THE UTILIZATION OF DISSOLVED OXYGEN AND NITRATES IN POLLUTED WATER

Thesis for the Degree of B. S.

R. F. Killeen

1935

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Sewage - Purification

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An Experimental Study of the Relation Between

the Time of Utilization of Dissolved Oxygen

and Nitrates in Polluted Water

A Thesis Submitted to

The Faculty of

MICHIGAN STATE COLLEGE

OF

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BY

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## Purpose of Project

The purpose of this experiment is to find the relation between the time of utilization of nitrates and dissolved oxygen in the decomposition of polluted water. In the aerobic stabilization of sewage by oxidation;the oxygen supply may be obtained from several sources: (1) The oxygen of the atmosphere is absorbed by the water the amount depending mainly on the temperature. (2) Certain plants will give off oxygen that is dissolved in the water. (3) The presence of certain salts such as nitrates in the water will aid in the process of oxidation. The relation of these oxygen resources concerning the time of utilization is important in the control of the polluted stream.

## Discussion of the problem

Few references concerning this question were found. Fuller,(I) states: "With respect to gaurding against objectionable odors, I think it is clearly necessary for the chemists an bacteriologists to keep in mind that putrefaction does not exist so long as oxygen remains at all. In fact you can go further than that, and say that so long as oxygen is available from nitrates, nitrites or other oxidized salts there is substantially no putrefaction."

It will be noted that nothing is said about which is used first the dissolved oxygen of the oxidized salts. However it is made clear that putrefaction does not begin until both the dissolved oxygen content and the nitrates have been used by the sewage. The word "substantially" infers that there is little if any putrefaction at the depletion of the oxygen supply. This therefore does not set any limit as to the beginning of putrefaction.

From data given by Fuller(II), it was shown that there were nitrates present in sewage samples where dissolved oxygen has been depleted. It can not be determined from this data, however, just when the nitrate and nitrite content are reduced. That is, it may have started at depletion of the dissolved oxygen or perhaps it may have depleted at the same time the dissolved oxygen was reduced.

The information given by H. Heukelekian (III) does not settle the question as to the time relation of the utilization of nitrates and dissolved oxygen and nitrites. He states: " The nitrates and nitrites were added as a potential source of oxygen and compared with actual amounts of dissolved oxygen. The nitrates and nitrites increased as the oxygen saturation was eighty percent or more. It would appear that pollution up to this point was not sufficient to have a detrimental effect on nitrification. When the average dissolved oxygen content dropped to sixty percent saturation there was a loss of nitrates. Probably not only was nitrification retarded but an actual loss of nitrates due to reduction might have taken place. Although it has been shown that the nitrates are not utilized until practically all the dissolved oxygen is consumed, it is possible, as indicated in the above discussion that localized anaerobic zones might be established in a medium which is not entirely defecient in dissolved oxygen."

This information is rather indefinite as to just when the nitrates are reduced. The author explains the discrepancy between the data concerning the loss of nitrates and the accepted fact that the nitrates are not utilized until the dissolved oxygen is depleted, by a theory that "localized anaerobic" conditions exist in which nitrates are reduced but no dissolved oxygen is utilized. It is possible however that the actual loss of nitrates might have commenced anywhere below the sixty percent saturation point, had there been no " anaerobic zones ".

It has been pointed out in the above discussion: (1) That putrefaction cannot exist until the dissolved oxygen and the nitrates have been reduced. (2) That nitrates are present after the dissolved oxygen has been exhausted. (3) There is evidence that below a sixty percent dissolved oxygen saturation point nitrates are reduced although it is commonly accepted that reduction does not begin until the dissolved oxygen is depleted.

Any conclusion as to the question under discussion would have to be indefinite if based upon the above references. Although the statements may be regarded as true they do not cover the same scope as would be desired. The statement made by Heukelekian that the nitrates are slowly used, reduction starting when the dissolved oxygen is less than sixty percent saturation is contrary to the other data found which seems to show that the nitrates were not used until possibly all the dissolved oxygen is depleted. It seems quite possible, however, that "anaerobic zones " might have been established around some of the larger particles, or in certain areas where contamination was especially heavy. That is, nitrates might have been used in these zones while there was dissolved oxygen present in the water as stated by Heukelekian above.

There are several practical points that hinge on the question under discussion- the relative time of the utilization of dissolved oxygen and nitrates also the onset of septic or anaerobic conditions. (Hydrogen sulphide gas is commonly used as an index of septic conditions.)

Probably the most likely point in this connection is the development of anaerobic conditions in a polluted stream. The stream provides a natural means of disposing of sewage and industrial wastes by dilution, allowing the wastes to decompose with the aid of oxygen then to become inert. At times, especially during low flow periods of the stream, septic conditions will occur causing an odor nuisance as well as becoming unsightly. Often the stream is used in many ways, both publicly and commercially and thereby affected seriously with the development of septic conditions. Some of the considerations that must be kept in mind in the regulation of a polluted stream as given by Metcalf and Eddy (IV):

A. Hygienic considerations.

1. Contamination of
    a. Private and public water supply.
    b. Natural ice.
    c. Shell fish.
    d. Water and bathing beaches.
2. Pollution resulting in
    a. Nuisance affecting public health and comfort.
    b. Impairment of recreational facilities.

B. Esthetic considerations, creation of conditions offensive to

1. The eye.
2. The sense of smell.

C. Economic considerations, damage to

1. Industrial water supplys.
2. Live stock.

3. Fish and other useful equatic life.

4. Property, with resulting depreciation of values.

5. Private and public river and harbor improvements and navigation. ( such as silting due to sewage deposits)

D. Legal considerations, interference with

1. Riparian owners.

In the development of septic conditions , the last three considerations (B,C,D) are all affected to some degree. It can be seen from this outline that the prevention of septic conditions is important to a variety of considerations. Therefore in streams where this consideration must be met it is important to prevent these anaerobic conditions from forming if possible.

A second point to be considered in the allowable pollution of a stream is the maintainance of fish life. The degree of pollution necessary to keep a stream fit for fish life may not necessarily be the same as that necessary to develop anaerobic conditions as mentioned above. That is, the condition of pollution of a stream is important concerning the fish life, as well as the prevention of septic conditions and the consequences that follow. Rudolfs, Heukelekian, Lackey, Zeller and Lacy (V) from studies on the Raritan river report as follows concerning fish life: "As long as pollution only is limited, that is, when the dissolved oxygen content of the river does not fall below sixty percent saturation at any time of the year, conditions are favorable for fish life, provided sludge deposits in the river or along the banks are of slight extent.

When the dissolved oxygen in the stream has reached about fifty percent saturation and sludge deposits are being formed below sewer outfalls and on shallow places, fish life will still exist to a more or less limited extent, although they will not multiply except in rather limited places. The more susceptible fish migrate.

If the dissolved oxygen content in the river during any time of the year falls below thirty percent saturation and sludge deposits become more or less permanent during the summer or at lower water flow so that local nuisance might be expected on account of odor, still a few fish like eels, which are able to exist on little oxygen would be present but all other types would disappear."

From this discussion it seems that the welfare of the fish depend on the dissolved oxygen content of the stream as well as the surrounding conditions of the stream bed. The limit thirty percent dissolved oxygen saturation as the limit of pollution that fish will endure appears to be generally accepted. It is important, then, that if the stream is to protect fish life this limit of pollution be observed.

Two of the importont problems in stream control, as pointed out above, are the prevention of septic conditions and the maintainance of fish life by keeping the minimum requirements of dissolved oxygen present at all times. The question of meeting these requirements bears directly on the relation of the time of utilization of nitrates and dissolved oxygen.

This relation is of importance concerning septic conditions as the time of utilization of the oxygen resources may help in preventing these conditions from developing. That is if the nitrates and dissolved oxygen are used prior to septic conditions then they will aid in the prevention of septic conditions and in some cases would no doubt actually prevent these conditions if present in large enough amounts. As stated by Fuller above, this is what likely happens. However, it is not stated definitely that some of these resources might not remain after septic conditions commence nor is there any reference as to which potential oxygen supply is first utilized, this point however is not important in this connection. It is evident that in this first case the full oxygen supply would not be available to prevent anaerobic conditions. The time of utilization of oxygen resources, however, is import- concerning the question of fish life. That is, it is desirable to maintain a certain definite limit of dissolved oxygen but as the relative time of utilization of the nitrates is unknown, it is not known whether their presence will aid the fish by giving up its oxygen to the dissolved oxygen present or not. Conditions would be favorable to fish life if the nitrates were reduced wholly or partially before the dissolved oxygen was used up.

Another reason for the importance of this relation is as an indicator of pollution. It is common to use either the dissolved oxygen content or the nitrate content as an index of pollution without regard to the condition being investigated. However if these two oxygen supplies are not utilized at the same time in the decomposition of sewage then each will be an indicator of a different stage of pollution. For example, if the dissolved oxygen is used up completely prior to the use of nitrates after which septic conditions follow, then the dissolved oxygen content would be a better index of pollution during the early stage, the nitrates during the latter stage of decomposition. If, however, the order of utilization is reversed, the opposite would be true concerning the proper index of pollution. Also, if the two oxygen supplies are used together then either one would be an index of the conditions being studied. If septic conditions occur before the entire utilization of nitrates, the oxygen control would be the best indicator as to when anaerobic conditions might be expected. If nitrates are used after the dissolved oxygen, the nitrate index would be incorrect, however it is not usually used.

It is the purpose of the sewage disposal plant to prevent these conditions, as well as other considerations mentioned in the outline given above. That is, to prevent the development of septic conditions and to protect the fish life. Of course the sewage plant is not entirely responsible for the prevention of the undesirable conditions. Other factors that also govern the stream conditions are: (1) The volume of flow. (2) The amount of aeration due to rapids, dams etc. (3) The presence of certain green plants that supply oxygen. (4) The surface area available for oxygen absorption the amount depending upon the temperature and the dissolved oxygen already present. In many streams these factors aiding purefication are enough to handle comparitively heavy loads with no undesirable conditions resulting. However the amount of purification accomplished by the sewage plant is often the element that controls the condition of the stream. It seems then, that the degree of the purification of the sewage plant effluent is an important factor in the control of the sanitary conditions that are found in the water way. Some of the important tests of sewage effluent which indicate river conditions are: The reduction of solids, the reduction of bacteriological oxygen demand, the reduction in bacteria count and the increase of oxidized salt content as well as the development of a dissolved oxygen in some cases. The first three tests indicate the plant effeciency concerning the pollution to be added to the water while the latter potential oxygen resources indicate the amount of pollution that may be expected to be combatted. It is through the utilization of these last named tests that the experiment is involved. Included in the group of oxidized salts are the nitrites and nitrates which are the most important in this respect. The control of these conditions from the sewage plant depend somewhat on the relation of the time of utilization of the oxygen resources.

The question to be answered, from a practical standpoint, is whether or not the high nitrate content produced from certain types of sewage plants is aiding in the prevention of the undesirable septic conditions and if so to what degree. From the material covered by the investigations given above, the answer would seem to be that the nitrate content in polluted water tends to retard septic conditions but does not help in maintaining a high dissolved oxygen content, thus the fish life is not aided by this potential oxygen supply. However, as pointed out before these references do not answer the question satisfactorily and the missing data must be supplied experimentally.

## Experimental

The sewage samples used were taken from the East Lansing sewage plant effluent channel. This sewage recieves only primary settling in Imhoff tanks.

The plan was to simulate polluted stream conditions where both nitrates and dissolved oxygen are present. The sewage samples used contained no nitrates and little dissolved oxygen and is generally considered weak in bacteriological oxygen demand. The nitrates were added to the samples in the form of potassium nitrate, the same amount being added to each. Various dilutions of the original sample were made with diluting water which had been stabilized and thus contained a fixed amount of dissolved oxygen. A wide range of dilutions was now available through which the nitrate content was constant but the amount of pollution was directly proportional to the dilution and the dissolved oxygen was inversely proportional to the dilution. Each dilution was tested immediately for dissolved oxygen content and also the nitrate content was checked to see if the dilutions contained the computed amounts. Three other samples were drawn from each dilution and were incubated for a period depending on the strength of the sewage. The incubations were made in closed bottles at room temperature and tested after the period of incubation- usually less than five days- for the same substances including the test for hydrogen sulphide. It was desired that the oxygen resource that was first depleted would occur in about the middle dilution- in order of strength- so that the relation with the other oxygen supply could best be observed. To do this it was necessary to make a trial test to determine what range of dilutions would best fit this condition. An arbitrary scale of dilutions was chosen for the first trial and the experiment finished. It was found that the dilutions were too low for the strength of sewage that was used, that is, only a small amount of dissolved oxygen was used up throughout the entire range of dilutions while none of the nitrates were used. A second trial was run this time using a higher range of dilutions. However there must have been a variation in the strength of the sewage as the range was again too low . On the next trial , however, the dissolved oxygen was utilized in all but the weaker dilutions and the nitrates were used after the depletion of the oxygen. Although no hydrogen sulphide test was run the characteristic odor indicating its presence was found in those dilutions in which the nitrates had been utilized. Almost the same range of dilutions was run on the last test and the results were similar to the previous test and in addition a hydrogen sulphide test was made. The proceedure of Theroux and Eldridge (Vl) was followed in making up the solutions and performing the tests that were made on each dilution. These were as follows:

(1) Dissolved oxygen (Winkler Method)

1. Add one c.c. of manganous sulphate solution by means of a pipette.
2. Add one c.c. of alkaline potassium iodide solution.
3. Insert the stopper and mix by inverting the bottle several times.
4. Allow the precipitate to settle half way and mix a second time.
5. Again allow to settle half way.
6. Add one c.c. of concentrated sulphuric acid, insert the stopper and mix immediately. Do not allow the bottle to

stand open after the addition of the acid.

7. Allow the mixture to stand at least five minutes.
8. Rapidly withdraw one hundred c.c. of the sample into a flask and titrate with twenty-five thousandths normal sodium thiosulphate using starch as an indicator near the end of the titration.

Note: This titration should not require over two minutes after the sample has been removed from the bottle. Should the blue color of the starch iodide return after once being decolorized, it should be disregarded.

Calculations:

c.c. thiosulphate x 2 equals p.p.m. dissolved oxygen.

(2) Nitrate Nitrogen ( phenoldisulphonic Acid Method)

1. Filter about thirty or thirty-five c.c. of the sewage through a filter paper.
2. Evaporate twenty-five c.c. of the filtrate to dryness on a water bath. ( Use a smaller amount if the nitrate content is high.)
3. Moisten the residue with one c.c. of phenoldisulphonic acid.
4. Dilute to about twenty c.c. with distilled water.
5. Add a fifty percent solution of sodium hydroxide until the maximum color is produced. ( Not over five or six c.c. will be required.)
6. Filter into a Nessler tube and wash the paper with water making up finally to fifty c.c.
7. Make up color standards containing three tenths, five tenths, seven tenths, one, one and one half and two c.c. of the standard nitrate solution and add two cc. of fifty percent

sodium hydroxide to each.

8. Dilute each to fifty c.c. and select the standard comparing with the sample.

Calculations:

$$\frac{\text{c.c. standard}}{\text{c.c. sample used}} \times 10 \text{ equals p.p.m. nitrate nitrogen.}$$

(Authors note. A color disc was used in the experiment in place of making up color standards as directed in step seven.)

(3) Hydrogen sulphide.

1. Syphon five hundred c.c. of the sample into a graduated cylinder.
2. Pipette ten c.c. of the twenty-five thousandths normal iodine solution into each of two erlenmeyer flasks.
3. Add one gram of potassium iodide to each flask.
4. To one add two hundred c.c. of distilled water.
5. To the other, syphon from the graduate two hundred c.c. of the sample.
6. Titrate both the distilled water blank and the sample with twenty five thousandths normal sodium thiosulphate, using starch as an indicator near the end of the titration.

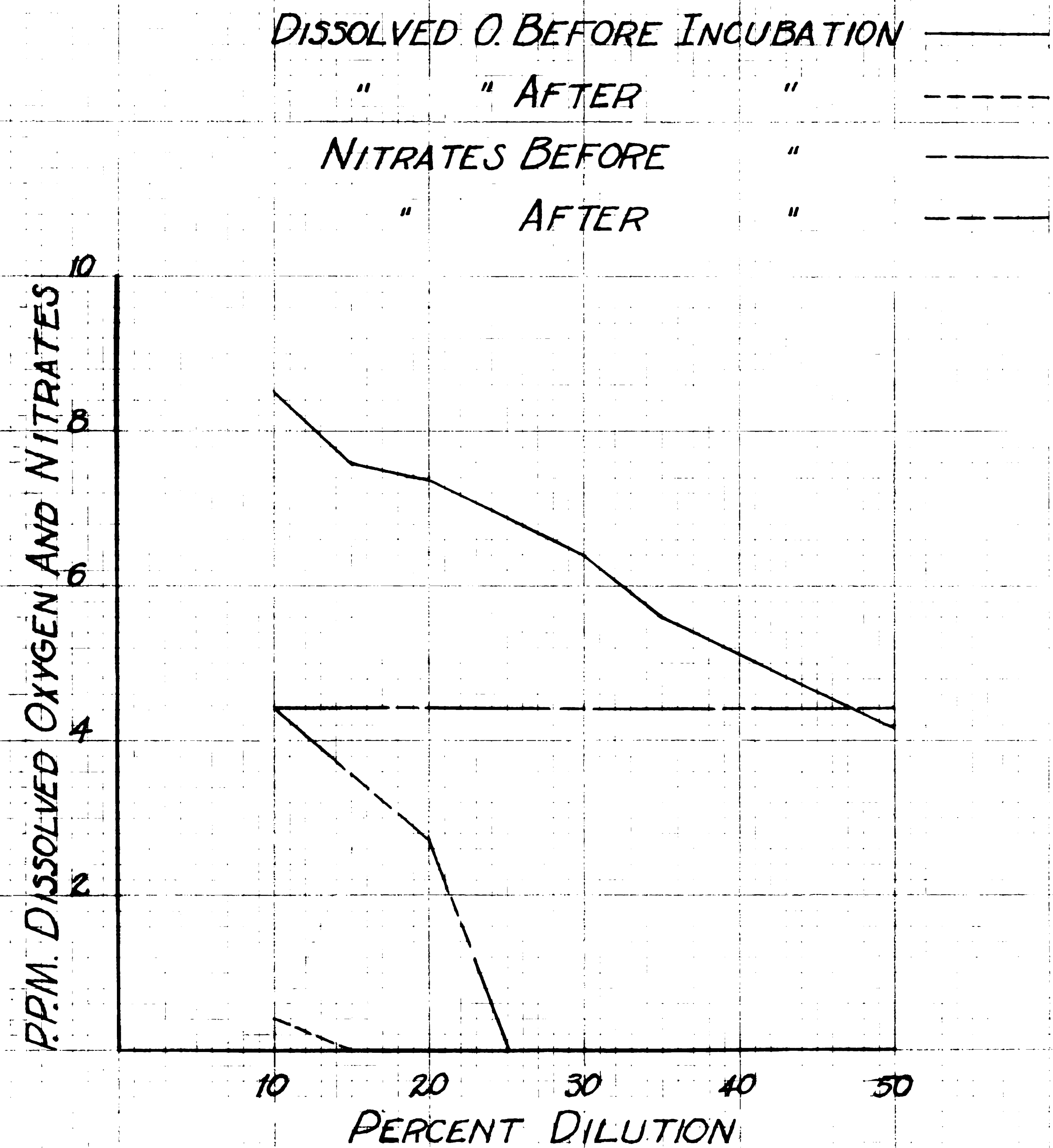
Calculations:

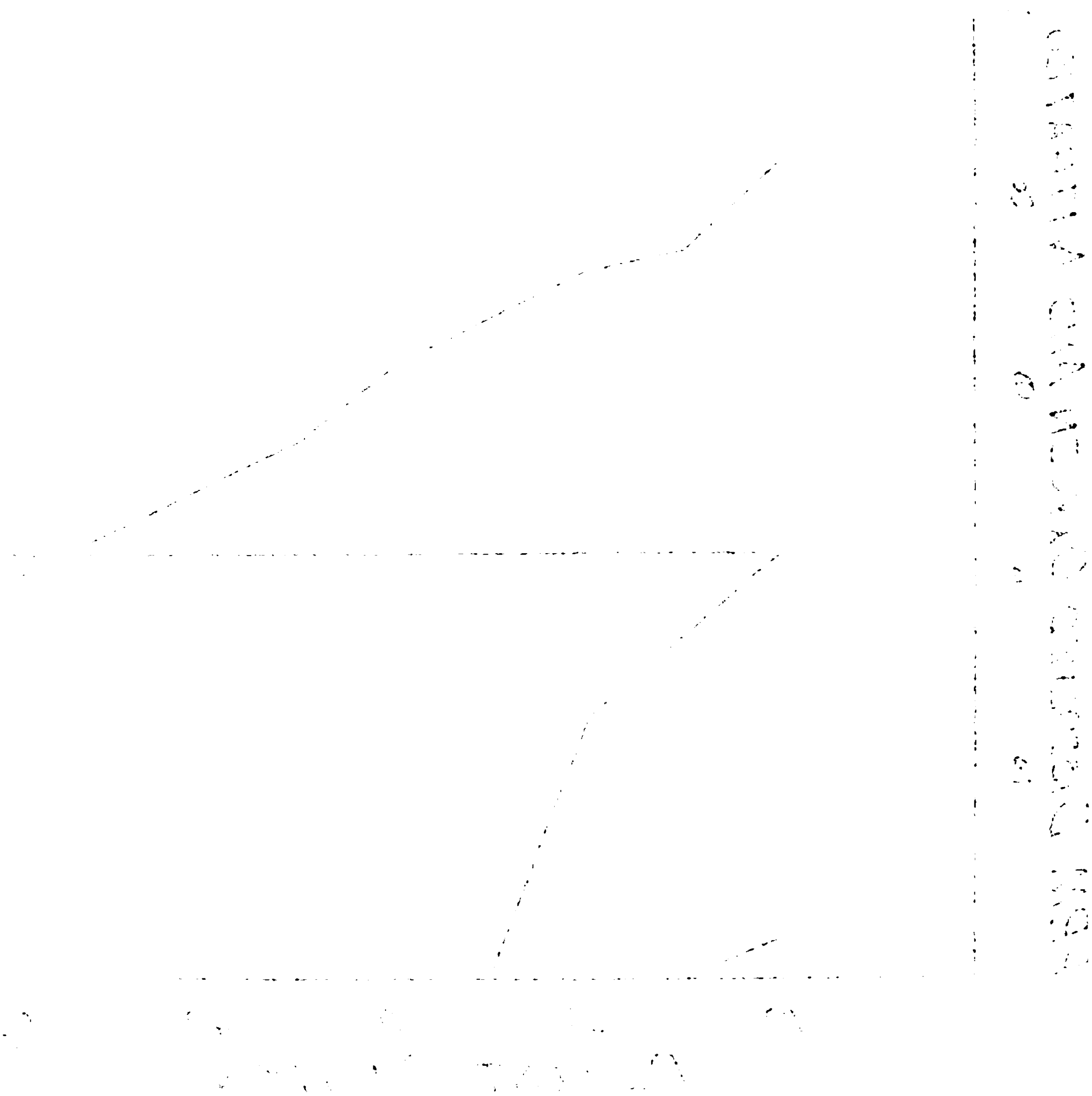
c.c. iodine used for sample - c.c. used for blank x .3408 equals p.p.m. of hydrogen sulphide.

Note : This method is for both free and combined hydrogen sulphide.

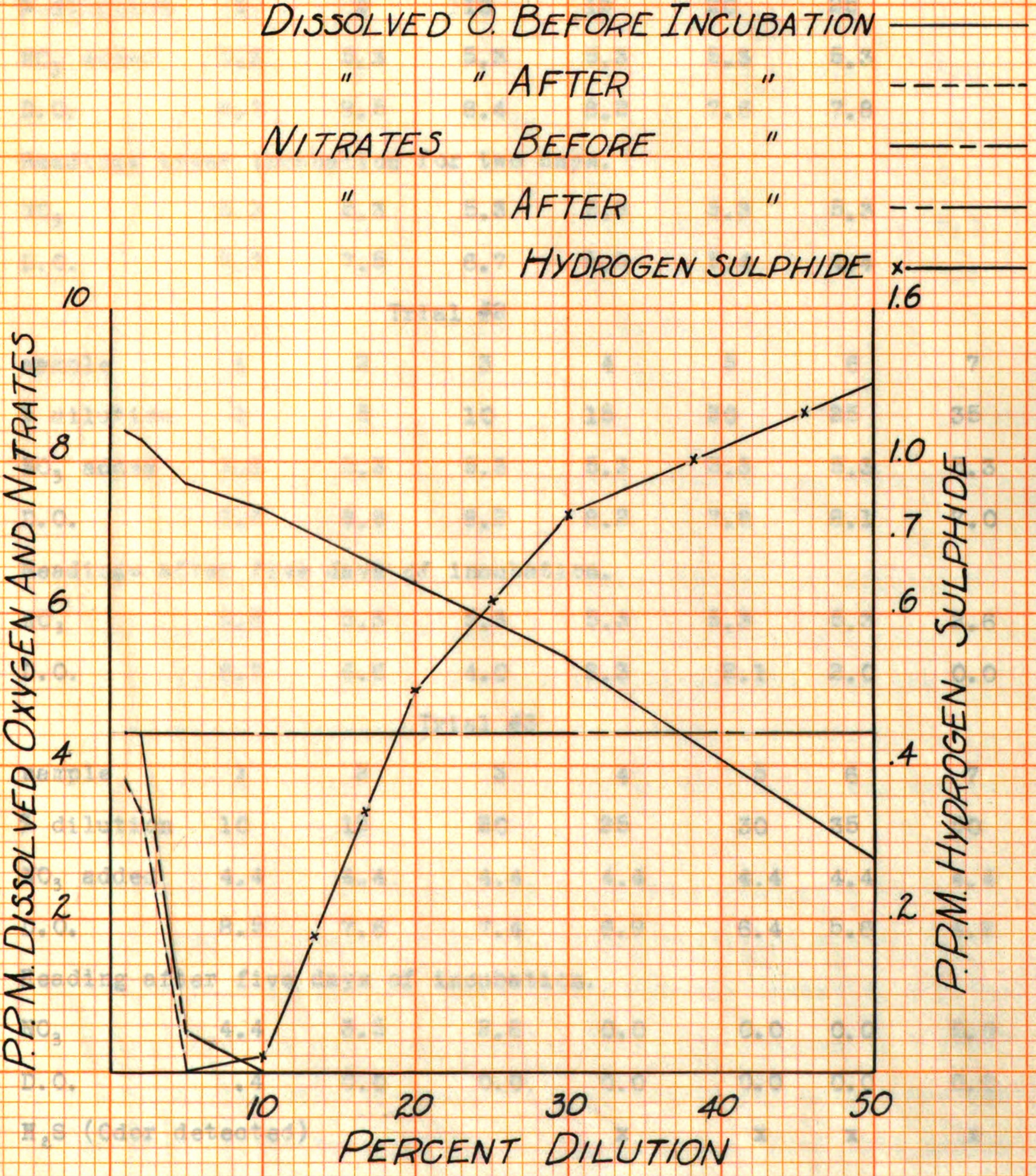
( Authors note. Inasmuch as the sample used was only two hundred c.c. the calculation factor was changed when computing the hydrogen sulphide content.)

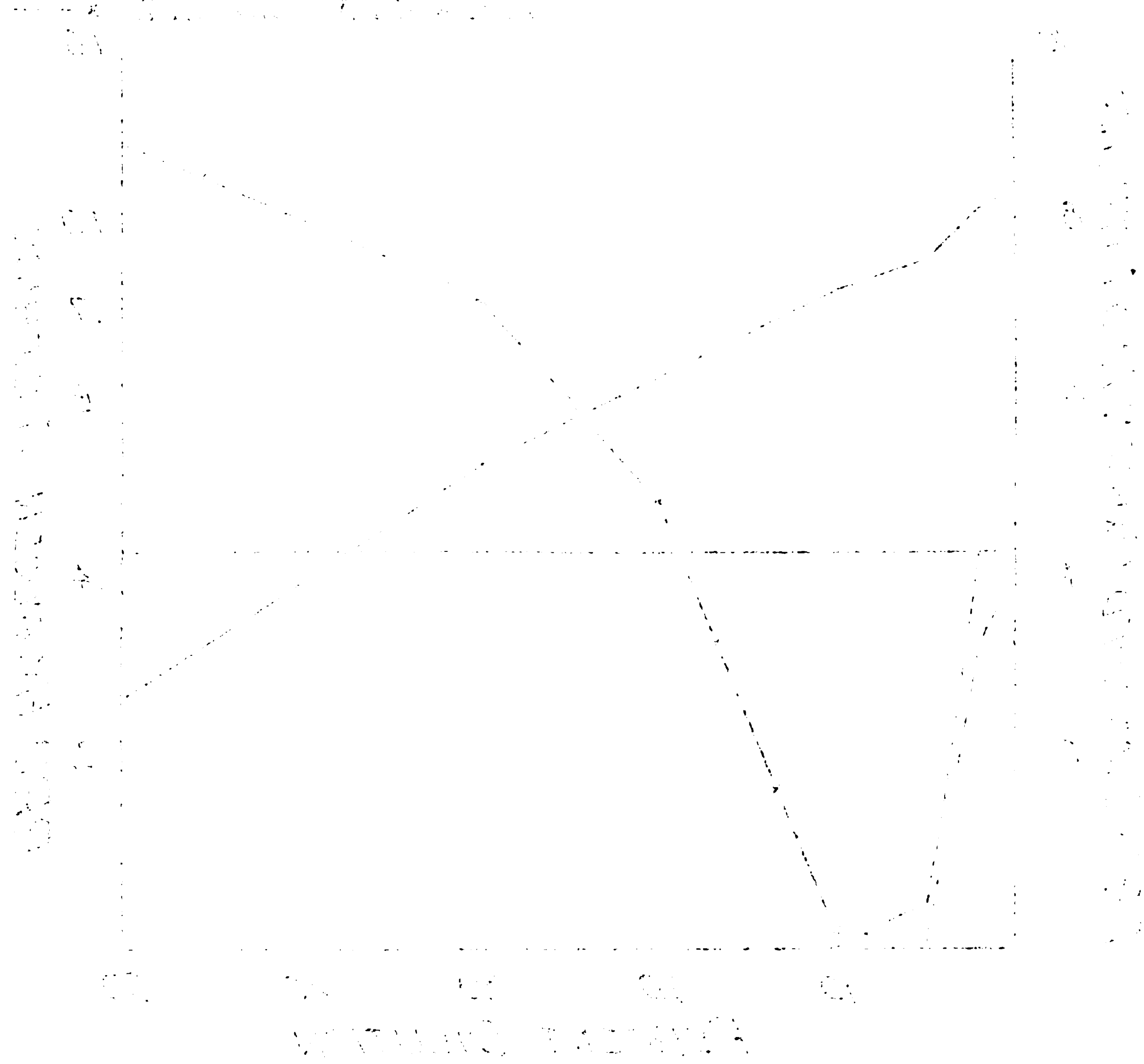
# UTILIZATION OF DISSOLVED OXYGEN AND NITRATES IN SEWAGE DILUTIONS INCUBATED FOR FIVE DAYS





# UTILIZATION OF DISSOLVED OXYGEN AND NITRATES ALSO PRODUCTION OF HYDROGEN SULPHIDE FROM SEWAGE DILUTIONS INCUBATED FOR FOUR DAYS





Data

Trial #1

| sample | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| % dilution | 1 | 5 | 10 | 15 | 20 | 25 |
| $NO_3$ added | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 |
| D.O. | 8.7 | 8.5 | 8.4 | 8.2 | 7.6 | 7.8 |
| Readings after incubation for two days. | | | | | | |
| $NO_3$ | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 |
| D.O. | 7.7 | 7.5 | 6.7 | 5.9 | 5.4 | 4.4 |

Trial #2

| sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| % dilution | 1 | 5 | 10 | 15 | 20 | 25 | 35 |
| $NO_3$ added | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 |
| D.O. | 8.6 | 8.6 | 8.2 | 8.2 | 7.8 | 8.1 | 7.0 |
| Readings after five days of incubation. | | | | | | | |
| $NO_3$ | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 5.3 | 2.6 |
| D.O. | 6.7 | 6.6 | 4.0 | 2.3 | 2.1 | 2.0 | 0.0 |

Trial #3

| sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| % dilution | 10 | 15 | 20 | 25 | 30 | 35 | 50 |
| $NO_3$ added | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 |
| D.O. | 8.5 | 7.6 | 7.4 | 6.9 | 6.4 | 5.6 | 4.2 |
| Reading after five days of incubation. | | | | | | | |
| $NO_3$ | 4.4 | 3.5 | 2.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| D.O. | .4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ (Odor detected) | | | | x | x | x | x |

Trial # 4

| sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| % dilution | 1 | 2 | 5 | 10 | 20 | 30 | 50 |
| $NO_3$ added | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 | 4.4 |
| D.O. | 8.4 | 8.3 | 7.7 | 7.4 | 6.4 | 5.2 | 2.8 |
| Reading after four days of incubation. | | | | | | | |
| $NO_3$ | 4.4 | 4.4 | 0.5 | 0.1 | 0.0 | 0.0 | 0.0 |
| D.O. | 3.8 | 3.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $H_2S$ | 0.0 | 0.0 | 0.0 | .2 | .5 | .8 | 1.3 |

Note all readings of D.O., $NO_3$ & $H_2S$ are in p.p.m.

See graphs for results of trials no. 3 & 4.

## Discussion of results

The data may be interpreted from the experimental data with the aid of the graphs as follows:

(1) All the dissolved oxygen was utilized before any reduction to the nitrates took place.

(2) Immediately after all the dissolved oxygen was used the nitrates were reduced.

(3) Immediately after all of the nitrates were utilized, septic conditions followed.

Inasmuch as all nitrates present in the sewage were in solution and not contained in suspended or settled solids there was no possibility for "localized anaerobic zones" to develop. This,therefore would not lead to false conclusions of supposing that the nitrates were utilized before any oxygen was used, as observed by Heukelekian, mentioned above. Also this proves that his assumption was correct concerning the fact that nitrates were not used prior to the use of dissolved oxygen as his data seemed to indicate.

Another point brought out by the experimental data, is that nitrates and dissolved oxygen must be utilized completely before the undesirable septic conditions will result. As a practical point this shows that all of the nitrates present in the effluent of a sewage plant will be utilized prior to the development of these conditions.

However, as it was pointed out in the data the nitrates are used after the dissolved oxygen is depleted and thus are unable to give up there potential oxygen until after the critical dissolved oxygen saturation point of about thirty percent has been reached, thus not aiding fish life.

The practice of using the dissolved oxygen content as an index of pollution is sound but it would not be exactly proper to use this test as an index of when septic conditions might be expected, but the nitrate test would show the true conditions. In general, the practical results might be summarized by stating that the presence of nitrates in a polluted stream will give up its oxygen supply to aid the prevention of anaerobic conditions but would not be available to aid in the protection of fish life.

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