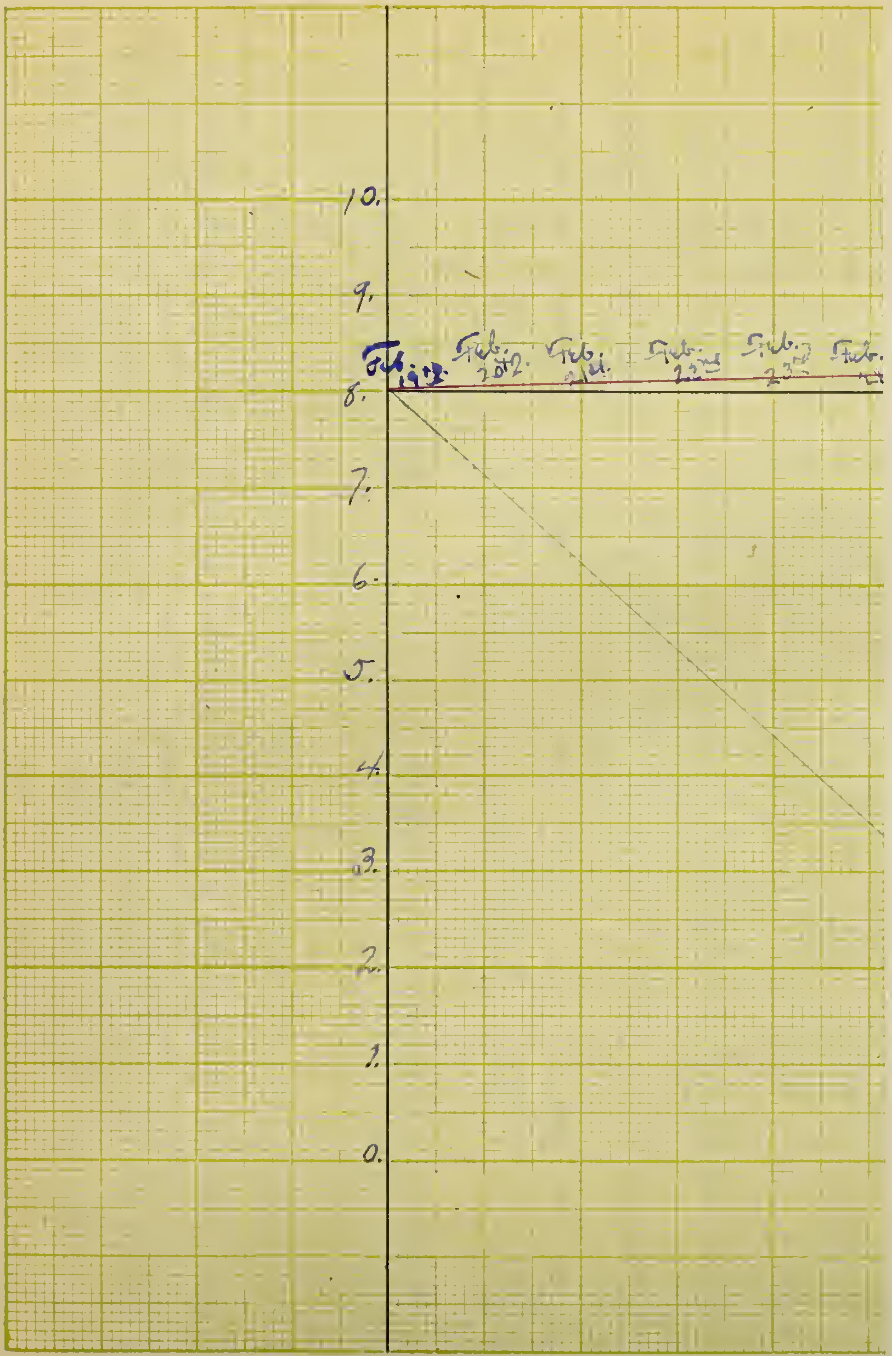
Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per. Million	Percentage Saturation
February. 19th. '01	Feb. 19th.	2°C	7.88	56.81
	2^35 P.M.		7.88	
" "	Feb. 25th.	"	2.5	18.02
	1^45 P.M.		2.5	
" "	Feb. 26th.	"	2.34	16.87
	2^15 P.M.		2.5	18.02
" "	March. 1st.	"	1.93	13.91
	2^05 P.M.		1.93	
" "	March. 4th.	"	2.6	19.03
	1^45 P.M.		2.6	
" "	March. 6th.	"	2.13	15.41
	2^10 P.M.		2.13	
" "	March. 8th.	"	0.81	5.8
	2^00 P.M.		0.81	
" "	March. 12th.	"	0.91	6.61
	2^30 P.M.		0.91	
" "	March. 15th	"	0.81	5.8
	2^10 P.M.		0.81	
" "	March. 18th.	"	1.01	7.98
	2^20 P.M.		1.01	

Series No 2- $HgCl_2$ added

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per M.	Percentage Saturation
February 19th.	Feb. 19th.	2°C	7.88	56.81
	3^{45} P.M.		7.88	
"	Feb. 25th.	"	8.04	57.97
	2^{30} P.M.		8.22	59.26
"	Feb. 26th.	"	8.31	59.91
	2^{45} P.M.		8.31	
"	March. 1st.	"	8.65	63.36
	2^{50} P.M.		8.65	
"	March. 4th.	"	8.63	62.27
	2^{10} P.M.		8.63	
"	March. 6th	"	9.87	71.19
	2^{30} P.M.		9.87	
"	March. 8th.	"	9.16	66.05
	2^{30} P.M.		9.16	
"	March. 12th.	"	9.87	71.19
	3^{00} P.M.		9.87	
"	March. 15th	"	8.55	61.64
	2^{40} P.M.		8.55	
"	March. 18th.	"	8.04	57.04
	2^{45} P.M.		8.04	
"	(sample + $(NH_4)_2S$ had been added)			
	March. 18th.	"	3.25	23.46
	4^{00} P.M		3.25	

Series No 3 - disinfected with $CHCl_3$

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million.	Percentage Saturation.
February 19th	Feb. 19th	2° C.	7.88	56.81
1901	3^{45} P.M.		7.88	
"	Feb. 25th	"	2.57	18.53
	3^{15} P.M.		2.57	
"	Feb. 26th	"	1.48	10.67
	3^{20} P.M.		1.48	
"	March. 1st	"	3.86	27.88
	2^{50} P.M		3.86	
"	March. 4th	"	3.05	22.09
	2^{30} P.M.		3.05	
"	March. 6th	"	2.85	20.54
	3^{20} P.M.		2.85	
"	March. 8th	"	2.64	19.08
	3^{20} P.M.		2.64	
"	March. 12th	"	2.13	15.41
	3^{30} P.M.		2.13	
"	March. 15th	"	2.44	17.61
	3^{45} P.M.		2.34	16.88
"	March. 18th	"	2.13	
	3^{20} P.M.		2.13	15.41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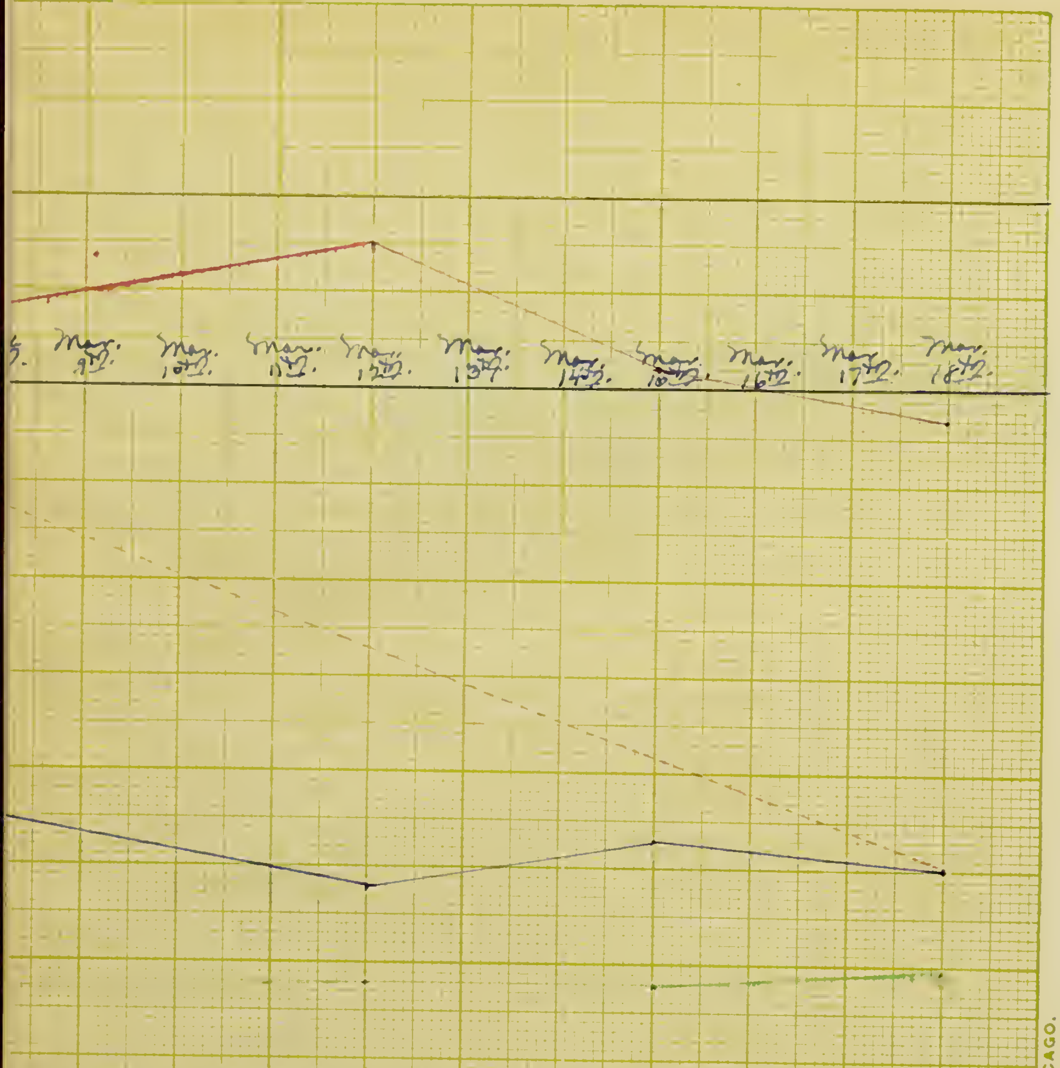
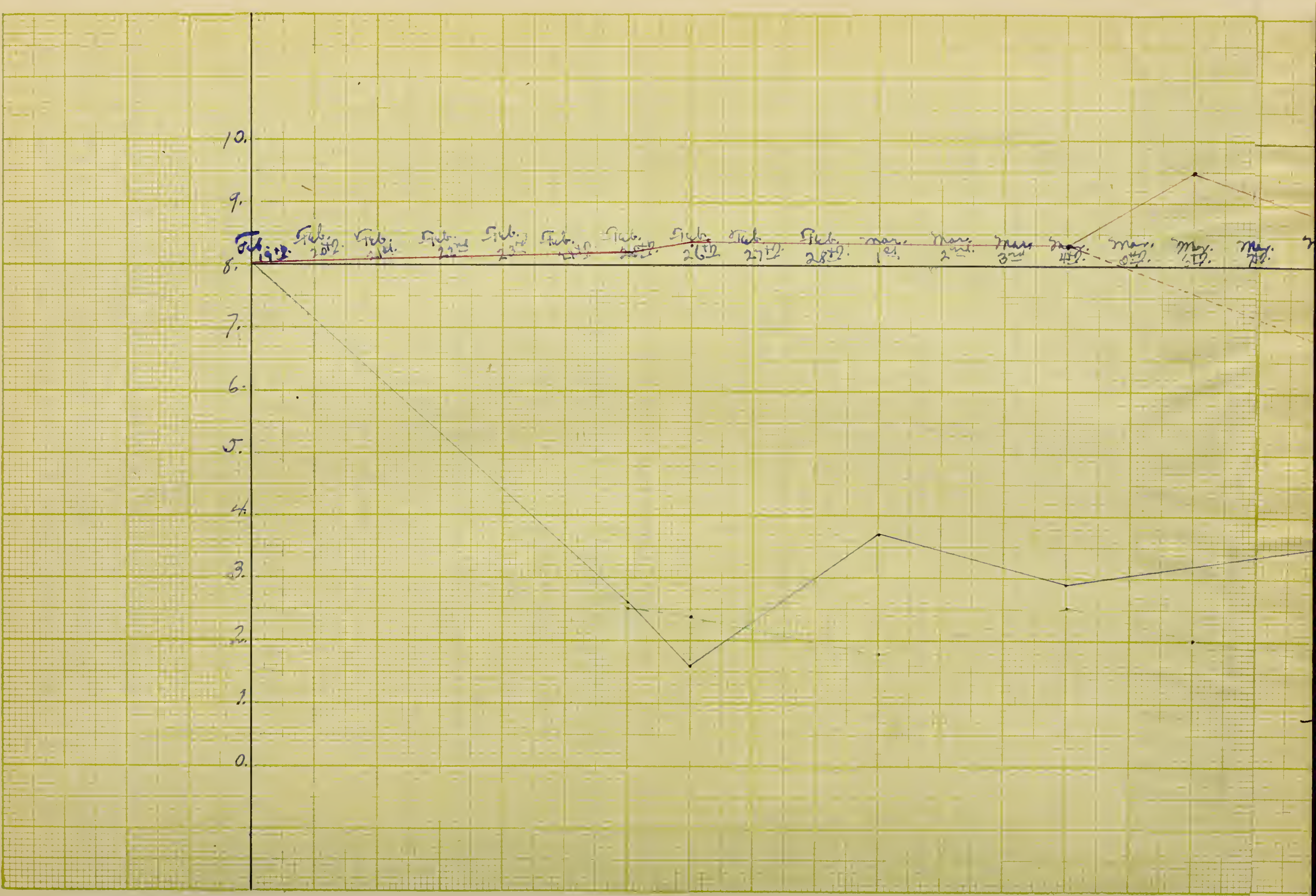


ot showing the disappearance of dissolved Oxygen in Champaign sewage
The red curve represents sewage sterilized with 1 cubic cent. of $HgCl_2$.
the dotted red curve is the sample to which $(NH_4)_2S$ was added.
The blue curve is sewage sterilized with chloroform.
The green curve is sewage in it's normal condition.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Under these conditions chloroform reduces but very little, the activity of the bacteria in sewage while mercuric chloride is a success as far as sterilization is concerned. In one case the degree of aeration of the sewage to which $HgCl_2$ had been added remained above the normal for 25 days and in the other case it lost but 1 part of oxygen per million on standing ten days. Upon adding mercuric chloride to the sewage a white cloudiness immediately appeared which, after standing for several days took on the form of a white curdy precipitate. The theory is that the $HgCl_2$ unites with the protoplasm of the bacteria in the sewage, producing a protoplasmate of mercury just as we have formed the albumenate of mercury when mercury is added to the white of an egg or other albumin containing substance. The formation, however of this compound of protoplasm of bacteria and mercury is said not to kill the bacteria, but simply arrests their activity while in this form. If, moreover, we can, by any means, break up this compound it is further stated that the bacteria resume their former activity. To test this view on the 4th of March it was experimentally determined how much ammonium sulphide would be necessary to add to one of the bottles sterilized

with $HgCl_2$ in order to exactly react with the $HgCl_2$ to form HgS and not leave any free $(NH_4)_2S$ in the water. It was found that it required 2.45 of a c.c. of $(NH_4)_2S$ to precipitate the mercury in 1 c.c. of the $HgCl_2$ solution. This amount was added to the middle of the sewage in the bottle, and the bottle was corked and allowed to stand for 14 days. After several days standing the white $HgCl_2$ changed to the black HgS and upon standing for 14 days and testing it was found that whereas the sewage which had been sterilised with $HgCl_2$ and had not had $(NH_4)_2S$ added contained 8.0 parts dissolved oxygen per million, the sample to which the $(NH_4)_2S$ had been added contained but 3.2 parts, and this seems to support the view that the bacteria in the sample to which the $(NH_4)_2S$ had been added, resumed their former activity and used up the oxygen.

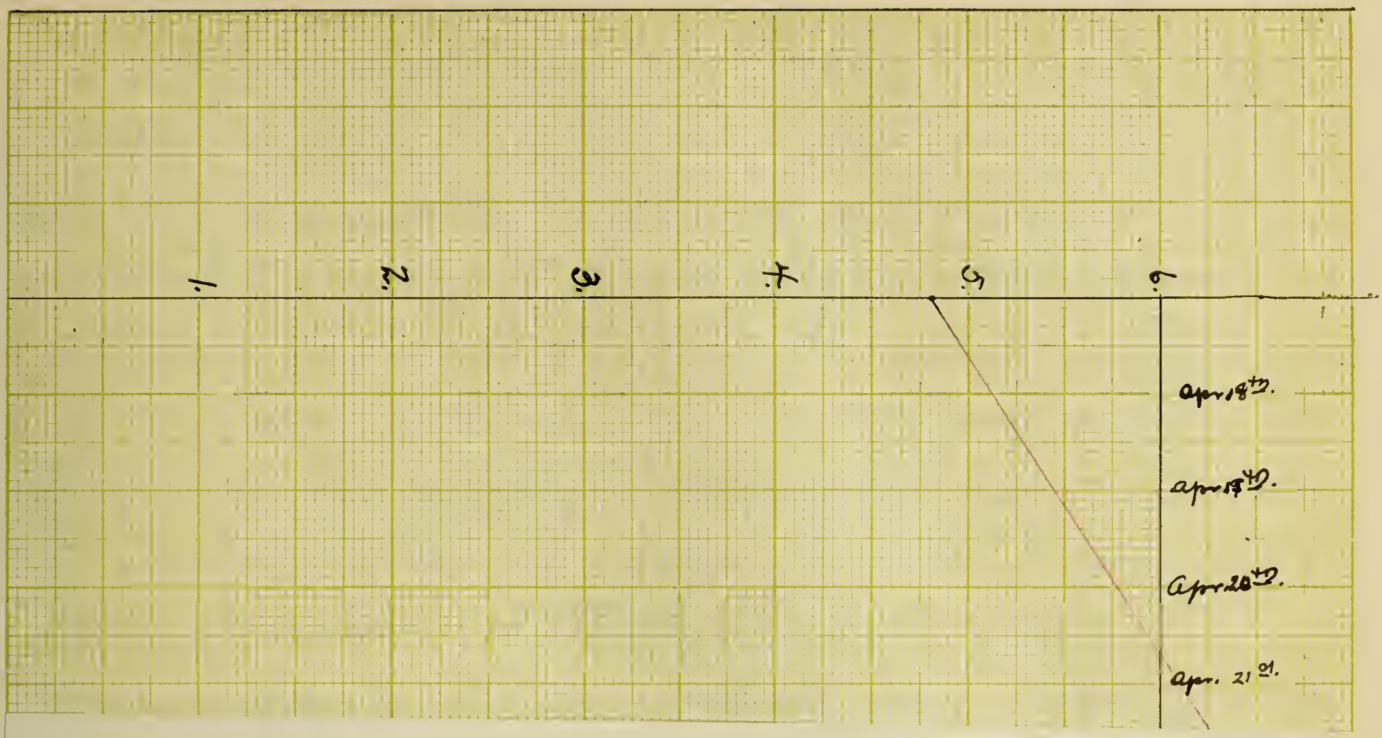
But to develop this fact more thoroughly I collected a sample of sewage on the 3rd of [illegible] and filled a 2 gallon bottle with it (The temperature was 18°C.) To this was added 25 c.c. of a saturated mercuric chloride solution. This large bottle was then placed in the dark and allowed to remain 12 days, when it was opened on the 15th [illegible], and [illegible]

71 percentage of saturation was determined. I then titrated 25 c.c. of the same $HgCl_2$ used above with a solution of $(NH_4)_2S$ using as an indicator $FeSO_4$ on a porcelain dropping plate, the presence of free $(NH_4)_2S$ in solution being shown by the precipitation of black FeS. It was found after 3 titrations that it would require 16.1 c.c. $(NH_4)_2S$ to precipitate the mercury added in 25 c.c. of solution. This amount was carefully added to the middle of the 2 gallon of sewage and the bottle was stoppered, then shaken to mix and allowed to stand for two days. The precipitate had now all turned to black HgS and I now opened the bottle, again determined its degree of aeration and then siphoned off, with frequent shaking to obtain [illegible] portions, to bottles of the sewage and black precipitate

Results:

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation
April. 3rd.	April. 3rd. 3^50 P.M.	15°C	6.55 6.55	61.84
(two days after adding $(NH_4)_2S$.) April. 17th.	April. 17th. 3^40 P.M.	..	4.83 4.83	43.6
.. ..	April. 23rd. 2^30 P.M.	..	6.75 6.75	63.73

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation
April. 17th.	April. 24th.	15°C	3.72	35.21
	2^{45} P.M.		3.72	
" "	April. 25th.	"	5.04	47.59
	2^{30} P.M.		5.04	
" "	April. 26th.	"	5.04	47.59
	9^{20} A.M.		5.04	
" "	April. 28th.	"	4.63	43.78
	3^{00} P.M.		4.63	
" "	April. 29th.	"	2.01	18.93
	3^{40} P.M.		2.01	
" "	May. 2nd.	"	0.8	7.62
	3^{20} P.M.		0.8	
" "	May. 7th.	"	1.31	12.18
	2^{30} P.M.		1.31	
" "	May. 10th.	"	1.4	13.32
	3^{20} P.M.		1.4	
" "	May. 13th.	"	0.9	8.56
	8^{50} A.M.		0.9	
" "	May. 14th.	"	0.46	4.4
	3^{40} P.M.		0.46	
" "	May. 15th.	"	0.93	8.8
	9^{30} A.M.		0.93	
" "	May. 16th. 10^{40} A.M.	"	0.91	8.68
" "	May. 17th. 10^{30} A.M.	"	0.51	4.91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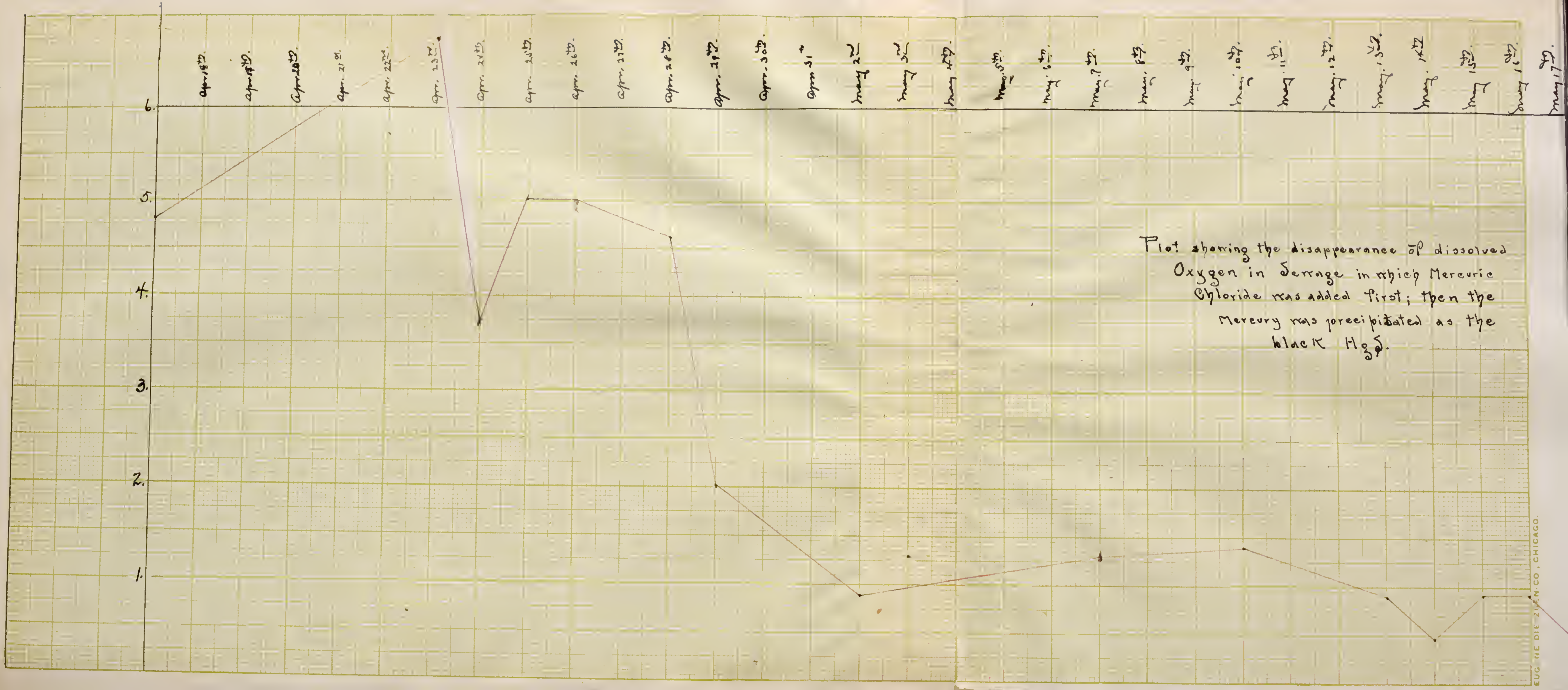


Plot showing the disappearance of dissolved Oxygen in Sewage in which Mercuric Chloride was added first; then the Mercury was precipitated as the black HgS.

The analyses show that, where in the same sewage to which $HgCl_2$ has been added still holds its oxygen undiminished in quantity for an indefinite period, if just enough ammonium sulphide is added to form mercuric sulphide of the mercury there is, after a certain period, an uncertain but gradual diminution in the degree of aeration; and the only plausible reason for this diminution is that the bacteria after a certain length of time resume their former activity, and I think the time during which no diminution of aeration occurs after adding the ammonium sulphide is occupied by the protoplasmate of mercury breaking up into mercury and bacterial protoplasm. (This is a theory which I have never seen advanced in works upon this subject.)

An article in the Chemical News stating that bacteria prey upon the phosphoric acid in a water, and that bacteria cannot live in a water which has all its phosphoric acid precipitated led to the following experiment.

On the 3rd of April, 190, I collected a gallon of sewage from the manhole on Green St., temperature was 15°C., determined its degree of aeration and then added enough strong ammonia to make it decidedly alkaline. I now added 30 c.c

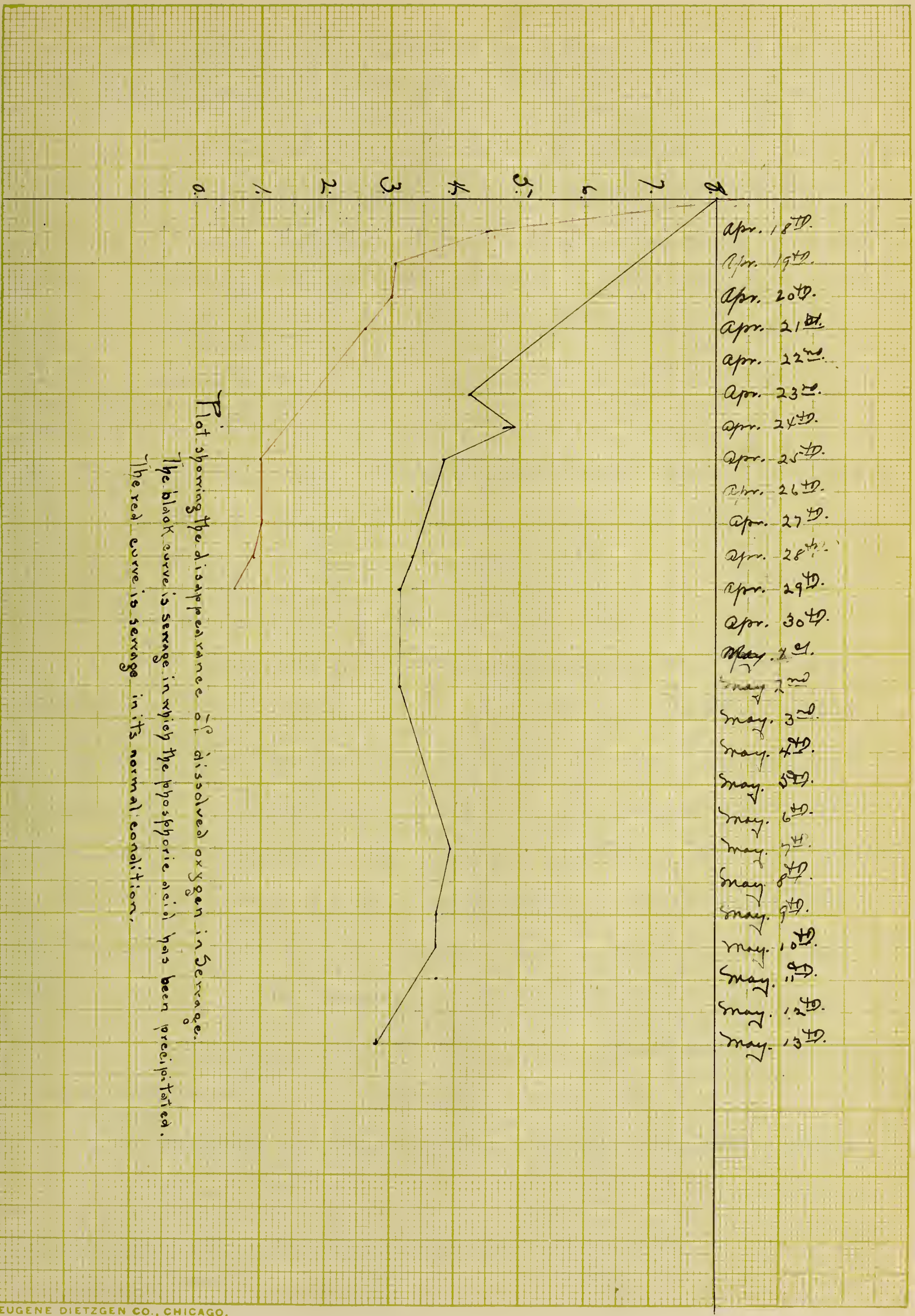
of magnesia mixture,* shook and let it stand fourteen days for the phosphoric acid to settle out.

On April 7th I filtered out the precipitated ammonium magnesium phosphate and reaerated the sewage with air. This was done, as described in the first part of this work, by passing air through the water, replacing the stopper in the bottle and shaking up the water with the air enclosed in the bottle. Having partly saturated it a series of eleven bottles were filled with it and stoppered to be tested from day to day.

* (11 grms. $MgCl_2$ + 2.8 grms. NH_4Cl + 5 c.c. NH_4OH and make up to 200 c.c.)

The tabulated results are as follows.

Date of Collection of Sample.	Date and hour of Examination.	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation.
April. 3rd	April. 3rd	15 °C.	6.55	61.84
(Resaturated)	3^{50} P.M.		6.55	
April. 17th.	April. 17th.	〃	8.0	75.54
	2^{40} P.M		8.0	
〃 〃	April. 23rd.	〃	4.23	39.97
	2^{00} P.M		4.23	
〃 〃	April. 24th.	〃	4.93	46.64
	2^{15} P.M.		4.93	
〃 〃	April. 25th.	〃	3.83	36.17
	1^{45} P.M		3.83	
〃 〃	April. 28th.	〃	3.32	31.41
	2^{40} P.M		3.32	
〃 〃	April. 29th.	〃	3.12	29.5
	3^{00} P.M.		3.12	
〃 〃	May. 2nd.	〃	3.12	29.5
	3^{00} P.M		3.12	
〃 〃	May. 7th.	〃	3.93	37.12
	2^{30} P.M.		3.93	
〃 〃	May. 9th.	〃	3.72	35.26
	1^{40} P.M.		3.72	
〃 〃	May. 10th.	〃	3.72	35.26
	2^{20} P.M.		3.72	
〃 〃	May. 13th.		2.8	26.51
	8^{50} A.M.		2.8	



Plot showing the disappearance of dissolved oxygen in Sewage.

The black curve is sewage in which the phosphoric acid has been precipitated.

The red curve is sewage in it's normal condition.

Comparing this table with the tables given for the disappearance of dissolved oxygen in normal sewage, we see that whereas the latter lose practically all their dissolved oxygen upon standing one week, the former contains at the end of seven days over one half its former amount and even at the expiration of a month still contains over a third of its oxygen. This seems to support the view that bacteria need phosphoric acid, as well as oxygen, for their growth and development, and that if the water doesnt contain any phosphoric acid the bacteria can not live, as life means a consumption of oxygen, and the oxygen has disappeared slowly.

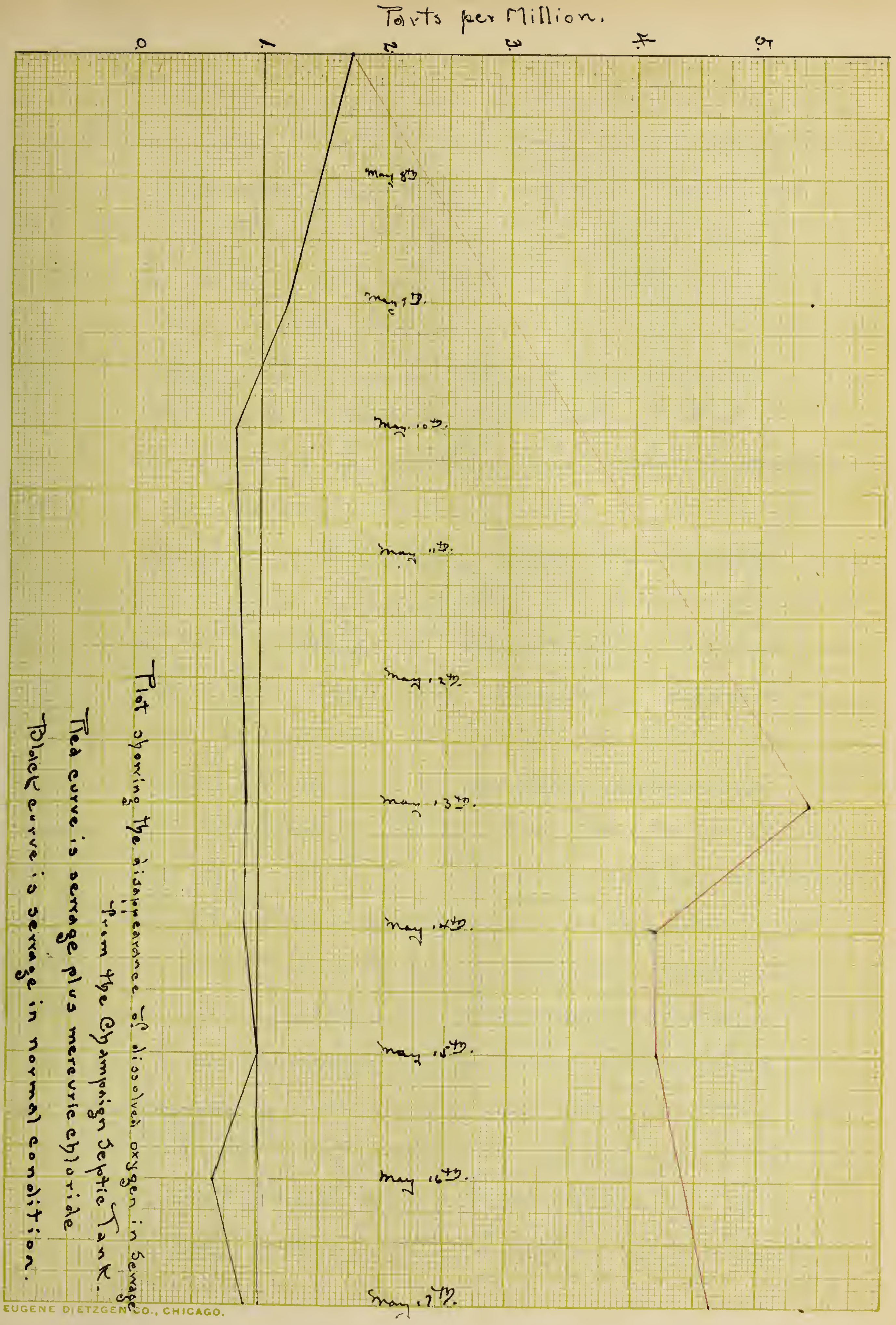
The next lot of sewage experimented upon, was collected the 7th of May, from Champaign Septic tank in Urbana, Ill. Sewage was collected at 2.00 P.M. and dipped with a bucket just before it passes over the board which separates the heavy matter from the liquid. It was taken to the laboratory, its percentage saturation determined and two series of eleven bottles each were made, one containing sewage in normal condition, and the other containing sewage sterilized with 1 c.c. $HgCl_2$.

The results of these two series are as follows.

Date of collection of Sample	Date and hour of examination	Temperature when collected	Parts dissolved Oxygen per Million	Percentage Saturation
May. 7th. '01	May. 7th	16°C	1.71	17.24
	5.00 P.M		1.71	
" "	May. 9th.	"	1.20	12.16
	1.40 P.M.		1.20	
" "	May. 10th.	"	0.8	8.12
	3.30 P.M.		0.8	
" "	May. 13th.	"	0.9	9.38
	1.40 P.M.		0.9	
" "	May. 14th.	"	0.9	9.38
	2.10 P.M.		0.9	
" "	May. 15th.	"	1.02	10.31
	8.50 A.M.		1.02	
" "	May. 16th.	"	0.65	6.58
	9.20 A.M.		0.65	
" "	May 17th.	"	0.91	9.15
	9.30 A.M.		0.91	

Sewage same as above, plus 1 c.c. $HgCl_2$ per. 300 c.c. Sewage.

" "	May. 7th.	16°C	1.71	17.24
	5.00 P.M.		1.71	
" "	May. 13th.	"	4.4	43.26
	2.20 P.M.		4.4	
" "	May. 14th.	"	3.17	31.90
	3.15 P.M.		3.17	
" "	May. 15th.	"	3.17	31.90
	9.50 A.M.		3.17	
" "	May 17th.	"	3.64	36.47



Plot showing the disappearance of dissolved oxygen in sewage from the Champaign Septic Tank.

Red curve is sewage plus mercuric chloride

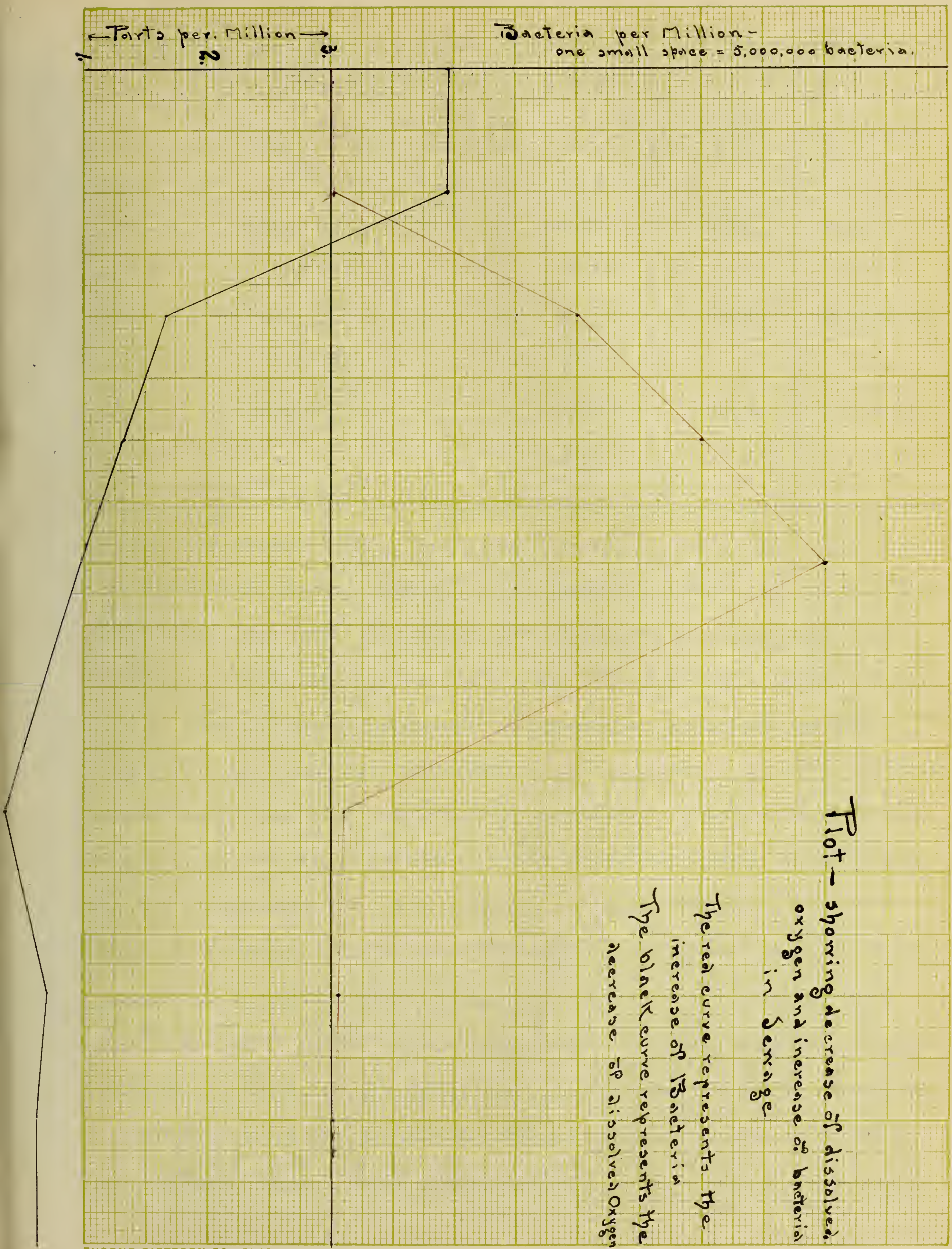
Black curve is sewage in normal condition.

The above experiments naturally led to the question, "Does the disappearance of oxygen and the multiplication of bacteria bear a constant ratio to one another?" It is a well authenticated fact that the bacteria in a water multiply in [illegible], consuming much oxygen in their growth, and it is the object of the following experimentation to count the colonies formed from day to day in the water, in addition to noting the rate of disappearance of the oxygen.

On the 14th of May, eleven small bottles were taken to the Champaign septic tank and filled at 11 A.M. with sewage, the temperature of which was 17 °C. The bottles were then carefully stoppered and brought to the laboratory. One of the bottles was then opened and its degree of aeration determined. The bottle and remaining sewage was then taken to the Bacteriological laboratory. I had previously sterilized three 250 c.c. Erlenmeyer flasks for one hour with dry heat at 150 °C. 100 c.c. of distilled water was now measured into each of the Erlenmeyer flasks, and the flasks and distilled water were again sterilized under pressure in a steam autoclave for twenty minutes. When cool they were removed from the autoclave, one c.c. of the sewage was added to one of them, and carefully mixed with the 100 c.c. of water, 1 c.c

of this was placed into the second sterilized flask and mixed, and 1 c.c. of this was then placed into the last flask, thus made a dilution of one part sewage to 1,000,000 parts stearilized water. I next melted up two stearilized tubes of "agar agar," cooled them down to nearly 40°C and then added one tenth of a cubic centimeter of the above diluted water to each tube, mixed and immediately poured said agar upon two stearilized Petri dishes. One of the dishes was put into the incubator to develope while the other was developed at the room temperature. This process was repeated every day after the percentage saturation had been determined. After a day or two standing, small white colonies appeared in the agar and these were counted and the day upon which they were found carefully noted. I also tried to find out which species, (detected by color and aspect of their colonies) multiplied and which diminished. The results follow -

Date of Collection of Sample	Date and hour of Examination	Temperature when Collected	Parts dissolved Oxygen per Million	Percentage Saturation	Number of Colonies per. c.c. of Sewage
May. 14th.	May 14th.	17° C	3.73	37.52	2,000,000
	1^{00} P.M.		3.73		
" "	May 15th.	..	3.70	37.22	3,000,000
	8^{00} A.M.		3.70		
.. ..	May 16th.	..	1.67	16.8	200,000,000
	9^{00} A.M.		1.67		



Plot – showing decrease of dissolved oxygen and increase of bacteria in Sewage

The red curve represents the increase of Bacteria

The black curve represents the decrease of dissolved Oxygen.

May 14th.	May 17th.	17°C	1.33	14.38	300,000,000
	10⁰⁰ A.M.		1.33		
" "	May. 18th.	"	0.98	9.96	400,000,000
	9³⁰ A.M.		0.98		
" "	May. 20th.	"	0.35	3.49	10,000,000
	10⁰⁰ A.M.		0.35		
" "	May. 21st.	"	0.70	7.18	4,000,000
	10⁰⁰ A.M.		0.70		
" "	May. 22nd	"	0.63	6.46	100,000
			0.63		
" "	May 23rd.	"	0.63		

To summarize the results obtained from the experiments upon sewage I found that the Winkler method cannot be used for sewage containing high nitrites and that, on the other hand, the Levy method gives satisfactory results. Mercuric chloride when added to sewage arrests the activity of the bacteria contained in the water, by uniting with the protoplasm of said bacteria. The bacteria are not killed by this reagent but are simply transformed into an inactive state, and if a suitable reagent, which will counteract the effect of the mercury, is added, the bacteria will, after an indefinite period, again become active. Phosphoric acid is necessary for the bacterial growth in sewage and other waters, and a water in which there isn't any phosphoric acid does not,

as a rule, contain lecithin for bacteria need phosphoric acid as a part of their food.

In all waters containing bacteria, if such water be enclosed in an air tight compartment, the bacteria will multiply indefinitely feeding upon the oxygen dissolved in the water, until the percentage of aeration has become a minimum then the bacteria begin to die and after a while we will have left only a few forms which cannot grow except in the absence of oxygen. Therefore does not, under these conditions, arrest the activity of the bacteria in sewage and all sewage when enclosed in an air tight compartment looses its oxygen, but obtained from the septic tank, losing its dissolved oxygen in a much shorter space of time than any other sewage collected. The reason is that it is a mixture of the sewage from every portion of the city of Champaign. But however diluted the sewage was I found that the mercuric chloride always arrested the bacterial action.

As a second part to this thesis some experimentation was conducted upon standard aerated distilled water, the object being to compare the results obtained with those given by Bunsen.

Two 2 litre bottles were half filled with freshly distilled water and vigorously shaken for five min-

ules, the air being renewed several times by filling up one bottle with the contents of the other and dividing into two portions, which are thus repeatedly shaken with fresh air. Finally one bottle being filled, the temperature of the water is taken, after which the bottle is allowed to stand stoppered half an hour to get rid of minute air bubbles.

(The water is made different temperatures by adding either heat or cold.)

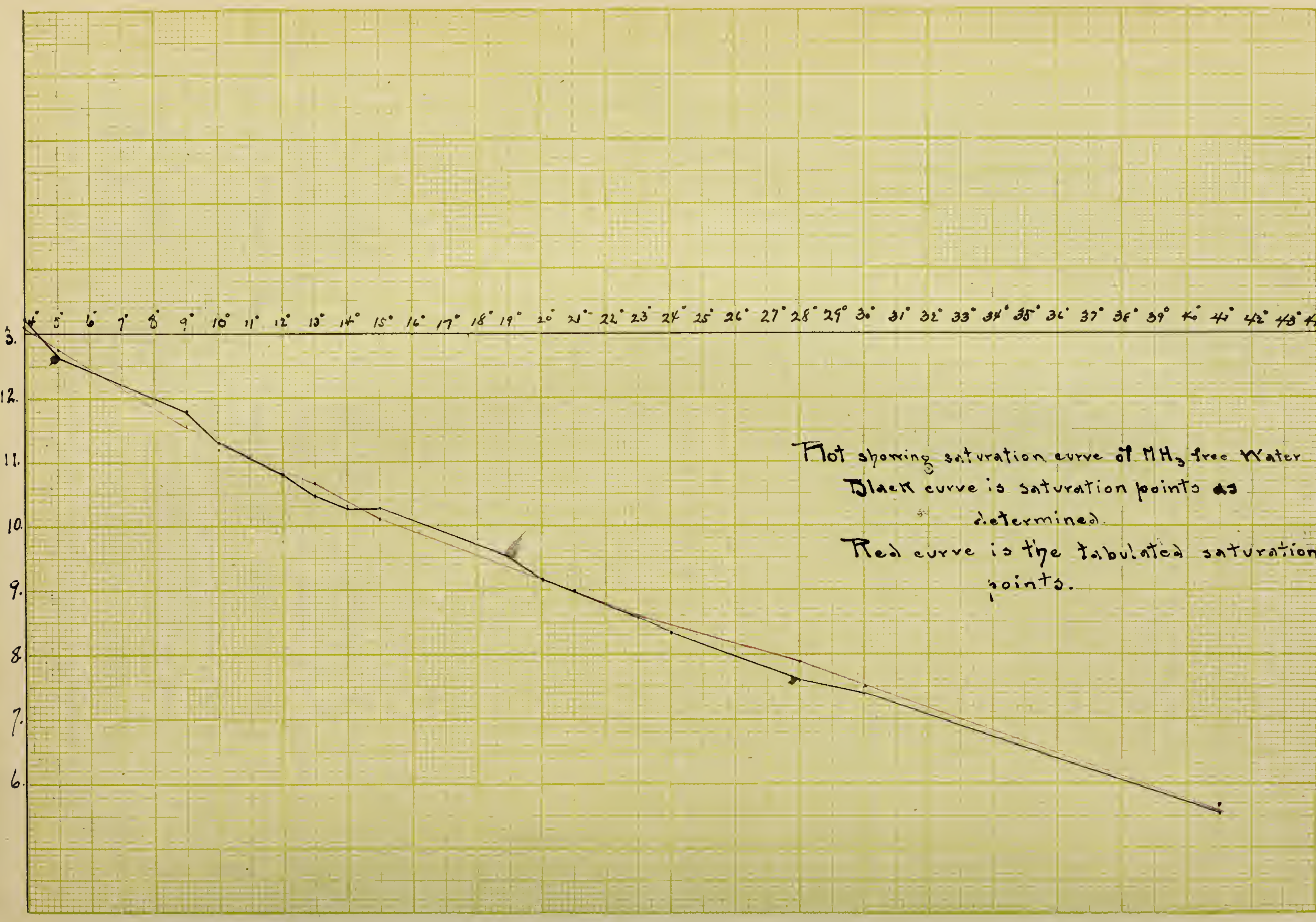
The table below given shows the results obtained.

These have all been run in duplicates.

Date	Temperature Centigrade	Time Saturated	Oxygen Found	Oxygen Tabulated	Percentage Saturation.
Feb. 20th.	13° C	40 minutes	10.15	10.59	94.52
" 21st.	15° C	" "	9.6	10.14	94.74
" 23rd.	12° C	" "	9.76	10.82	90.22
" "	18.6° C	" "	9.2	9.4	97.97
" 24th.	18.9° C	" "	9.55	9.5	100.01
" "	20.0° C	" "	9.27	9.19	100.87
" 25th.	19.5°	" "	8.40	9.20	91.30
" 27th.	12.0°	" "	10.83	10.82	100.09
" "	28.0°	" "	7.63	7.90	96.58
" 28th.	9.0°	" "	11.8	11.58	101.98
" "	47.0°	" "	5.85		
" "	41.0°	" "	6.52		

Saturation of NH3 free water cont.

Date-	Temperature Centigrade	Time saturated	Oxygen found	Oxygen tabulated	Percentage saturation
March 5th.	15°	40 minutes	10.48	10.44	100.48
" "	4°	1 "	13.23	13.15	100.63
" 7th.	5°	" "	12.62	12.78	98.76
" 11th.	10°	" "	11.30	11.31	99.91
" "	20°	" "	9.16	9.19	99.69
" 13th.	24°	" "	8.34	8.51	98.09
" 19th.	30°+	" "	7.43	7.50	99.05
" "	13°	" "	10.48	10.59	99.01
" 21st.	14°+	" "	10.28	10.30	99.8
" "	23°	" "	8.55	8.67	98.16
" 22nd.	19.8°	" "	9.2	9.2	100.00
			9.26		
" "	20.7°	" "	9.03	9.04	100.01
			9.06		
			9.07		
" 27th.	21.0°	Levy method " "	9.0	8.97	100.33
" "	"	Winkler method " "	8.5	"	94.76
" 28th.	22.0°	Levy method	8.84	8.84	100.00
			8.84		
			8.84		
" "	"	Winkler	8.33	8.84	94.32
			8.32		94.11
			8.34		94.34



Plot showing saturation curve of NH_3 free Water

Black curve is saturation points as determined.

Red curve is the tabulated saturation points.

The results obtained from the standard aerated water were quite satisfactory, nearly all of them being but a small amount above or below the tabulated amount, and a comparison of the Levy and Winkler methods for these standard ammonia free waters showed the results obtained from the Levy method about 0.5 parts above those of the Winkler.

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