CIVIL ENGINEERING STUDIES

SANITARY ENGINEERING SERIES NO. 13

THE EFFECT OF ORGANICS EXTRACTED FROM GROUND WATER ON THE RATE OF OXIDATION OF IRON

By
B. A. MARSH

Supported By
NDEA (TITLE IV) PROGRAM
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
and
DIVISION OF WATER SUPPLY AND POLLUTION CONTROL
U. S. PUBLIC HEALTH SERVICE
RESEARCH PROJECT WP-17

DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
OCTOBER, 1962

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Department of Civil Engineering
University of Illinois
Urbana, Illinois

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ABSTRACT

In many communities throughout central Illinois, water treatment plants experience difficulty in reducing the iron content of their finished water to within the U. S. Public Health Service Drinking Water Standards of 0.3 mg/l.

Many investigators have associated iron removal difficulties with the presence of organic matter in the raw water. The organic matter is believed to form "chelates" or "complexes" with iron which keep the iron in solution and, thus, prevent precipitation of iron during treatment.

The purpose of this study was to determine the effect, if any, of a series of organic extracts on the oxidation rate of iron and on the rate of change of soluble iron to the insoluble form. To do this, field studies were made at Atwood and Clinton, Illinois.

The extracts used were secured by Lloyd R. Robinson, Research Assistant, using an acidified and unacidified carbon filter arrangement. The extracts were prepared in solutions of one milligram of organic matter per milliliter. Each extract was added to raw water, with a few exceptions, in a concentration of 5 mg/l. Composite samples were also prepared, using the extracts in approximate proportions to the concentrations in which they were extracted from the raw water. These were added to the raw water in concentrations of 5 mg/l and 25 mg/l. One extract which was found to have a chelation effect in laboratory experiments was added to raw water in a concentration of 50 mg/l.

In addition to the extracts, two other compounds, ammonium chloride and tartaric acid, were used. The ammonium chloride was used because it was suspected that some of the extracts contained large amounts of this

compound. The tartaric acid was used since it is known to be a good chelator of iron.

The bathophenanathroline procedure was used to determine ferrous iron and the orthophenanthroline procedure was used to determine total iron. A radioactive tracer, Iron - 59, was used, with a membrane filter arrangement, to measure the rate of change of soluble iron to the insoluble form.

The results of this study indicate that following aeration, these extracts increased the oxidation rate and the rate of change of soluble iron to insoluble iron. The only significant retardation in the rate occurred when the extract solution added lowered the pH. Of significant interest, also, was the fact that the tracer study, which measured soluble iron, consistently showed a greater rate of conversion to insoluble iron than the bathophenanthroline study, which measured the rate of conversion of ferrous iron to ferric iron. This suggests that some of the soluble ferrous iron can be filtered out, possibly by adsorption on previously precipitated iron.

ACKNOWLEDGMENTS

The author wishes to acknowledge the financial support received through a Graduate Fellowship, National Defense Education Act, Title IV, Department of Health, Education and Welfare. Much of the equipment and materials used in the experimental work was provided by Research Grant WP-17, Division of Water Supply and Pollution Control, U. S. Public Health Service, entitled "Fundamental Factors in Treatment of Iron Bearing Waters."

The author also wishes to take this opportunity to express his thanks to Dr. R. S. Engelbrecht, adviser, and Dr. J. T. O'Connor for the assistance, encouragement, and guidance, without which this work could not have been satisfactorily accomplished.

The help of Mr. L. R. Robinson and Mr. M. M. Ghosh is also gratefully appreciated, as is the assistance and cooperation of the water treatment plant operators of the water plants where the samples were collected.

Special thanks also go to the author's wife, Dolores, for the many long hours spent proofreading and typing this manuscript.

This report was submitted as a thesis in partial fulfillment of the requirement for the degree of Master of Science in Sanitary Engineering under the direction of Dr. R. S. Engelbrecht, Professor of Sanitary Engineering.

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I. INTRODUCTION

A. Nature and Importance of the Problem

The presence of iron in water supplies has been a source of many problems. These problems are world-wide, but they vary in magnitude and with locality. In the United States, and particularly in the central states where deep wells are the source of water for many communities, the problems are especially acute. For example, in Illinois, 70 per cent of the public water supplies contain iron in excess of the United States Public Health Service limit of 0.3 mg/l. Current data indicates that one-third of the plants supplying this water are not reducing the iron content to a satisfactory level.[3]

According to Weston[11] the first attempt at deferrization, or removal of iron from water, was made in Germany in 1868. Despite the antiquity of the subject, there is still considerable difference of opinion and uncertainty about the factors which affect the presence of iron in water and its removal.[2,4]

Technical literature, during the past half century, has contained many publications dealing with the problem of iron removal from water supplies. Most of them have been case histories of treating difficult waters or descriptions of unique treatment plants. As a result, a number of unit processes and combinations of these processes have been reported as effective in the removal of iron from water supplies.[6]

There is still a great need for information about the ability of certain substances in water which exert a "chelating" or "complexing" effect on iron. It is these substances, including organics, which are generally believed to interfere to a large extent with the usual iron removal processes.[4]

In different iron-bearing natural water supplies, the ferrous ion may be present in association with one or more of the following: (a) bicarbonates; (b) sulfates; (c) organics.

Waters containing chelated iron generally are surface waters, but some shallow wells and, occasionally, deep wells will yield highly colored waters containing iron in a chelated form.[7]

Reports indicate that iron in a chelated form is either not precipitated or only partially precipitated by aeration even when the pH is raised above 10. Nor is it removed in passing through a zeolite filter. One well water with a color of 35 and an iron content of 3.5 mg/l had less than one mg/l of iron removed by aeration, lime treatment, settling, and filtration. Another water with a color of 450 and an iron content of 12 mg/l showed no iron removal after aeration, lime treatment, and a 5-day detention time.[7,8]

There are many conflicting theories concerning the effect of organic compounds on the oxidation and removal of iron. Stumm and Lee[10] maintain that, generally, most organic impurities are known to hasten the oxidation reaction, but under such conditions the iron removal is very slow.

Applebaum[1,2] and Nordell[7,8] report that organic matter in iron-bearing waters inhibits and slows down the oxidation reaction. Such organics must be removed by prechlorination or special coagulants before filtration.

Weston, in his review of iron removal practices in 1909, speaks of organic matter or humus in water and its effect on iron removal as follows:

> "Humus is the active principle of leaf-mould, and the name has been given to a mixture of various substances of indefinite composition which have resulted from the decomposition of organic matter in the partial or complete absence of oxygen. It is necessary to distinguish the main classes of humus matter from one another. Even in recent literature, statements have been made which show a lack of appreciation of any difference in humus compounds. Some of these are albumins; some are gums; some are organic acids; some are acids in combination with calcium, manganese, iron, etc.; some combine with iron to form a brown-colored compound. From a water purification standpoint, however, there are three classes, those in solution, those in colloidal solution, and those in colloidal suspension.
>
> The first class probably affects the deferrization process but little. Not much is known of this class, and their existence is doubted by many chemists. They may impart taste or odor to a water, which can be removed by aeration, ozonation, or absorption.
>
> The second class, humus matter in colloidal solution, is a great hindrance to the precipitation of iron. These gelatinous or gummy bodies are not precipitated by aeration. They remain in solution until absorbed by suspended matter or by the action of filtering material, or until they are destroyed by bacterial action. What is worse, a small amount of these gelatinous bodies will hinder the precipitation of a larger amount of iron. They are more apt to be present in seepage water from near the surface than in the dark brown water from deep wells, leading one to believe that the more recent the decomposition of organic matter, the larger will be the proportion of these humus bodies in colloidal solution. They yield readily to treatment with ozone.
>
> The third class, humus matter in colloidal suspension, is easily removed by sand filtration."[11]

The only conclusion that can be drawn from the foregoing observations is that the presence of organic probably affects the oxidation and/or the removal of iron from water.

B. Theoretical Considerations

Ground waters are normally devoid of oxygen and supersaturated with carbon dioxide. When water containing carbon dioxide is aerated, the carbon dioxide is driven off. When this happens, the pH of the water increases and oxygen is dissolved in the water. In the presence of dissolved oxygen, any ferrous ions present will begin to oxidize to ferric ions and precipitate as the hydroxide.

The ferrous ion found in natural water may be thought of as ferrous bicarbonate. The oxidation reaction of this compound is as follows:

$$4\ Fe(HCO_3)_2 + O_2 + 2\ H_2O \longrightarrow 4\ Fe(OH)_3 + 8\ CO_2$$

Ferric hydroxide is insoluble and, thus, is precipitated. If there is nothing present in the water to interfere with this reaction, it will proceed as shown.

In waters containing organic matter, some of the ferrous ions may be found in a chelated or complexed form. It is believed that, when this occurs, the ferrous ion is in association with two organic anions. The ferric chelate is thought to be a more stable form than the ferrous chelate; and, in the presence of dissolved oxygen, the ferrous ion is oxidized to the ferric ion, which becomes associated with one more organic anion. The ferric chelate or complex is believed to be soluble and, therefore, will not precipitate.

As previously stated, there are some people who believe that the presence of organics in water will hinder the oxidation reaction, while others believe that organics actually enhance this reaction.

C. Purpose of the Study

The purpose of this study can be divided into two parts.

1. When iron is found in waters from deep wells, it is in the ferrous or reduced state due to the absence of dissolved oxygen. Upon aeration, the ferrous oxidizes to the ferric state if there is nothing present to inhibit this oxidation.

Therefore, the primary purpose of this study is to determine the effect, if any, of organic matter on the rate of oxidation of iron. It is desired to know if the organic matter affects this oxidation rate or if, instead, it actually affects the rate of change of soluble iron to the insoluble form.

2. The second part of this study is a comparison of the rate of oxidation of ferrous ions to ferric ions and the rate of conversion of soluble iron to insoluble iron. The analytical techniques employed were:

a. the bathophenanthroline procedure for ferrous iron determination;

b. a radioactive iron tracer, Iron - 59, was used to follow the rate of change of soluble to insoluble iron. By counting the gamma radiations, after filtration of the samples, an indication of the amount of soluble iron present could be obtained. The sensitivity of the tracer allowed the rate of iron removal to be followed well below the limits of bathophenanthroline sensitivity.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Preparation of Organic Compounds

The organic compounds used in this study were prepared from a series of organic compounds extracted from the water supplies of four central Illinois municipalities. These municipalities were Atwood, Clinton, Oakwood, and Philo. Two of these, Atwood and Clinton, were chosen for field study. The Oakwood water has an extremely rapid oxidation rate, while at Philo the iron content was very low. Also, at Philo the organic content was very low and, consequently, the amount extracted was very low.

The organic extracts were secured by Lloyd R. Robinson,[9] using the carbon filter technique. The water was run through an unacidified filter and an acidified filter in series, at the rate of 1 gallon per minute. The filters were then subjected to a series of solvent extractions to remove the adsorbed organics. The solvents used in these extractions were: (a) water; (b) ethyl alcohol; (c) ethyl alcohol and hydrochloric acid; (d) ethyl alcohol and ammonia; and (e) chloroform. The extracts were then dried to remove the solvents. The organics obtained were given and will be hereinafter referred to by the following designations:

Unacidified Filter	Acidified Filter
H_2O - A	H_2O - B
ETOH - A	ETOH - B
ETOH + HCl - A	ETOH + HCl - B
ETOH + NH_3 - A	ETOH + NH_3 - B
CHLORO - A	CHLORO - B

For purposes of this study, these dried extracts were dissolved as completely as possible in distilled water by prolonged stirring on a magnetic stirrer. The solutions were so prepared as to contain one

milligram of organic per milliliter. Some difficulty was experienced in dissolving the ETOH + HCl and the CHLORO extracts in pure distilled water.

One sample of the ETOH + HCl extract was dissolved as completely as possible in distilled water. Another was partially dissolved in a small amount of reagent grade HCl and diluted to 100 ml with distilled water. This was then stirred and the organic was completely dissolved. The result of the use of HCl was that the pH of that sample was approximately 1.2, as compared to a pH of 3 to 4 of the other samples. The sample which was dissolved in distilled water is designated as ETOH + HCl - A_1.

The CHLORO - B extract was dissolved in 10 ml of 0.2 N KCl and 10 ml of an organic solvent, Dioxane. The sample was then made up to 100 ml with distilled water. It was necessary to dissolve the CHLORO - A extract in a solution containing 50 per cent 0.2 N KCl and 50 per cent Dioxane.

All of the extract preparations mentioned thus far were used in field studies carried out at Atwood and Clinton, Illinois, with one exception. That exception was that there was no H_2O - A extract used with the Clinton water. All of these preparations were added in concentrations of 5 mg/l. Thus, for 8 liters of water, 40 ml of extract preparation were added.

Two composite samples of organic matter were also prepared for each study, using each extract in proportions approximating those in which they were extracted from the carbon. Those samples were given the designations of COMPOSITE - 1 and COMPOSITE - 2 and were added to the water in concentrations of 5 mg/l and 25 mg/l, respectively. The approximate concentration of organics in Atwood raw water is 10 mg/l and that in Clinton raw water is 12 mg/l.

In addition to the extracts, two other compounds, ammonium chloride and tartaric acid, were used in the field studies at Clinton, Illinois. The ammonium chloride was used because it was found that the ETOH + HCl extracts contained over 75 per cent of this compound, and it was desired to know the effect of this in pure form.

The tartaric acid was used since it is known to be a good chelator of iron. For this reason, it was desired to know the effect it would have on the oxidation rate. Both the tartaric acid and the ammonium chloride were added in concentrations of 5 mg/l.

Also, at Clinton an experiment was made using 50 mg/l of the ETOH + NH_3 - B extract. This was designated as ETOH + NH_3 - B_1. The reason for using this was that Lloyd Robinson[9] found this extract to be a strong chelator in laboratory investigations conducted in the Sanitary Engineering Laboratory at the University of Illinois.

B. Iron Determinations

1. Sampling Technique

The samples were collected directly from the well, while the pump was in operation.

The procedure used was as follows:

a. A battery jar with a capacity of approximately 9 liters was completely filled with the raw water and covered.

b. Two samples, a 10 ml and a 25 ml, were taken simultaneously for ferrous iron and total iron determinations, respectively.

c. The pH was taken by means of electrodes inserted in rubber stoppers in the cover of the jar.

d. The jar was then drained to the 8 liter level in the experiment on the raw water. When the organics were added, the volume was reduced to allow the final volume to be 8 liters.

e. The sample was aerated for 2 minutes at 8,000 cubic centimeters per minute by means of an air compressor and a carborundum air diffuser.

f. Immediately after aeration, a sample was taken for ferrous iron determination and the pH was recorded.

g. 500 ml was then taken from the battery jar for the tracer study and, also, a sample was taken for dissolved oxygen determination.

h. At the same time that the tracer was added, a sample was taken for ferrous determination and a sample was also taken for total iron determination. The sample taken for total iron was filtered so as to indicate the amount of soluble iron at that instant. This sample then became the reference point for the tracer study.

2. Ferrous Iron Determination by Bathophenanthroline

The determination of ferrous iron using bathophenanthroline (4,7 - diphenyl - 1,10 - phenanthroline) was that outlined by Lee and Stumm,[5] with some minor variations. Some small variations were also made in the recommended reagents. The detailed procedure is given in Appendix A.

3. Total Iron Determination by Orthophenanthroline

The determination of total iron by orthophenanthroline*[1] (1,10 - phenanthroline) was as outlined in the 11th Edition of Standard Methods,[9] with minor modifications. The detailed procedure is given in Appendix A.

4. Soluble Iron Determination

The method used in determining soluble iron employed an isotope of iron, Iron - 59, as a tracer.

In the tracer study, 500 ml of the test sample was taken from the battery jar immediately after aeration, and placed in an 800 ml beaker. The beaker was placed on a magnetic stirrer and, with the stirrer in operation, 5 drops of the tracer solution were added with a dropper. This amount of tracer was chosen since it would give a count rate of between 1700 and 2000 counts per minute on a Gamma Scintillation Counter.*[2]

The sample was then flash mixed for one minute. Immediately after mixing, a 10 ml sample was taken. This was placed without filtering in a plastic counting tube. The count rate of this sample would represent the total amount of soluble iron present at the time the tracer was added.

---

*1 Both bathophenanthroline and orthophenanthroline are products of the G. Frederick Smith Chemical Company, Columbus, Ohio.

*2 Nuclear Measurements Corporation, Minneapolis, Minnesota. This model has a two-inch, well-type sodium iodide crystal.

One minute after the mixing was completed, another 10 ml sample was taken. This sample was vacuum filtered through a 0.22 micron filter*3 into a plastic counting tube. From this point, the samples were taken and filtered at various intervals for 60 to 90 minutes. All pipetting of radioactive materials was done with a 10 ml volumetric pipette equipped with a rubber pipetter bulb.

The counting tubes were then taken to the laboratory where they were counted in the Gamma Scintillation Counter.

---

*3 A cellulose nitrate filter manufactured by Millipore Filter Corporation, New Bedford, Massachusetts.

III. EXPERIMENTAL RESULTS

A. Effect of Organics on Iron Oxidation Rate

The results obtained in this study are given in both tabular and graphical form. The tables are contained in Appendix B, while the figures plotted from the data in the tables appear in the text.

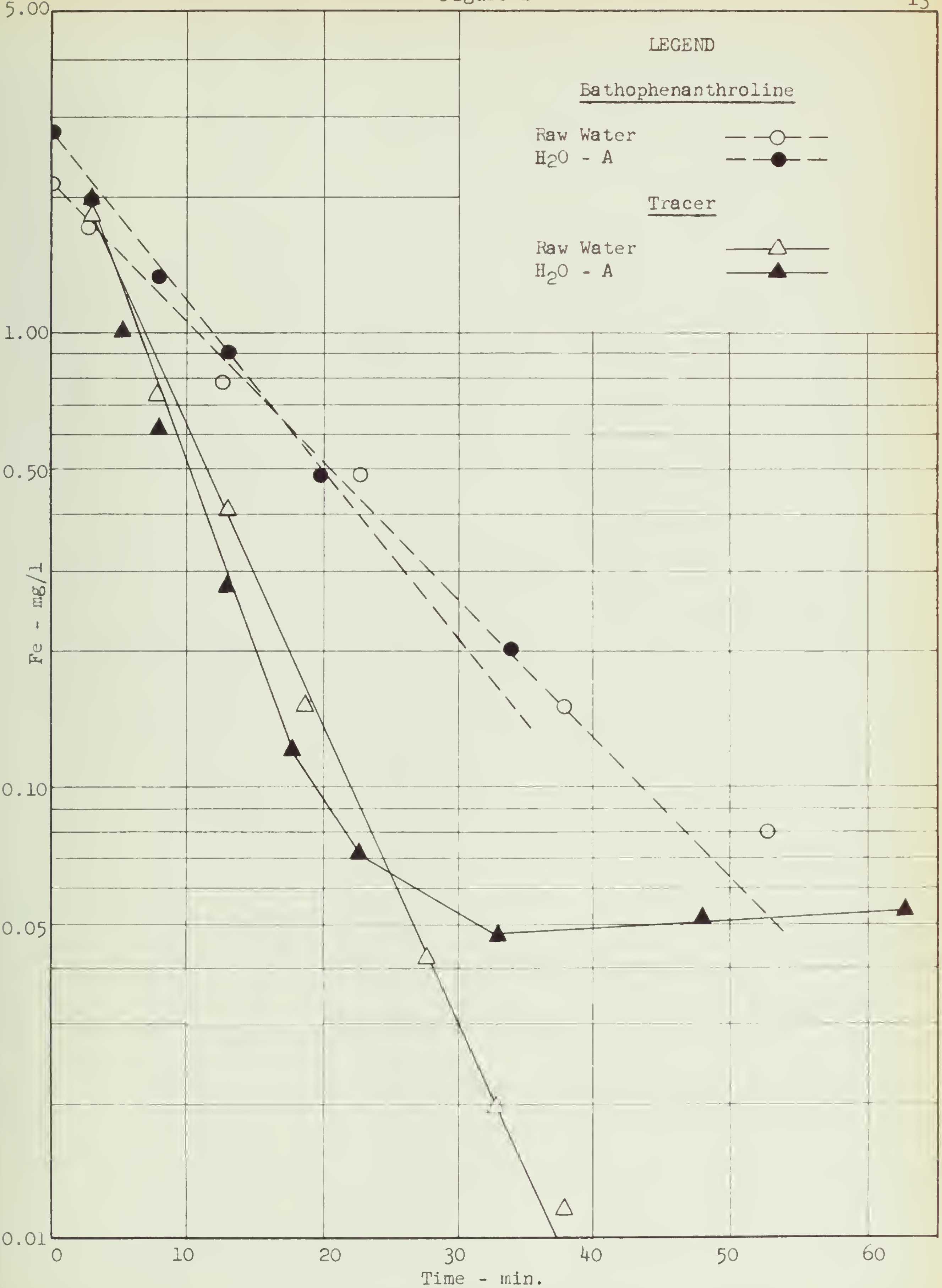
The curves obtained for the rate of oxidation of ferrous iron by bathophenanthroline are shown as dashed lines, while those for the conversion of soluble to insoluble iron as obtained by the tracer study are shown as solid lines.

The reference point for the tracer study was from a sample taken at the instant the tracer was added. This sample was filtered immediately and analyzed for total iron. This gave the soluble iron present at the time the tracer was added. In three or four instances, the orthophenanthroline analysis for total iron gave a result of zero or considerably less than the ferrous iron indicated by the bathophenanthroline determination. Whenever this occurred, the bathophenanthroline value was taken since there must have been at least that amount of soluble iron present.

The oxidation rate of iron in the raw waters of Atwood and Clinton is shown on Figures 1 and 3. The oxidation rate in raw water is reproduced on each graph for ease of comparison with the curves for waters containing added organic extracts.

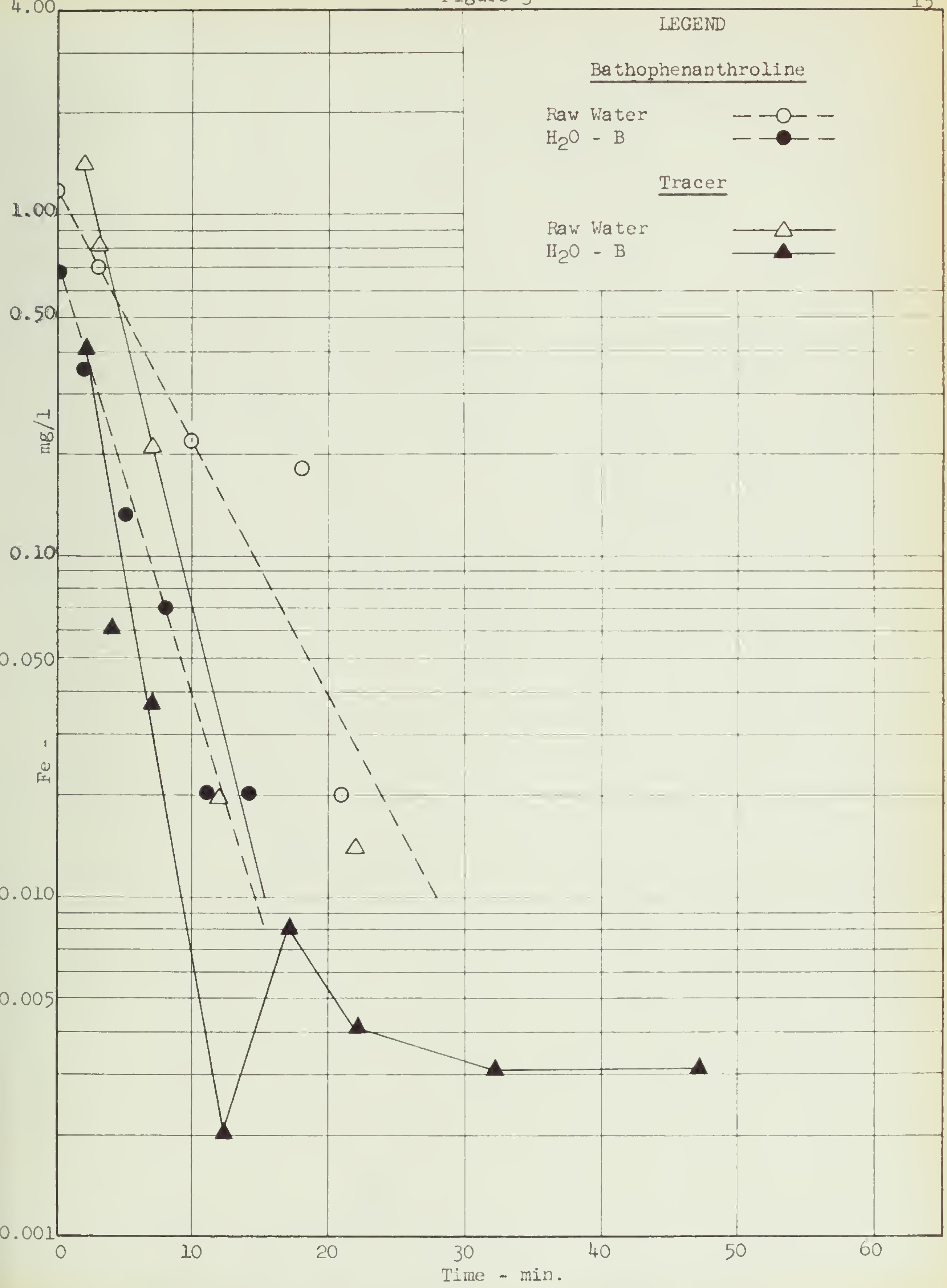
Figure 1 shows that H_2O - A extract has no appreciable effect on the oxidation rate. It should be noted, however, that the tracer curve begins to flatten out after 25 minutes. This occurs at about 0.05 mg/l of soluble iron. This is an indication that some small amount of iron might remain in solution.

Figure 1



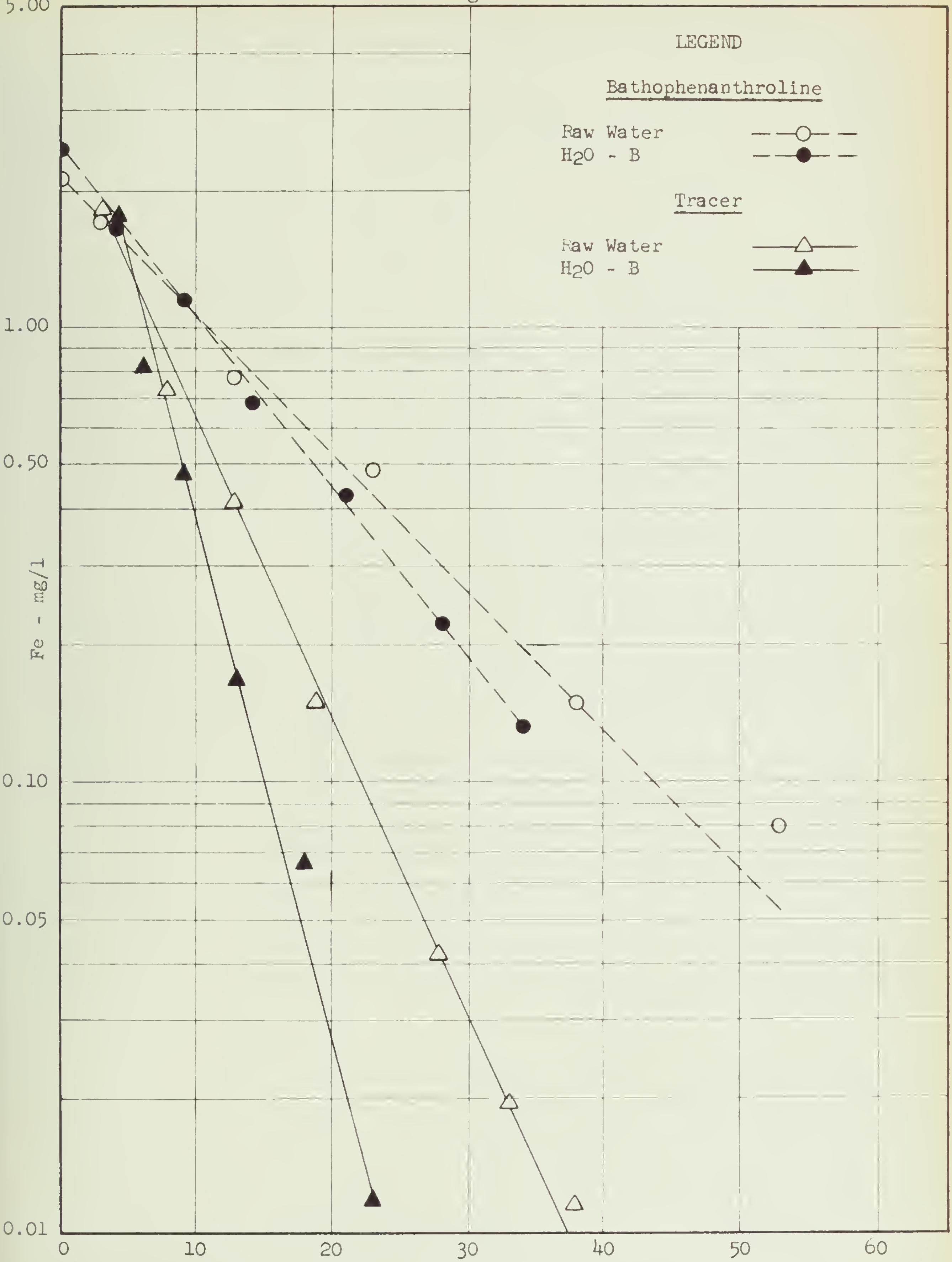
COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD H_2O - A EXTRACT ADDED

Figure 3



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD H_2O - B EXTRACT ADDED

Figure 2



COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD H_2O - B EXTRACT ADDED

It may be assumed that this represents chelated iron, but it is safe to say that it is of small consequence since it is well below the U. S. Public Health Service Drinking Water Standards of 0.3 mg/l.

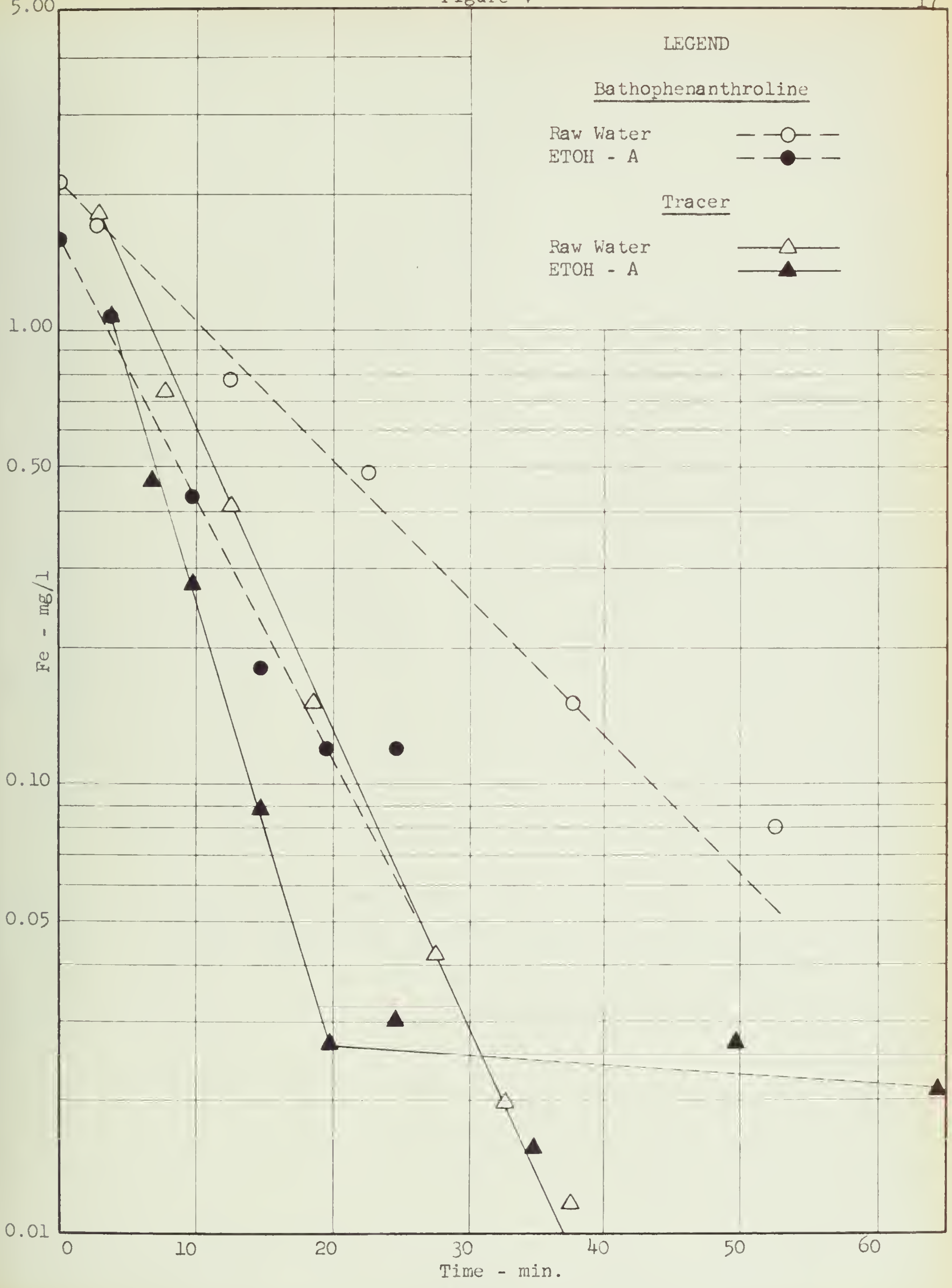
There was no H_2O - A extract for Clinton.

The addition of the H_2O - B extracts has little effect on the iron oxidation rate as shown in Figures 2 and 3. There is a slight difference in the bathophenanthroline curves for Clinton, however, with the H_2O - B extract increasing the oxidation rate by a small amount. The leveling-out effect is noticed again in the tracer curve for Clinton H_2O - B extract. This occurs at a very low concentration; about 0.003 mg/l where the limit of analytical sensitivity is approached. This is well below the bathophenanthroline sensitivity.

The effect of the addition of the ETOH - A on Atwood water is quite apparent from the bathophenanthroline curves shown in Figure 4. The organic additive had a definite accelerating effect on the oxidation rate. This difference is not quite so pronounced in the tracer curves, indicating that the rate of change of soluble iron to insoluble iron was less affected by the organic extract than was the rate of oxidation. A leveling-out effect is shown again by the tracer curves. For Atwood, this occurs at about 0.025 mg/l of soluble iron. For Clinton, this occurs at a concentration of about 0.009 mg/l.

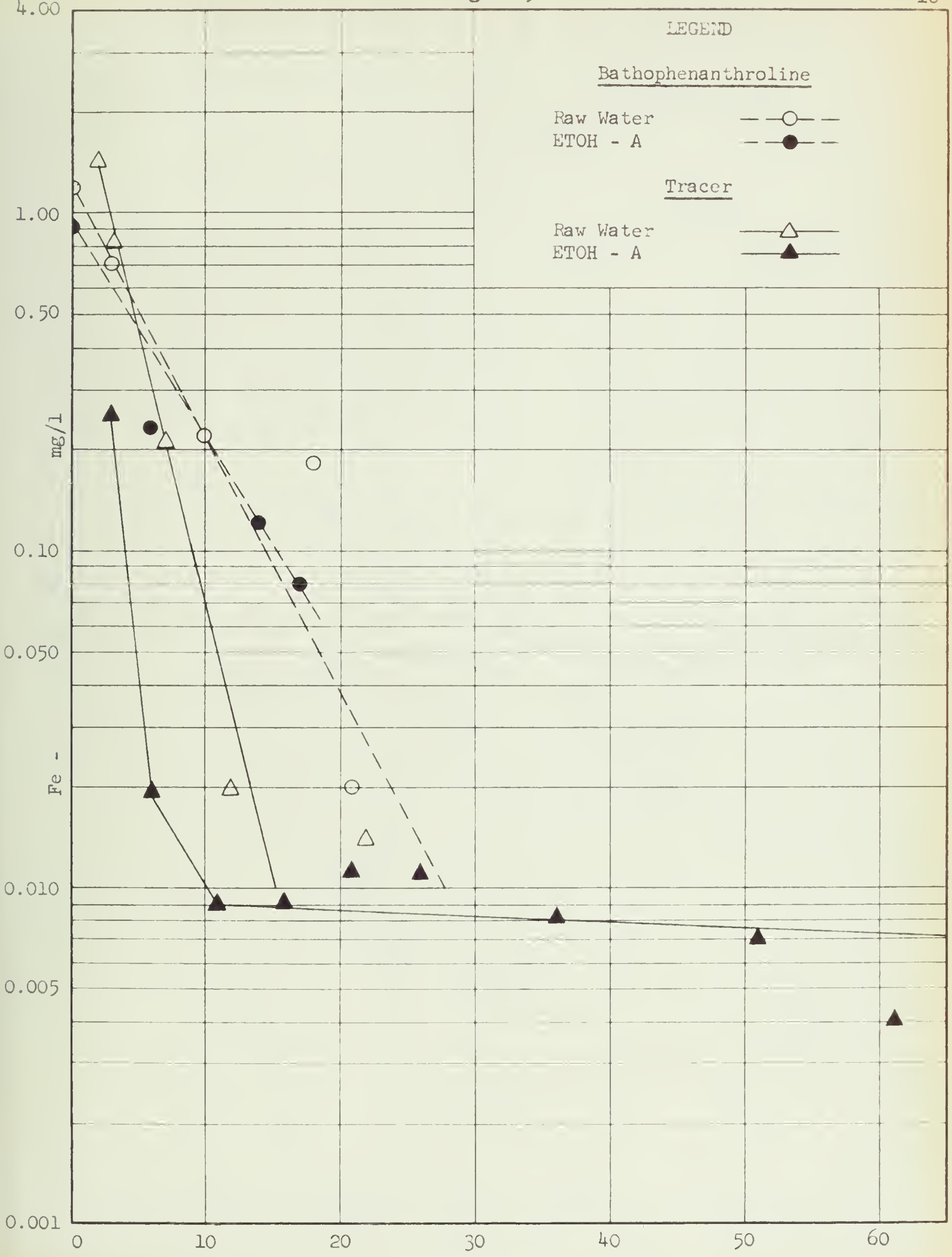
Figures 6 and 7 compare the oxidation rates in raw water and in water in which ETOH - B extracts are added. The curves are nearly identical with those for the ETOH - A extracts. The leveling off of the tracer curves occurs at almost exactly the same place. It is possible that these two extracts contain the same organic constituents.

Figure 4



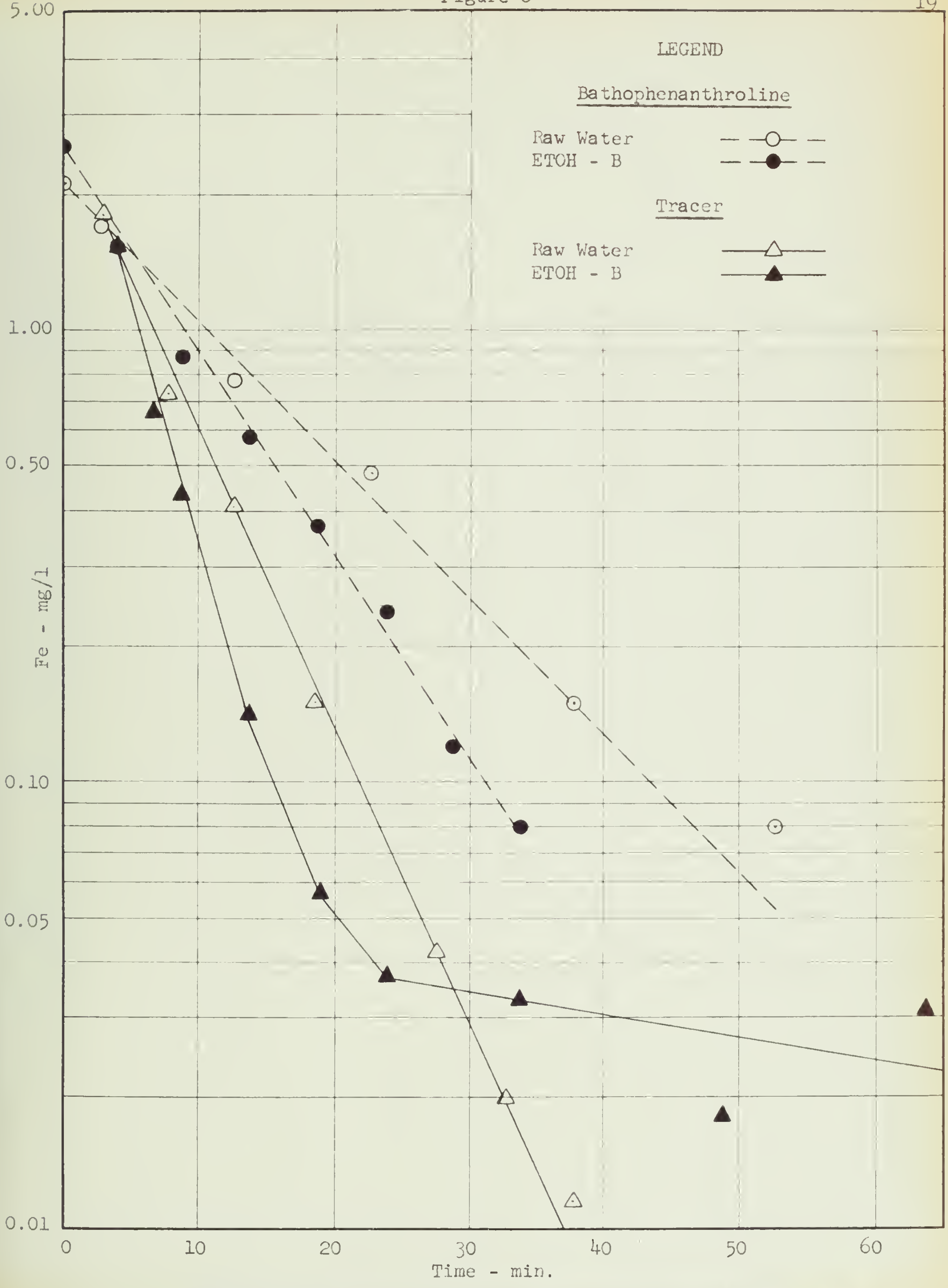
COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD ETOH - A EXTRACT ADDED

Figure 5



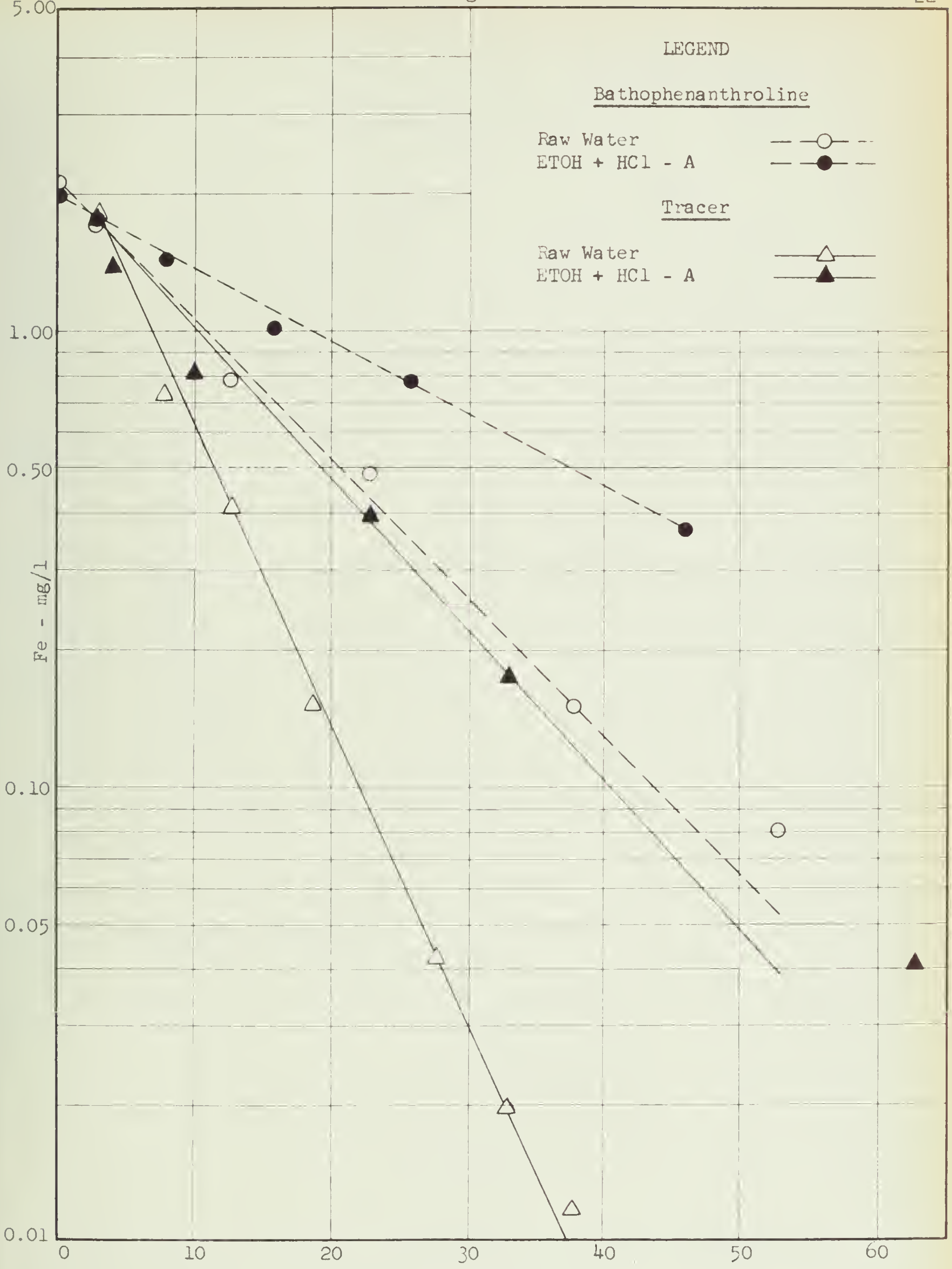
COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD ETOH - A EXTRACT ADDED

Figure 6



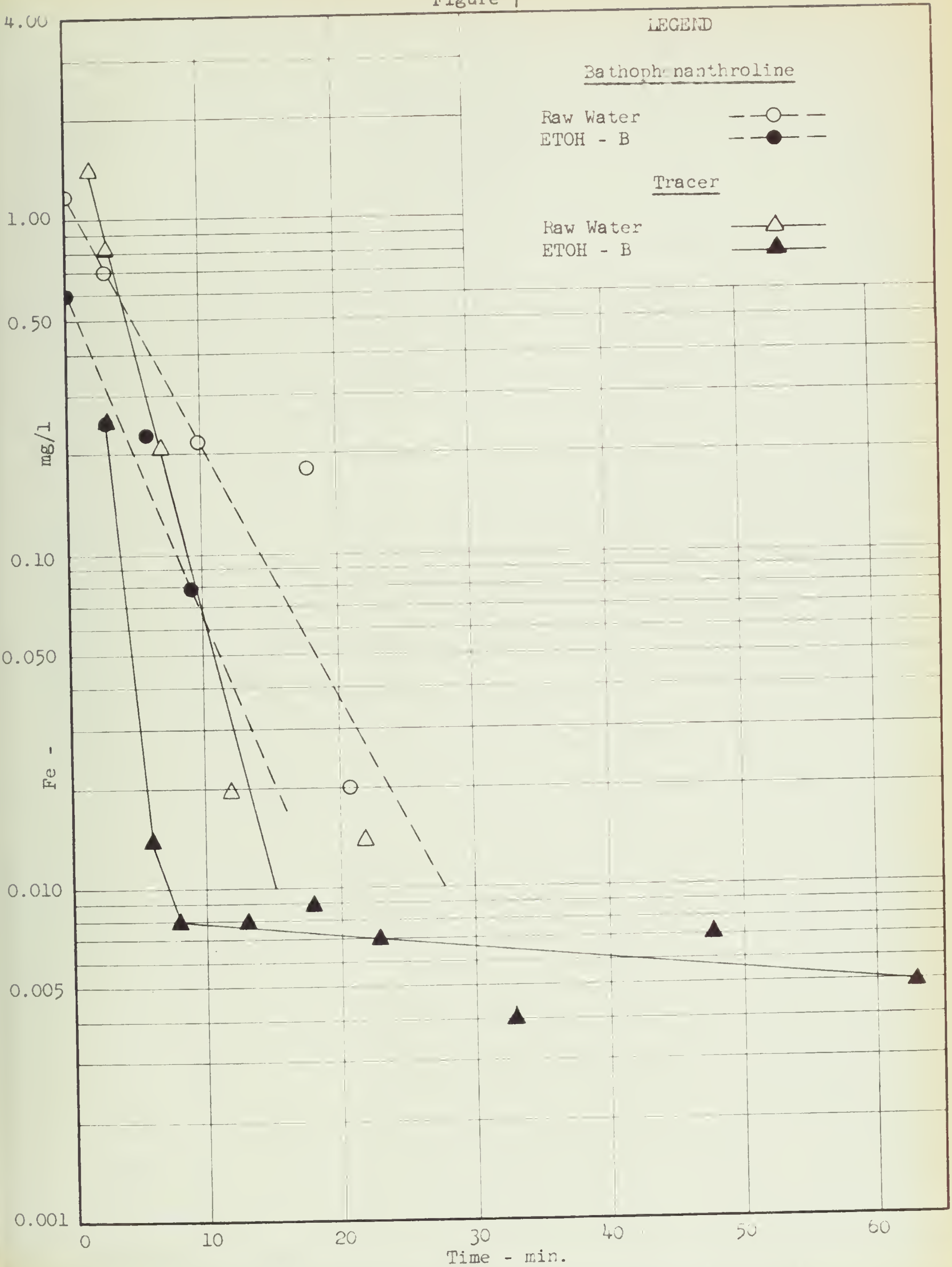
COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD ETOH - B EXTRACT ADDED

Figure 8



COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD ETOH + HCl - A EXTRACT ADDED

Figure 7



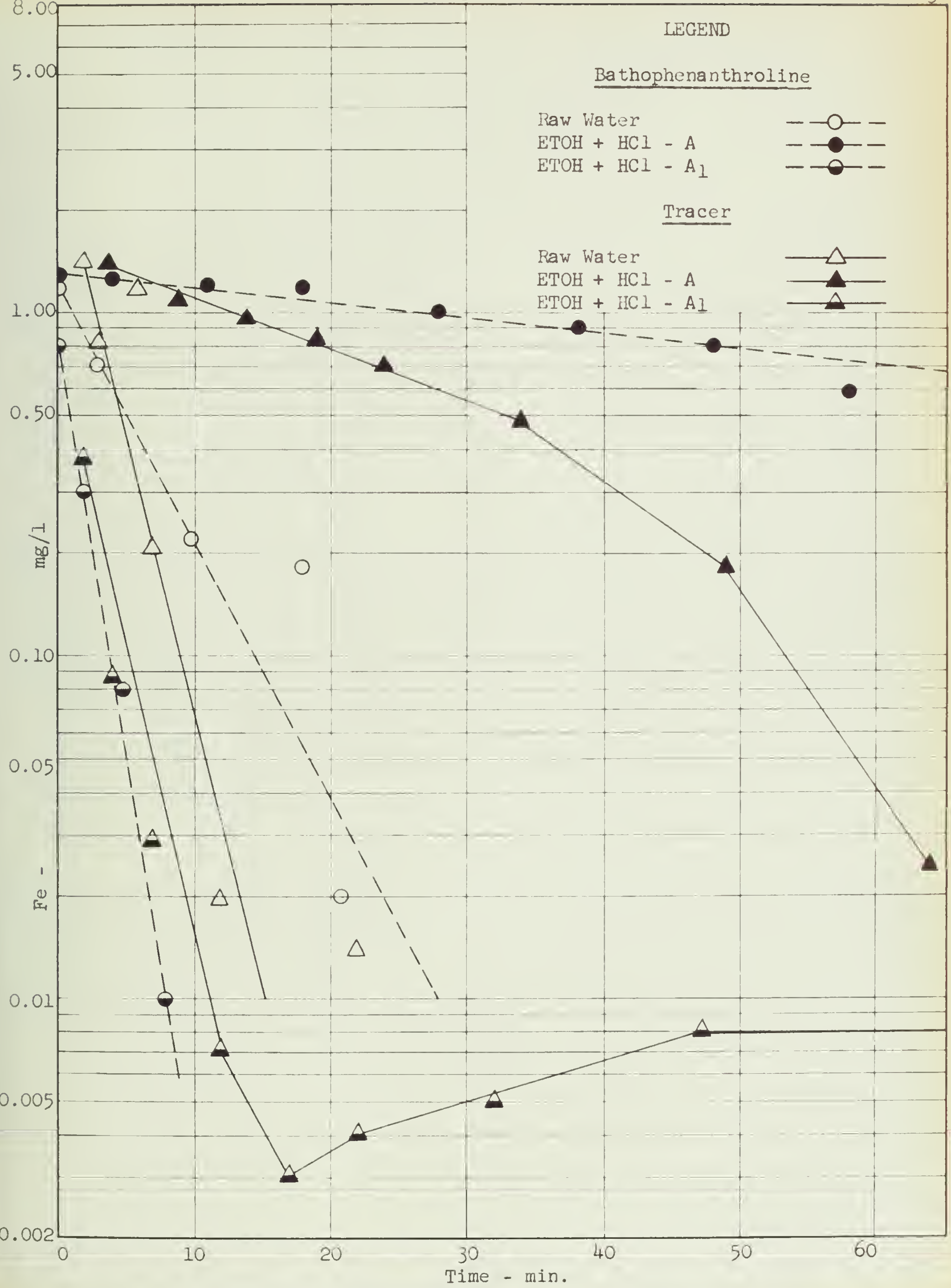
COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD ETOH - B EXTRACT ADDED

A very significant retardation of iron oxidation due to the ETOH + HCl - A extract is seen from Figure 8. This extract was dissolved in approximately 2 ml HCl and diluted to 100 ml with distilled water. The pH of the extract solution was about 2. The retarding effect is most likely due to the low pH value attained after aeration. In most of the other experiments, pH values increased during aeration by 0.4 to 0.6 units above the initial pH. In this test, a gain in pH of only 0.2 of a unit was achieved after aeration.

The difference in oxidation rates due to pH is clearly demonstrated in Figure 9. The two extracts shown on this graph are ETOH + HCl - A and ETOH + HCl - A_1. The former was made with 5 ml HCl and 95 ml distilled water. It had a pH of 1.12. The latter was made with distilled water only. The pH of this solution was 3.0. When the ETOH + HCl - A_1 extract was added and the sample aerated, the pH increased as it had with all the previous extracts. The effect was to enhance oxidation slightly. In contrast to this, when the ETOH + HCl - A was added and the sample aerated, the pH dropped from 7.20 to 6.85. The effect of this was to reduce the rate of oxidation substantially. This is shown clearly by both the bathophenanthroline curves and the tracer curves. The tracer curve for ETOH + HCl - A_1 exhibits a tendency to level off at about 0.005 mg/l.

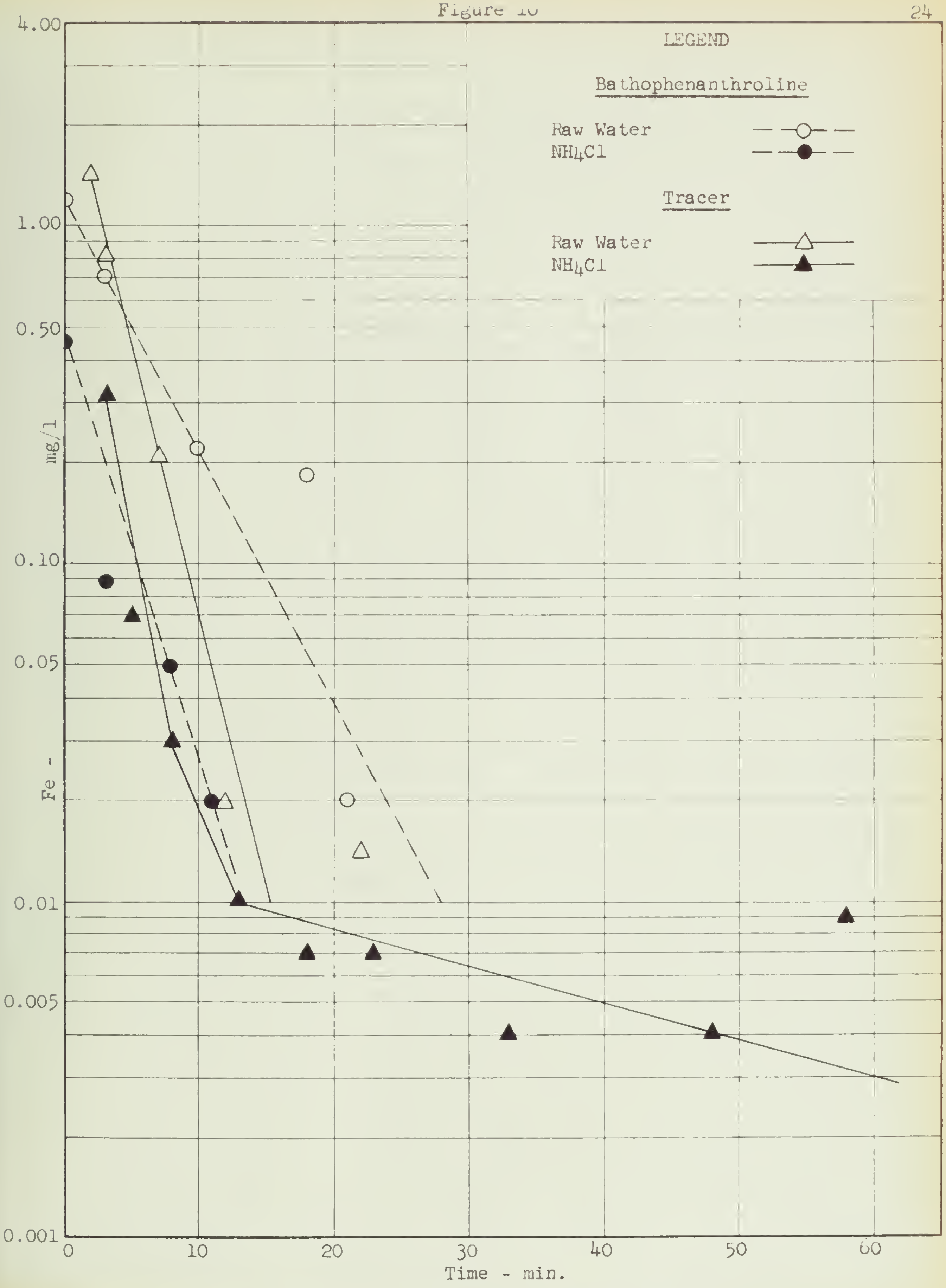
Figure 10 is the plot of the experiment using ammonium chloride. As explained previously, it was suspected that the ETOH + HCl extracts were at least 75 per cent ammonium chloride. As expected, the results of this test were very similar to those obtained in the experiment using the ETOH + HCl - A_1 which was made up with only distilled water. The tracer curve shows a tendency to level off at approximately the same place as that for the ETOH + HCl - A_1, also.

Figure 9



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THOSE WHICH HAVE HAD ETOH + HCl - A and ETOH + HCl - A_1 EXTRACTS ADDED

Figure 10



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD NH_4Cl EXTRACT ADDED

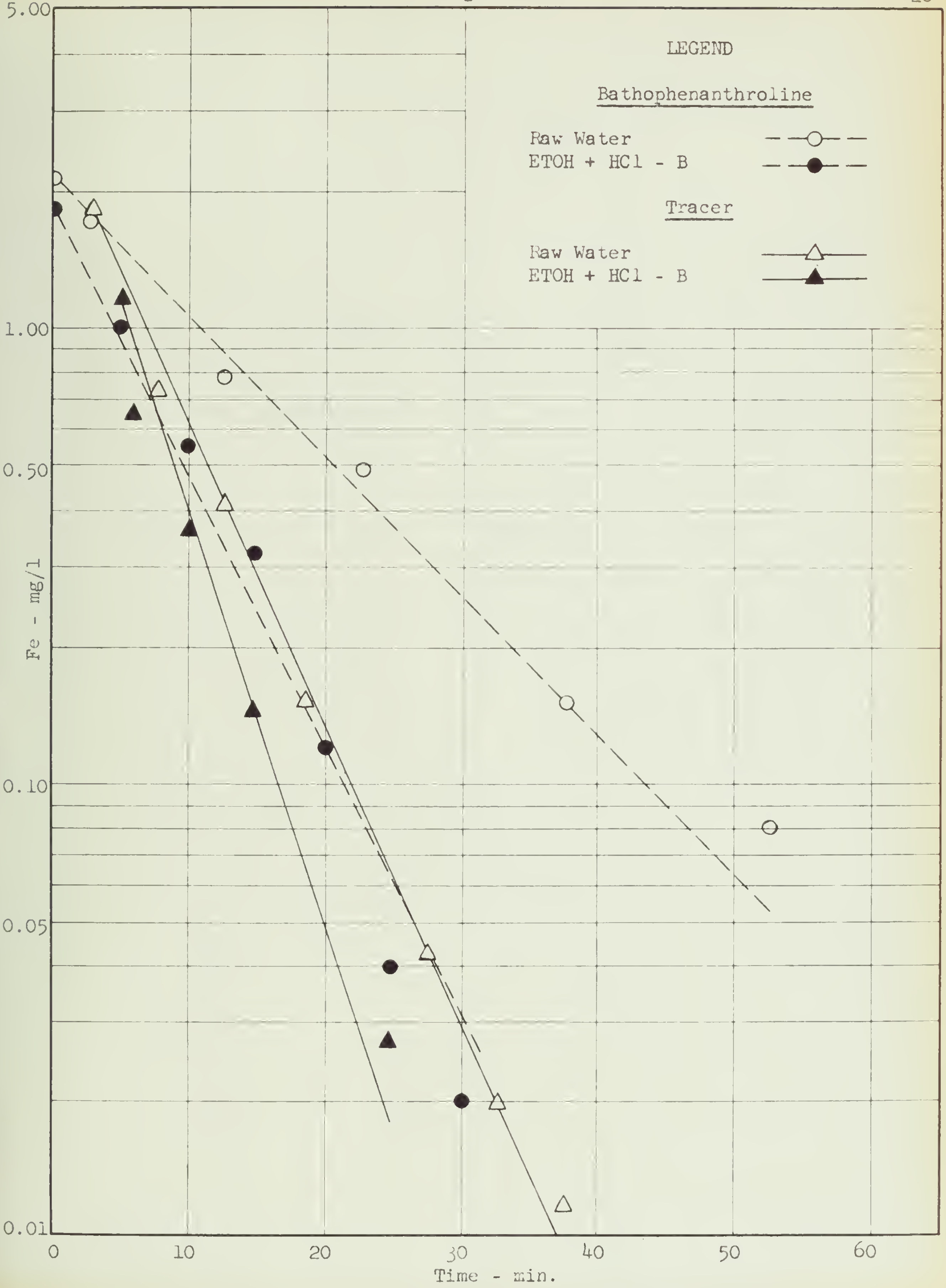
The results using ETOH + HCl - B extract plotted on Figure 11 for Atwood show a definite increase in oxidation rate with added organic. This same extract solution for Clinton was made with HCl and distilled water, and it exhibits very much the same retardation as the Clinton ETOH + HCl - A. This is shown on Figure 12. Again, it may be that both the A and the B extracts contain the same organic constituents.

Figures 13 and 14 are for the ETOH + NH_3 extracts. For the Clinton water, there was no appreciable difference between the oxidation rate of the raw water and that which had the added organic. There is, however, a leveling-off of the tracer curve at about 0.005 mg/l. The effect of the ETOH + NH_3 extract on the oxidation of Atwood water is shown very definitely on Figure 13. The extract increased the rate markedly. The tracer curve shows a tendency to level off a little higher than that for Clinton.

The curves for ETOH + NH_3 - B, shown on Figures 15 and 16, exhibit practically no effect on oxidation rate whatsoever. The tracer curves do show a tendency to level off. For Atwood, this is about 0.035 mg/l of soluble iron, and for Clinton this is at about 0.005 mg/l.

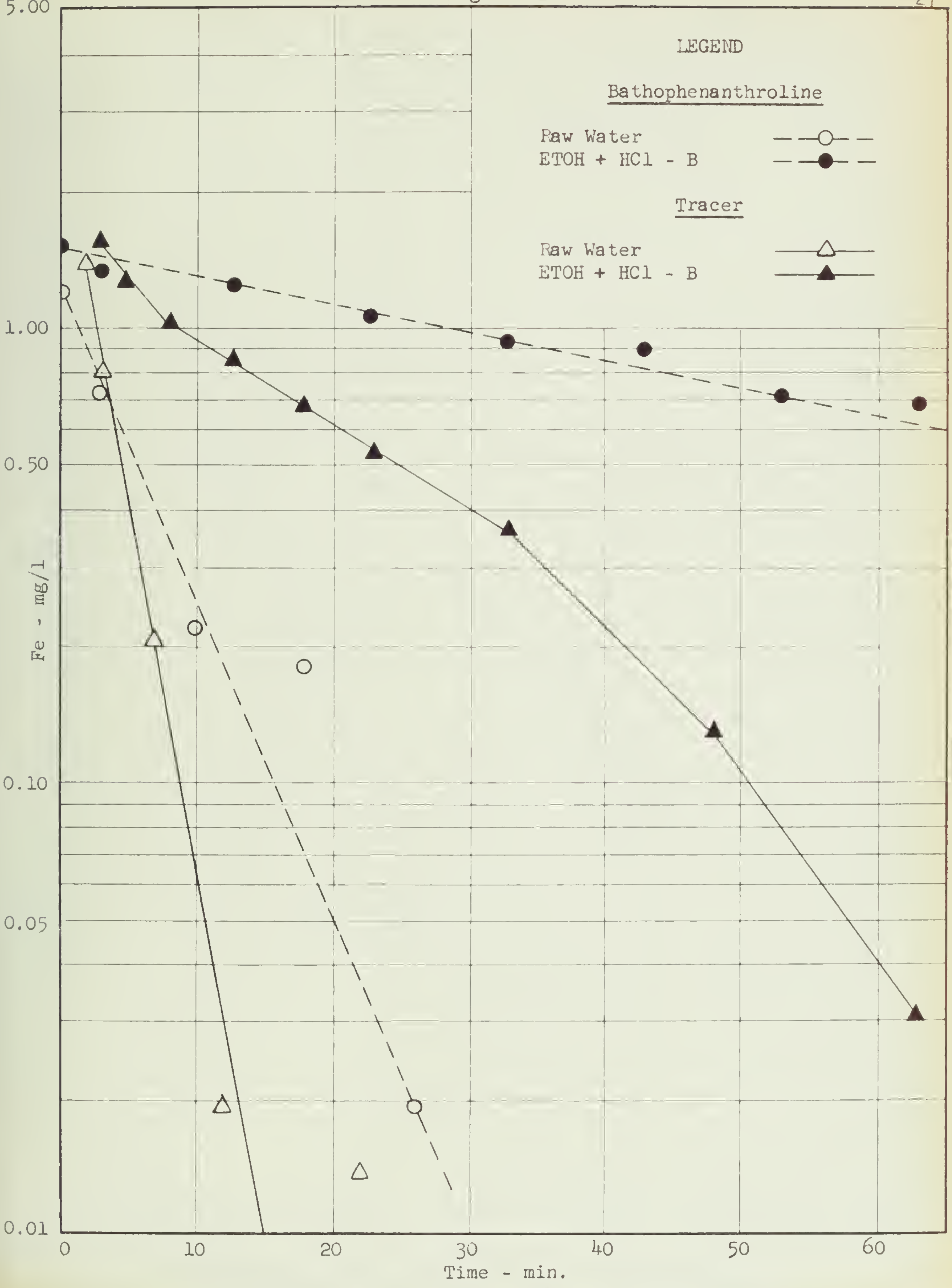
An additional test was made at Clinton with the ETOH + NH_3 extract. This was done with a concentration of 50 mg/l of the extract added to the raw water. The effect of ETOH + NH_3 - B_1, as shown on Figure 17, was practically the same as the test with 5 mg/l of the extract. The only significant difference appears in the tracer curves. The curve for ETOH + NH_3 - B_1 begins to level off at a concentration ten times larger than that for ETOH + NH_3 - B. This occurs at about 0.07 mg/l which is still well below the limit of 0.3 mg/l.

Figure 11



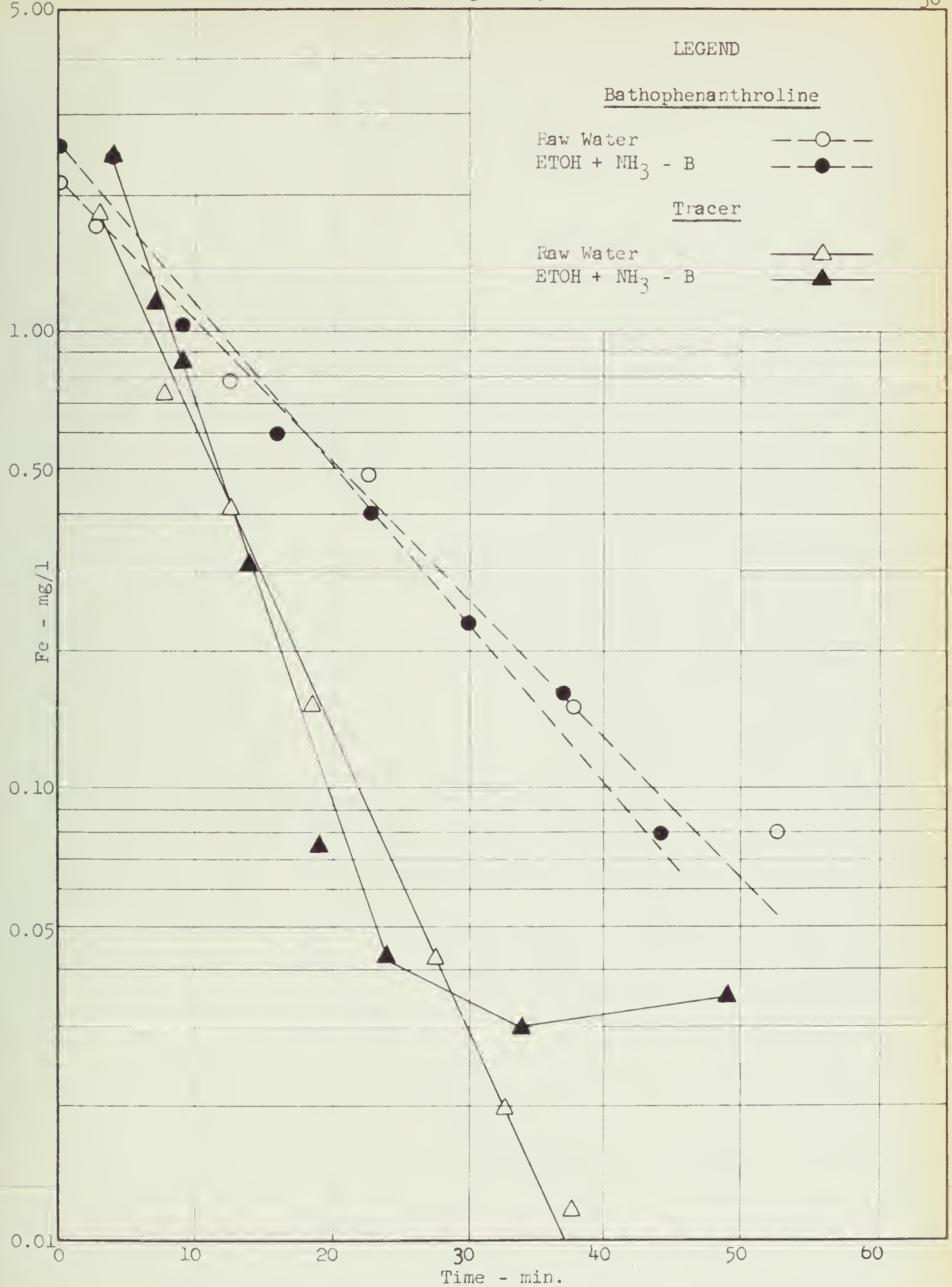
COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD ETOH + HCl - B EXTRACT ADDED

Figure 12



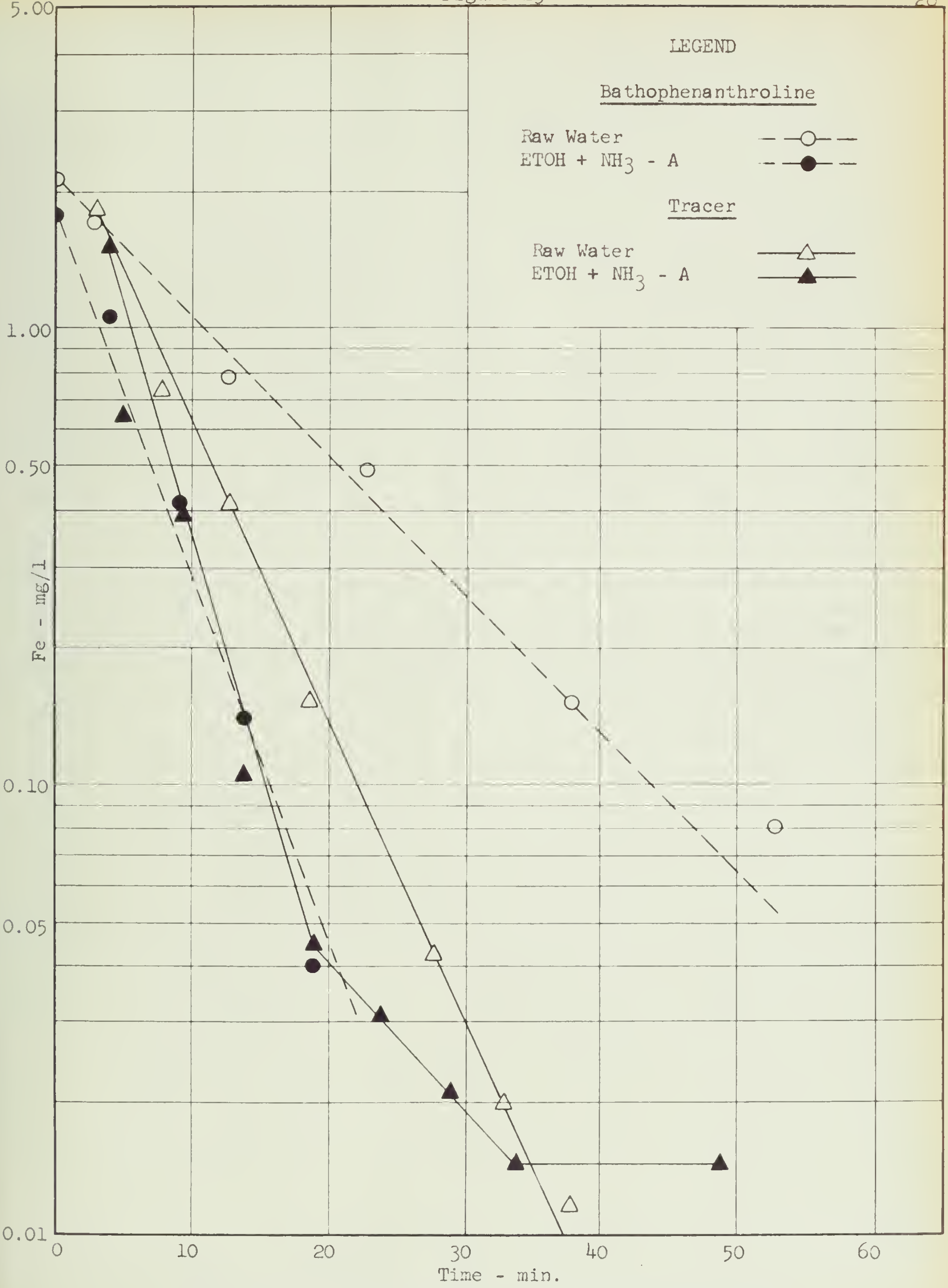
COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD ETOH + HCl - B EXTRACT ADDED

Figure 15

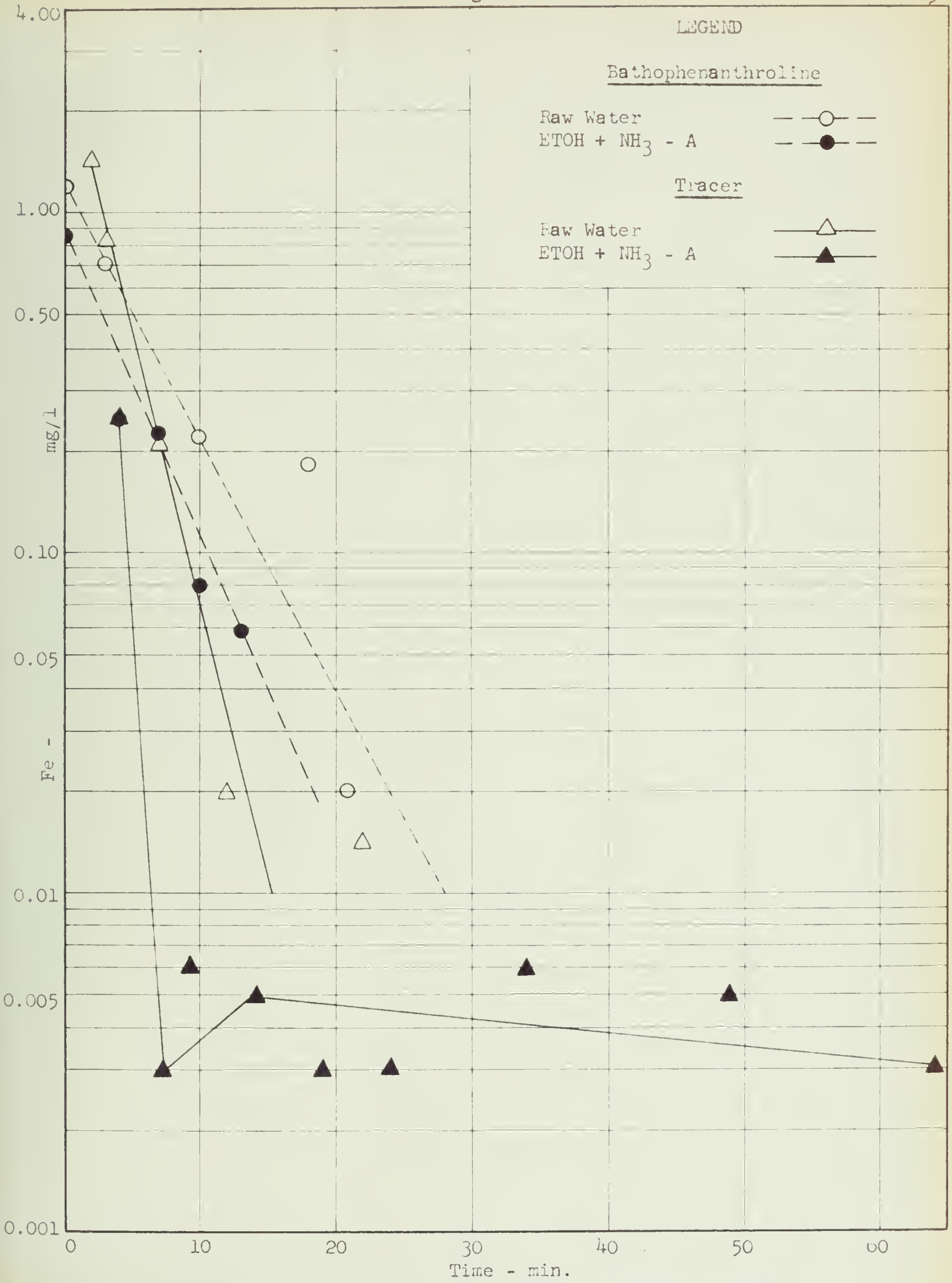


COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD ETOH + NH_3 - B EXTRACT ADDED

Figure 13

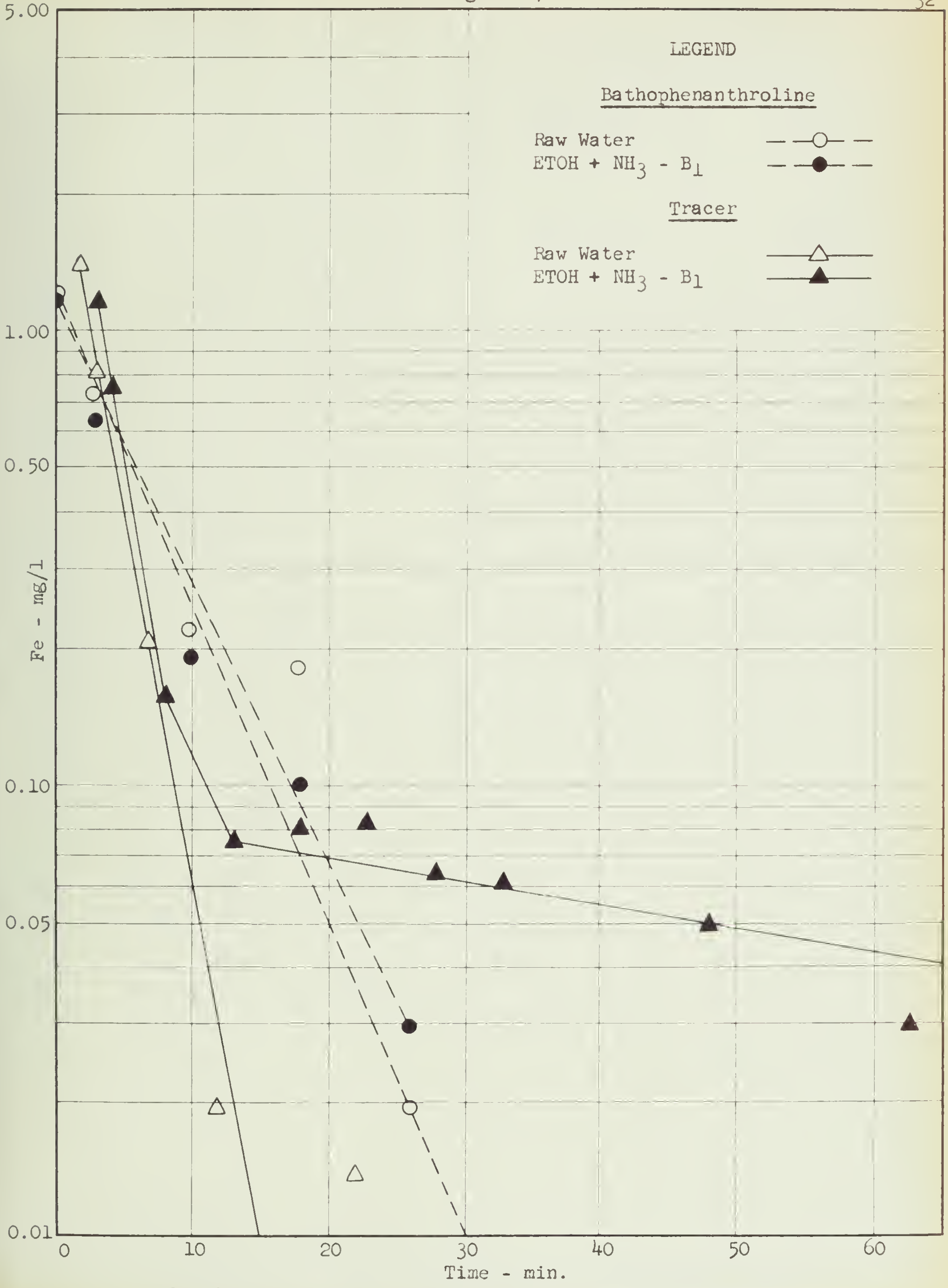


COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD ETOH + NH_3 - A EXTRACT ADDED



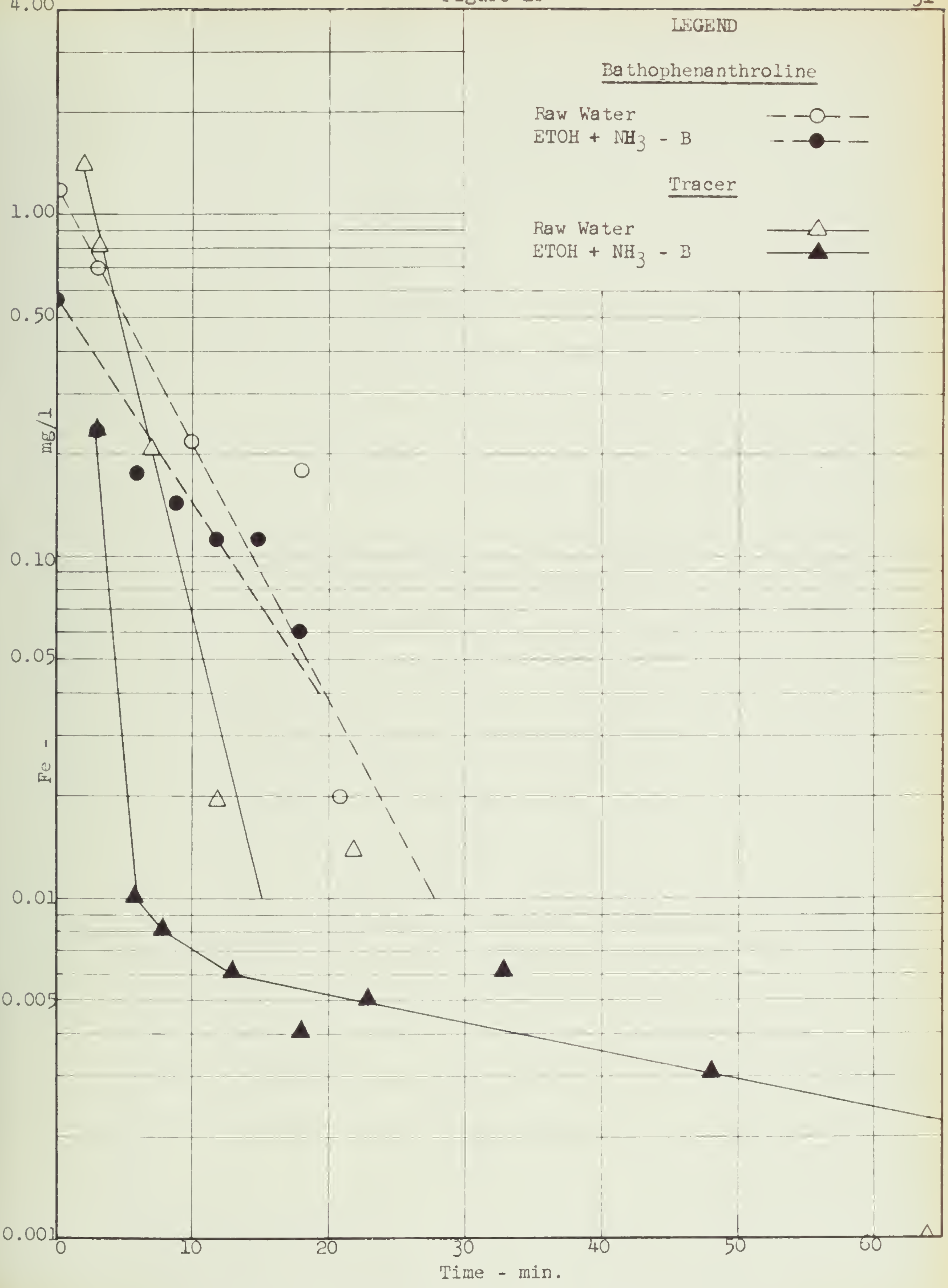
COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD ETOH + NH_3 - A EXTRACT ADDED

Figure 17



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD ETOH + NH_3 - B1 EXTRACT ADDED

Figure 16



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD ETOH + NH_3 - B EXTRACT ADDED

The fact that the ETOH + NH_3 - B_1 extract caused the tracer curve to level off at a concentration ten-fold higher than the ETOH + NH_3 - B extract indicates that chelation is taking place. The iron is being held in solution at a higher level of concentration due to the high concentration of organics. It is interesting to note that a ten-fold increase in organic concentration appears to hold ten times the amount of iron in solution.

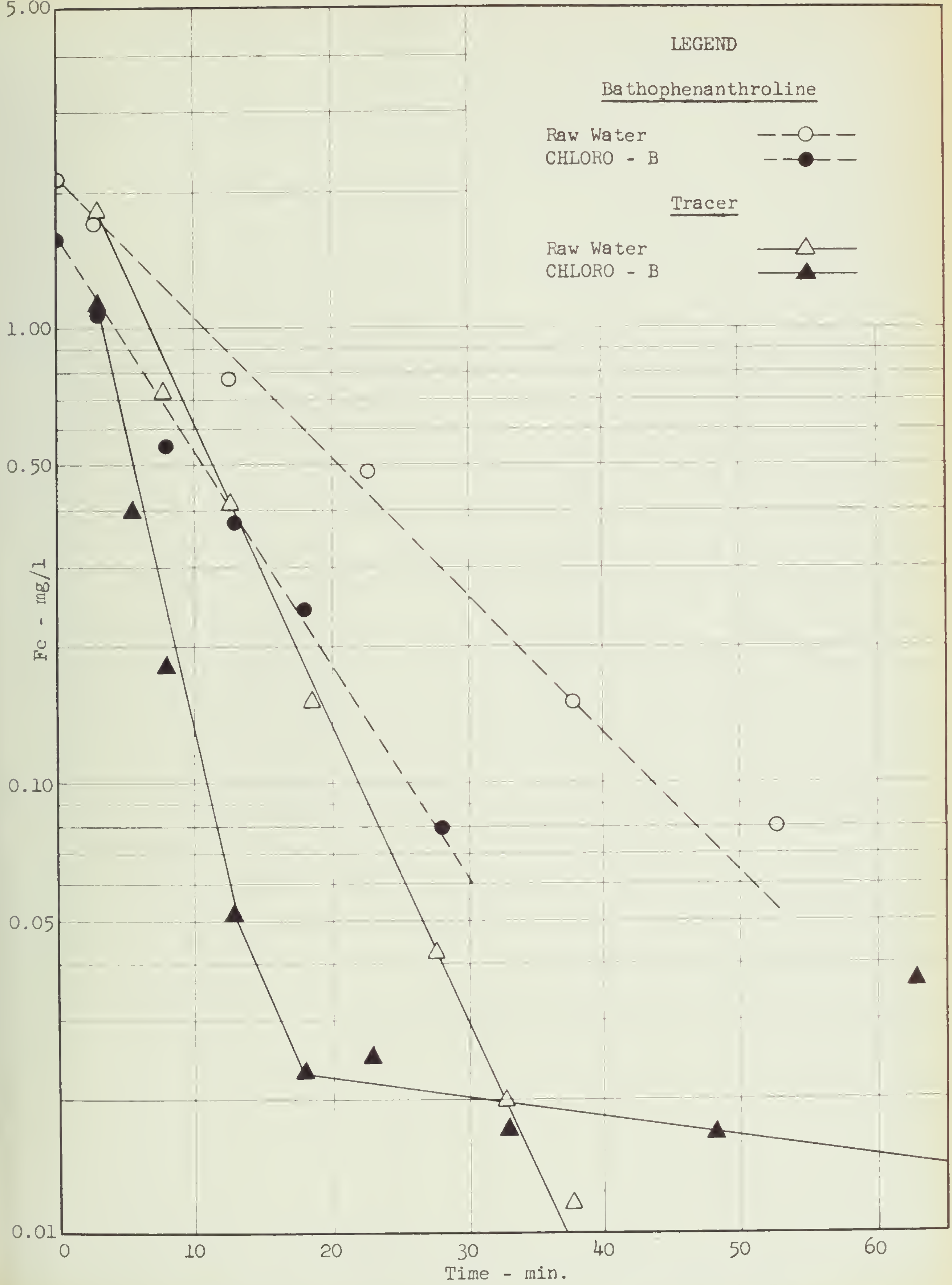
No graphs were constructed for the CHLORO - A extracts for either Atwood or Clinton. The effect of the dioxane contained in these extract solutions was to disperse the air bubbles so finely, while the sample was aerating, that the dissolved oxygen content increased rapidly and to a very high value. At the same time, the pH increased rapidly. The result was that the iron oxidized at such a rapid rate that there was no, or practically no, ferrous iron remaining at the end of the 2 minutes aeration time. There was a trace of ferrous iron in the Atwood CHLORO - A test, but it disappeared within 6 minutes after aeration. The results of these runs are tabulated on Tables 21 and 22.

There was no graph plotted for the Clinton CHLORO - B extract for the same reasons given above for the CHLORO - A extracts. The results of this test are tabulated on Table 24.

Figure 18 shows the curves on the CHLORO - B extract for Atwood. The increase in oxidation rate is quite apparent. The tracer curve again indicates a tendency to level off at a concentration of about 0.02 mg/l of iron.

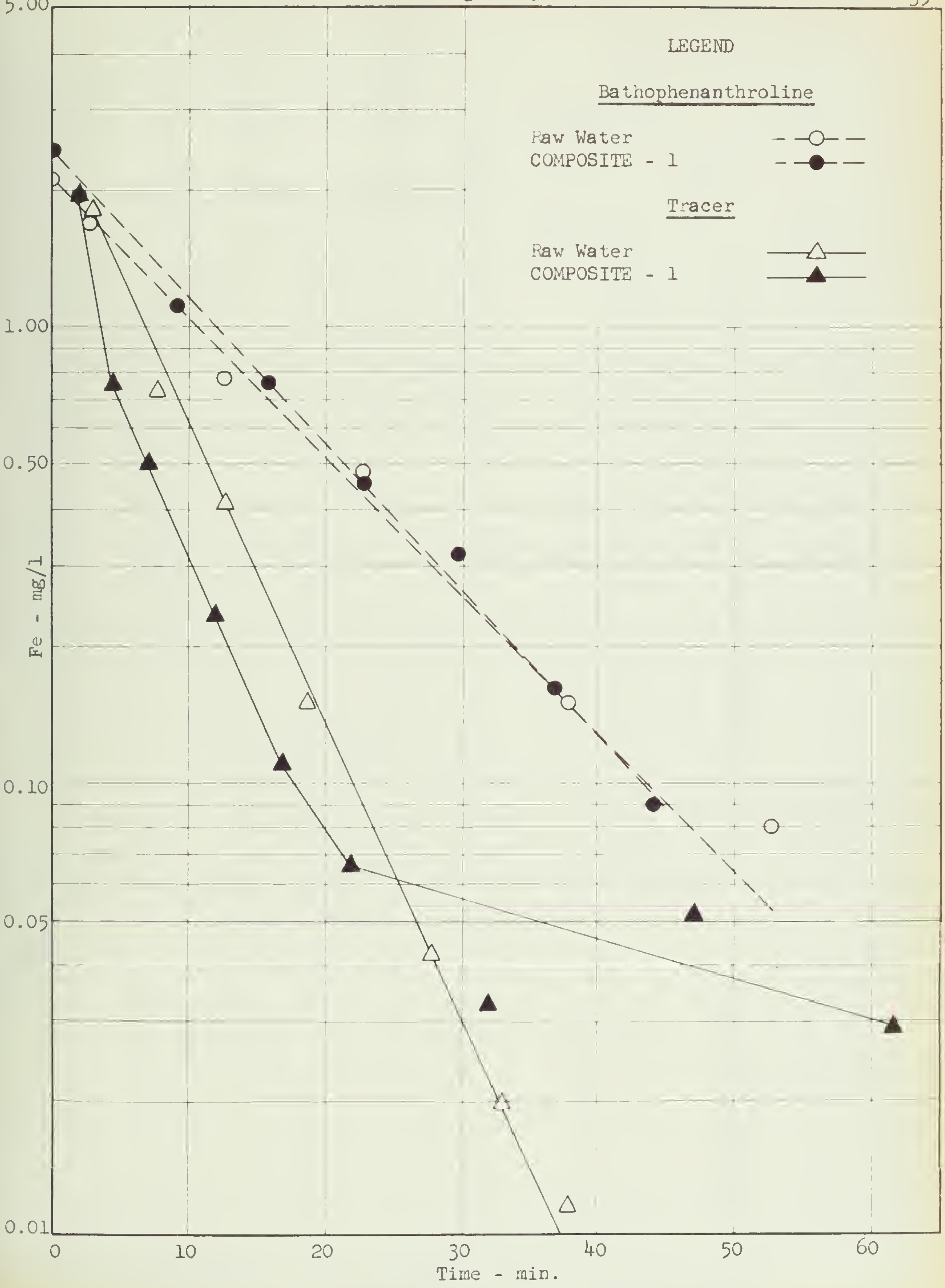
The curves for COMPOSITE - 1 are shown on Figures 19 and 20. There is no effect shown for the Atwood extract except a tendency for the tracer

Figure 18



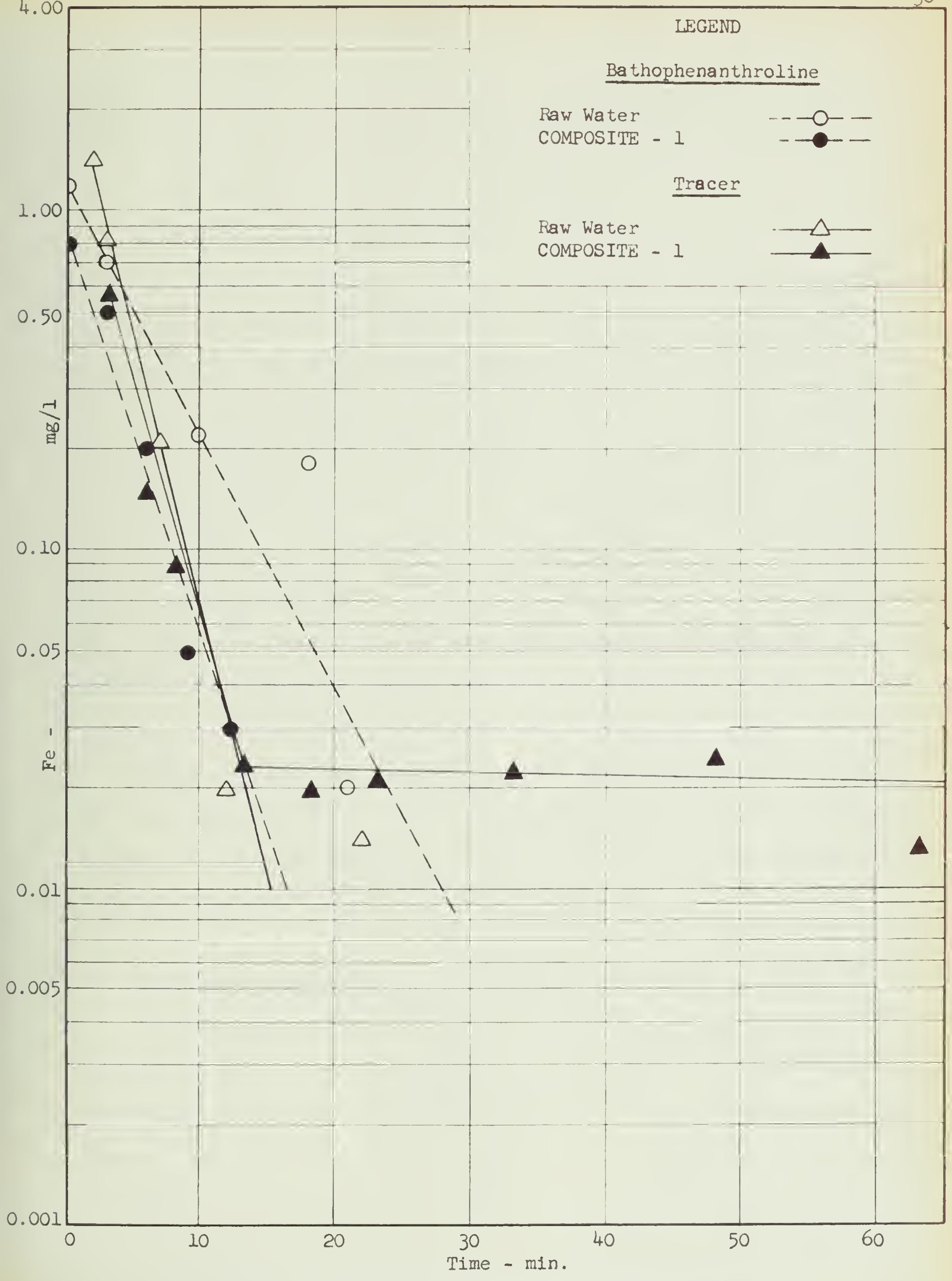
COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD CHLORO - B EXTRACT ADDED

Figure 19



COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER WITH THAT WHICH HAS HAD COMPOSITE - 1 EXTRACT ADDED

Figure 20



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD COMPOSITE - 1 EXTRACT ADDED

curve to level off at about 0.06 mg/l. A slight accelerating effect is shown on the bathophenanthroline curve for the Clinton extract. The tracer curve also shows a leveling out at about 0.02 mg/l.

COMPOSITE - 2 had opposite effects on the waters of Atwood and Clinton. Figure 21 indicates that this composition of extracts enhanced the oxidation rate of the Atwood water. Again, the tracer curve begins to flatten out at about 0.03 mg/l of soluble iron concentration.

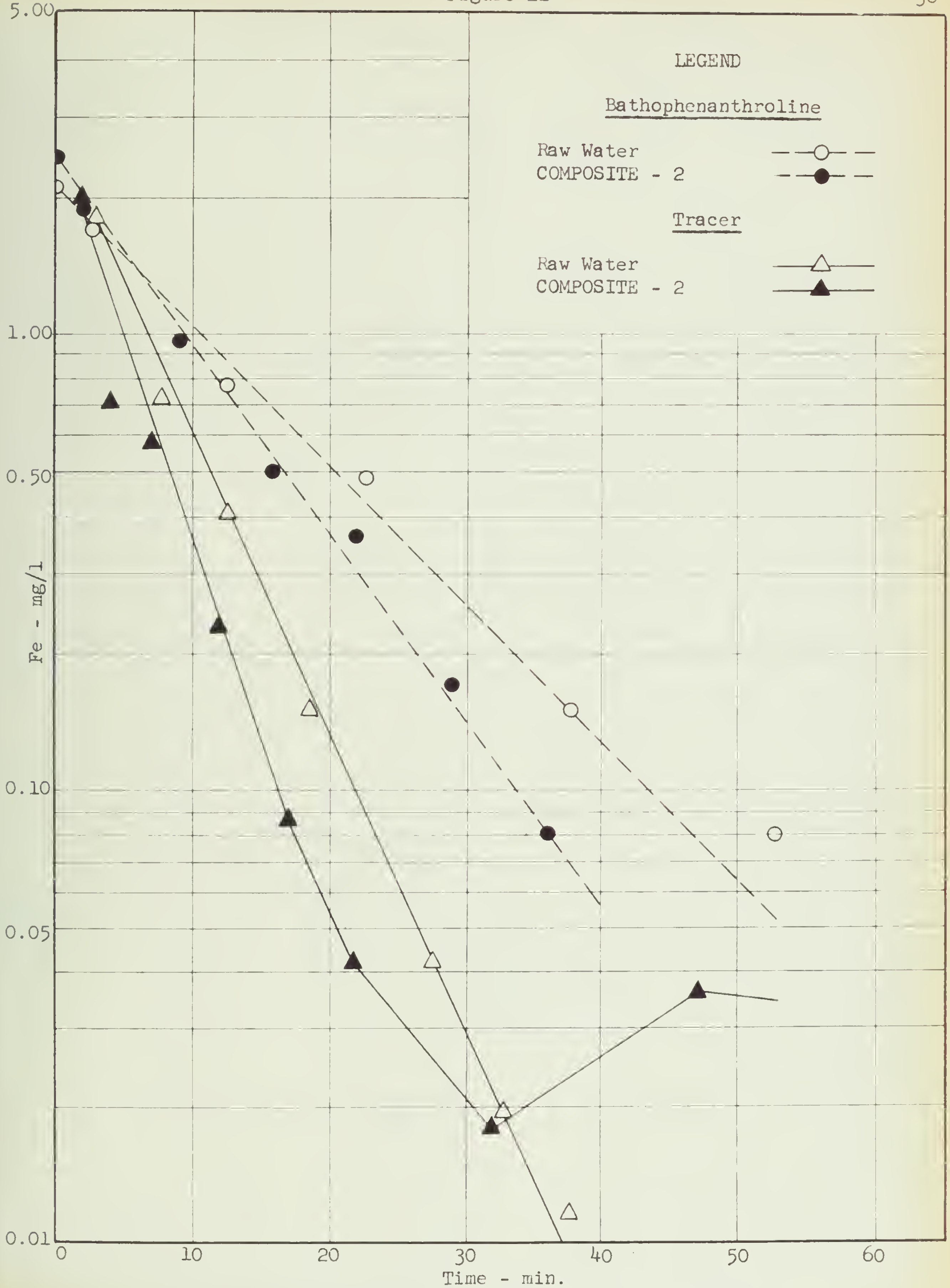
The opposite effect is shown on Figure 22 for the Clinton COMPOSITE - 2. The result was that the oxidation rate was slowed quite noticeably. This can be explained by the fact that this composite sample had a pH of 3.0, and, when 200 ml were added to the 7.8 liters to make a concentration of 25 mg/l, the pH dropped to 6.75 after aeration. However, the pH rose slightly with time and the oxidation rate was somewhat faster than that shown by the ETOH + HCl extracts that had the same effect on pH. The tracer curve shows a tendency to level out at about 0.04 mg/l.

Figure 23 shows the results of the 5 mg/l of tartaric acid added to the Clinton raw water. The effect was to slow the oxidation rate only slightly. The tartaric acid did not maintain any measurable amount of iron in solution.

B. Comparison of Bathophenanthroline and Tracer Curves

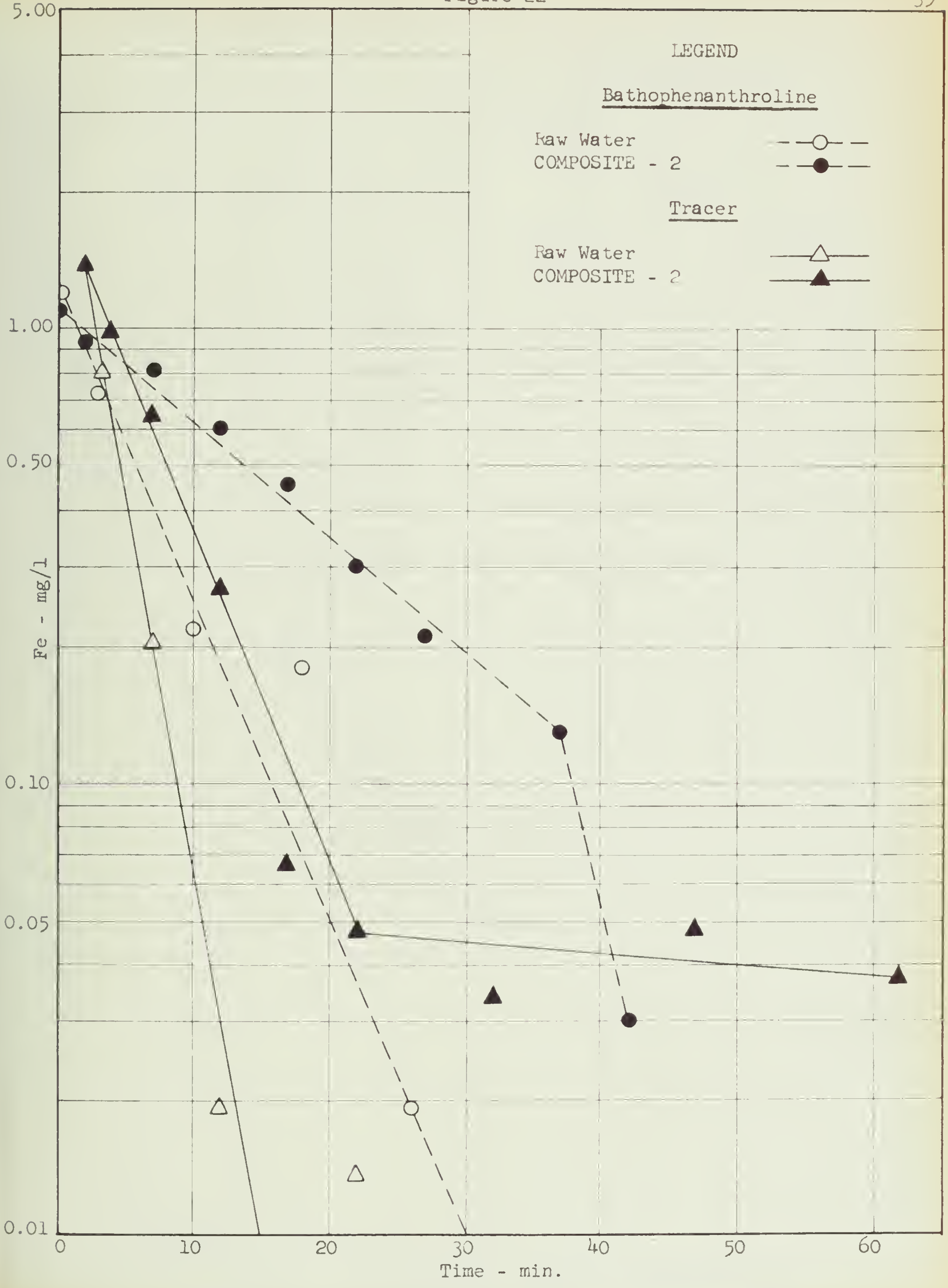
The bathophenanthroline procedure used in this study was for the measurement of ferrous iron. Ferrous iron is soluble iron, and it is generally believed that it will not filter out when it is in this reduced state.

Figure 21



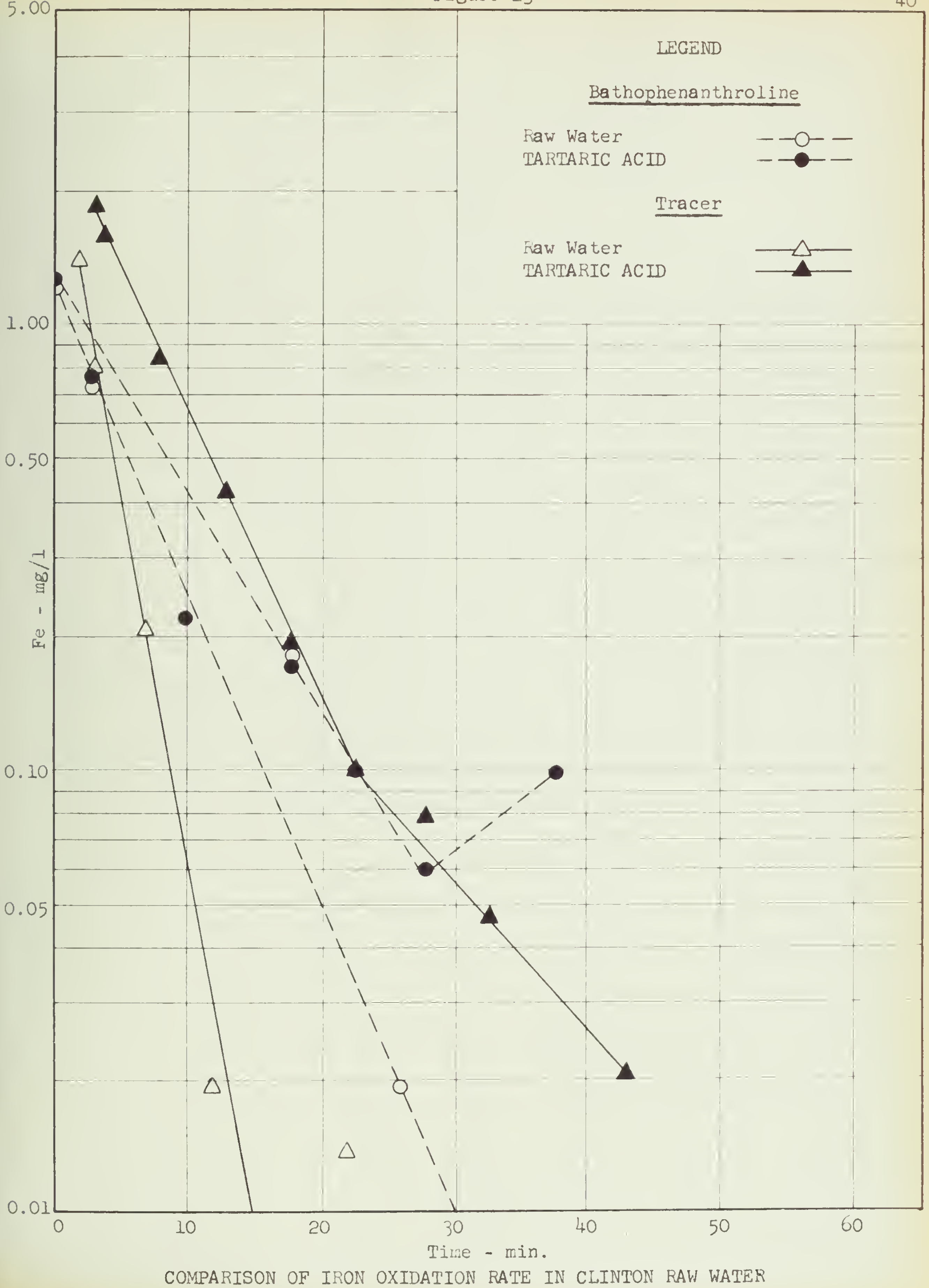
COMPARISON OF IRON OXIDATION RATE IN ATWOOD RAW WATER
WITH THAT WHICH HAS HAD COMPOSITE - 2 EXTRACT ADDED

Figure 22



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD COMPOSITE - 2 EXTRACT ADDED

Figure 23



COMPARISON OF IRON OXIDATION RATE IN CLINTON RAW WATER WITH THAT WHICH HAS HAD TARTARIC ACID EXTRACT ADDED

The tracer study used in this investigation was for the purpose of measuring the soluble iron. Chelated ferric iron is believed to be soluble and, also, cannot be filtered out.

Throughout this investigation, there was an obvious difference in the curves plotted for the bathophenanthroline study and those plotted for the tracer study. This was to be expected since the amount of soluble iron should exceed or equal the amount of ferrous iron at any given time. What was not expected was that, for practically every extract, the curve for soluble iron was below that for ferrous iron. This would seem to indicate that there was less soluble iron than ferrous iron. It must be assumed that when the tracer samples were being filtered through the 0.22 micron membrane filter, some of the ferrous iron was either filtered out directly or oxidized on the filter and then filtered out. This would also explain why several of the filtered samples intended for a reference point for the tracer study contained less iron than the corresponding bathophenanthroline sample.

IV. CONCLUSIONS

A. Effect of Organics on Iron Oxidation Rate

The results of this study tend to show that the presence of organics in the water supplies in central Illinois, even in concentrations higher than they occur naturally, does not inhibit the oxidation and removal of iron. Their presence does, in fact, hasten the oxidation process.

The only inhibitive factor found was that of pH. When an extract solution was added that lowered the pH, the oxidation was slowed down. Most of this lowering of pH was due to the solvents used to dissolve the dried extract rather than to the extract itself.

Even the use of 5 mg/l of a good chelator such as tartaric acid did not hold the iron in solution at a level above the U. S. Public Health Service Drinking Water Standard of 0.3 mg/l for a significant length of time. A 50 mg/l dose of the ETOH + NH_3 - B which was found to be a good chelator in synthetic waters in the laboratory failed to produce any hindering effect on the oxidation rate, although it did exhibit a chelating effect greater than the 5 mg/l dose of the same extract.

B. Comparison of Bathophenanthroline and Tracer Curves

The difference between the curves produced by the bathophenanthroline study and those produced by the tracer study is so consistantly reproducible that it can only be concluded that some of the ferrous iron is either being filtered out directly or is being oxidized on the filter and then filtered out.

If it is oxidized on the filter, it might be due to the contact with the ferric iron which is being filtered out.

Whichever is occuring, filtration of ferrous iron or oxidation and filtration of the ferrous iron on the filter, the fact remains that a problem presents itself which can only be resolved by further study.

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APPENDIX A

Iron Determination Reagents and Procedures

1. Ferrous Iron Determination

The reagents used in the bathophenanthroline procedure are as follows:

a. bathophenanthroline - 0.001 M solution, prepared by dissolving 0.332 g 4,7 - diphenyl - 1,10 - phenanthroline ($C_{24}H_{16}N_2$) in 500 ml ethyl alcohol and 500 ml distilled water;

b. sodium acetate - 10 per cent, iron-free solution, prepared by dissolving 100 g sodium acetate in one liter of distilled water;

c. isoamyl alcohol - commercially prepared;

d. pure ethyl alcohol - commercially prepared.

The procedure followed in the ferrous iron determination was as described below:

a. 4 ml of sodium acetate buffer were pipetted into a 125 ml separatory funnel.

b. 10 ml of the water sample were pipetted into the separatory funnel. The tip of the pipette was kept beneath the surface of the liquid at all times.

c. 15 ml of bathophenanthroline were added to the separatory funnel and the mixture slightly shaken.

d. 10 ml isoamyl alcohol were added to the mixture and shaken well to obtain complete mixing of the constituents.

e. After allowing the mixture to separate, the lower, aqueous layer was drawn off and discarded. The colored extract was transferred from the separatory funnel to a 50 ml volumetric

flask and the funnel was washed down two or three times with pure ethyl alcohol. The flask was then filled to the mark with ethyl alcohol. The per cent transmission was then determined on the Beckman D. U. Spectrophotometer,*[4] using a wave length of 533 millimicrons, and the reading compared with a standard curve to determine the amount of ferrous iron present in the sample.

2. Total Iron Determination

The reagents used in this determination were as follows:

a. reagent grade hydrochloric acid - commercially prepared;

b. hydroxylamine hydrochloride - a 10 per cent solution, prepared by dissolving 10 g $NH_2OH \cdot HCl$ in 100 ml distilled water;

c. ammonium acetate buffer solution, prepared by dissolving 250 g $NH_4C_2H_3O_2$ in 150 ml of distilled water, adding 700 ml glacial acetic acid, and diluting to one liter;

d. orthophenanthroline solution, prepared by dissolving one g 1,10 - phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) in one liter of distilled water and heating to 80° C.

The procedure used in determining total iron by orthophenanthroline is as follows:

a. 2 ml concentrated HCl were placed in a 100 ml flask.

b. 25 ml of the water sample were pipetted into the flask.

c. 1 ml of hydroxylamine hydrochloride was added to the flask.

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*4 Manufactured by Beckman Instruments, Fullerton, California.

APPENDIX A Continued

d. The sample was boiled for 5 minutes and then allowed to cool.

e. 10 ml of ammonium acetate buffer were added.

f. 10 ml of orthophenanthroline were added and the flask was filled to the mark with iron-free distilled water.

g. The per cent transmittance was measured on the Beckman D. U. Spectrophotometer at a wave length of 512 millimicrons. The reading was compared to a standard curve to determine the iron concentration.

APPENDIX B

Tabulated Data

Table 1

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE None

ALKALINITY 485 mg/l as $CaCO_3$

								Tracer Study	
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.60	3.16	7.31		Before aeration			
2	0	2.14		7.61	6.1	After aeration*			
3	3	1.67	1.80			Tracer added	1	0	1.800
4	13	0.77					2	0.5	1.320
5	23	0.48					3	5	0.730
6	38	0.15					4	10	0.140
7	53	0.08		7.60			5	15	0.150
							6	20	-
							7	25	0.042
							8	30	0.020
							9	35	0.012
							10	40	0.0

*Throughout the study, all aeration was for 2 minutes at 8 liters/minute

Table 2

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE None

ALKALINITY 430 mg/l as $CaCO_3$

								Tracer Study	
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.85	1.84	7.56		Before aeration			
2	0	1.18		7.83	6.7	After aeration			
3	3	0.71	0.80			Tracer added	1	0	1.410
4	10	0.22					2	1	0.800
5	18	0.18					3	5	0.208
6	26	0.02		7.89			4	10	0.0197
							5	15	-
							6	20	0.0137
							7	25	0.0

Table 3

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE H_2O - A ALKALINITY Not measured

No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	Tracer Study No.	Tracer Study Time min.	Tracer Study Soluble Iron-mg/l
1		3.30	3.60	7.15		Before aeration			
2	0	2.80		7.60	6.4	After aeration			
3	3	1.94	1.92			Tracer added	1	0	1.940
4	8	1.31					2	2	1.007
5	13	0.89					3	5	0.611
6	20	0.48					4	10	0.276
7	27	0.28					5	15	0.120
8	34	0.20		7.60			6	20	0.071
							7	30	0.047
							8	45	0.052
							9	60	0.054
							10	90	0.075

APPENDIX B Continued

Table 4

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE H_2O - B

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		3.02	3.24	7.10		Before aeration			
2	0	2.41		7.65	7.0	After aeration			
3	4	1.63	1.72			Tracer added	1	0	1.720
4	9	1.12					2	2	0.810
5	14	0.67					3	5	0.470
6	21	0.42					4	10	0.176
7	28	0.24					5	15	0.066
8	35	0.12		7.70			6	20	0.012
							7	30	0.185
							8	45	0.013
							9	60	0.0057

Table 5

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE H_2O - B

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.33	1.68	7.50		Before aeration			
2	0	0.67		8.00	7.5	After aeration			
3	2	0.35	0.40			Tracer added	1	0	0.400
4	5	0.13					2	2	0.060
5	8	0.07					3	5	0.036
6	11	0.02					4	10	0.002
7	14	0.02					5	15	0.008
8	17	0.0		7.60			6	20	0.004
							7	30	0.003
							8	45	0.003
							9	60	0.0

Table 6

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE ETOH - A   ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.46	2.64	7.15		Before aeration			
2	0	1.58		7.55	7.8	After aeration			
3	4	1.08	1.08			Tracer added	1	0	1.080
4	10	0.43					2	2	0.467
5	15	0.18					3	5	0.277
6	20	0.12					4	10	0.088
7	25	0.12		7.50			5	15	0.0268
							6	20	0.0300
							7	30	0.0157
							8	45	0.0268
							9	60	0.0212
							10	90	0.0206

Table 7

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH - A   ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.67	1.56	7.30		Before aeration			
2	0	0.90		7.70	7.1	After aeration			
3	3	0.25	0.0			Tracer added	1	0	0.250
4	6	0.23					2	3	0.019
5	14	0.12					3	5	0.009
6	17	0.08					4	10	0.009
7	20	0.0		7.50			5	15	0.011
							6	20	0.010
							7	30	0.008
							8	45	0.007
							9	60	0.004
							10	90	0.008

Table 8

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE ETOH - B ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		3.20	3.36	7.10		Before aeration			
2	0	2.56		7.55	7.4	After aeration			
3	4	1.52	1.44			Tracer added	1	0	1.520
4	9	0.89					2	2	0.656
5	14	0.58					3	5	0.434
6	19	0.37					4	10	0.141
7	24	0.24					5	15	0.0567
8	29	0.12					6	20	0.0374
9	34	0.08		7.55			7	30	0.0330
							8	45	0.0183
							9	60	0.0320
							10	105	0.0348

Table 9

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH - B ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.67	1.60	7.50		Before aeration			
2	0	0.60		8.20	7.8	After aeration			
3	3	0.25	0.0			Tracer added	1	0	0.250
4	6	0.23					2	3	0.014
5	9	0.08					3	5	0.008
6	12	0.0		8.10			4	10	0.008
							5	15	0.009
							6	20	0.007
							7	30	0.004
							8	45	0.007
							9	60	0.005
							10	90	0.004

APPENDIX B Continued

Table 10

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE ETOH + HCl - A

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.17	2.64	7.25		Before aeration			
2	0	1.98		7.45	7.0	After aeration			
3	3	1.75	1.75			Tracer added	1	0	1.750
4	8	1.45					2	1	1.390
5	16	1.02					3	7	0.800
6	26	0.78					4	10	0.790
7	46	0.37					5	15	0.560
8	76	0.06		7.40			6	20	0.400
							7	30	0.176
							8	60	0.042
							9	90	0.0091
							10	150	0.0137

Table 11

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH + HCl - A

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.25	1.72	7.20		Before aeration			
2	0	1.26		6.85	7.3	After aeration			
3	4	1.26	1.40			Tracer added	1	0	1.400
4	11	1.20					2	2	1.160
5	18	1.18					3	5	1.080
6	26	1.00					4	10	0.940
7	38	0.90					5	15	0.840
8	48	0.80					6	20	0.700
9	58	0.58					7	30	0.480
10	88	0.33		6.90			8	45	0.180
11	118	0.14					9	60	0.024
12	238	0.0		7.45			10	90	0.150

APPENDIX B Continued

Table 12

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH + HCl - A_1 ALKALINITY 390 mg/l as $CaCO_3$

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.00	1.54	7.45		Before aeration			
2	0	0.81		7.80	7.1	After aeration			
3	2	0.30	0.38			Tracer added	1	0	0.380
4	5	0.08					2	2	0.086
5	8	0.01					3	5	0.029
6	11	0.0		7.70			4	10	0.007
7	14	0.0					5	15	0.003
							6	20	0.004
							7	30	0.005
							8	45	0.008
							9	120	0.008

Table 13

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE NH_4Cl ALKALINITY 430 mg/l as $CaCO_3$

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.10	1.60	7.40		Before aeration			
2	0	0.45		7.70	7.35	After aeration			
3	3	0.09	0.32			Tracer added	1	0	0.320
4	8	0.05					2	2	0.070
5	11	0.02					3	5	0.030
6	14	0.0					4	10	0.010
7	17	0.0		7.70			5	15	0.007
							6	20	0.007
							7	30	0.004
							8	45	0.004
							9	60	0.009
							10	90	0.007

Table 14

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE ETOH + HCl - B

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.46	3.12	7.15		Before aeration			
2	0	1.80		7.70	7.8	After aeration			
3	5	1.00	1.15			Tracer added	1	0	1.150
4	10	0.55					2	1	0.640
5	15	0.32					3	5	0.355
6	20	0.12					4	10	0.144
7	25	0.04					5	20	0.027
8	30	0.01					6	30	0.0073
9	35	0.0		7.60			7	45	0.0102
							8	60	0.0
							9	90	0.0102

Table 15

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH + HCl - B

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.50	1.60	7.00		Before aeration			
2	0	1.50		6.70	7.75	After aeration			
3	3	1.32	1.52			Tracer added	1	0	1.520
4	13	1.22					2	2	1.240
5	23	1.05					3	5	1.020
6	33	0.91					4	10	0.840
7	43	0.88					5	15	0.670
8	53	0.70					6	20	0.530
9	63	0.67					7	30	0.350
10	73	0.052		6.70			8	45	0.126
11	103	0.20					9	60	0.030
12	133	0.0					10	90	0.020

APPENDIX B Continued

Table 16

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE ETOH + NH_3 - A ALKALINITY 465 mg/l as $CaCO_3$

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.46	2.88	7.15		Before aeration			
2	0	1.80		7.60	7.7	After aeration			
3	4	1.06	1.15			Tracer added	1	0	1.150
4	9	0.41					2	1	0.640
5	14	0.14					3	5	0.390
6	19	0.04					4	10	0.104
7	24	0.0		7.80			5	15	0.045
							6	20	0.031
							7	25	0.021
							8	30	0.0147
							9	45	0.0147
							10	105	0.0049

Table 17

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH + NH_3 - A ALKALINITY 415 mg/l as $CaCO_3$

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.67	1.56	7.80		Before aeration			
2	0	0.85		8.20	7.25	After aeration			
3	4	0.25	0.04			Tracer added	1	0	0.250
4	7	0.22					2	3	0.003
5	10	0.08					3	5	0.006
6	13	0.06		8.20			4	10	0.005
							5	15	0.003
							6	20	0.003
							7	30	0.006
							8	45	0.005
							9	60	0.003
							10	90	0.003

Table 18

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE ETOH + NH_3 - B ALKALINITY 470 mg/l as $CaCO_3$

								Tracer Study	
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		3.33	3.52	6.90		Before aeration			
2	0	2.62		7.60	7.0	After aeration			
3	4	2.48	2.08			Tracer added	1	0	2.480
4	9	1.03					2	3	1.150
5	16	0.60					3	5	0.860
6	23	0.41					4	10	0.310
7	30	0.23					5	15	0.075
8	37	0.16					6	20	0.043
9	44	0.08		7.60			7	30	0.030
							8	45	0.035
							9	60	0.0086
							10	90	0.014

Table 19

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH + NH_3 - B ALKALINITY 410 mg/l as $CaCO_3$

								Tracer Study	
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.11	1.52	7.70		Before aeration			
2	0	0.56		8.10	7.4	After aeration			
3	3	0.23	0.06			Tracer added	1	0	0.230
4	6	0.17					2	3	0.010
5	9	0.14					3	5	0.008
6	12	0.11		8.10			4	10	0.006
7	15	0.11					5	15	0.004
8	18	0.06					6	20	0.005
9	21	0.0					7	30	0.006
							8	45	0.003
							9	60	0.001
							10	120	0.003

APPENDIX B Continued

Table 20

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE ETOH + NH_3 - B1* ALKALINITY 385 mg/l as $CaCO_3$

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.04	1.96	7.50		Before aeration			
2	0	1.15		7.80	6.6	After aeration			
3	3	0.63	1.16			Tracer added	1	0	1.160
4	10	0.19					2	1	0.740
5	18	0.10				*50 mg/l of	3	5	0.155
6	26	0.03		7.80		organic added	4	10	0.074
							5	15	0.080
							6	20	0.082
							7	25	0.064
							8	30	0.061
							9	45	0.049
							10	60	0.029

APPENDIX B Continued

Table 21

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE CHLORO - A ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		3.25	3.28	6.90		Before aeration			
2	0	0.13		7.55	8.4	After aeration			
3	3	0.08	0.39			Tracer added	1	0	0.390
4	6	0.0					2	2	-
							3	5	-
							4	10	0.0067
							5	15	0.0086
							6	20	0.0038
							7	30	0.0067

Table 22

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE CHLORO - A ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		0.82	1.60	7.00		Before aeration			
2	0	0.0	0.0	7.85	9.4	After aeration			
						Tracer added	1	0	0.0
							2	3	
							3	5	
							4	10	
							5	15	
							6	20	

Table 23

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE CHLORO - B ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		2.77	2.88	6.90		Before aeration			
2	0	1.57		7.55	9.0	After aeration			
3	3	1.06	1.12			Tracer added	1	0	1.120
4	8	0.55					2	2	0.390
5	13	0.37					3	5	0.176
6	18	0.24					4	10	0.051
7	23	0.13		7.60			5	15	0.023
8	26	0.08					6	20	0.025
							7	30	0.017
							8	45	0.017
							9	60	0.037
							10	90	0.021

Table 24

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE CHLORO - B ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		0.95	1.52	7.50		Before aeration			
2	0	0.0		7.85	9.0	After aeration			
3	3	0.0	0.0			Tracer added	1	0	0.0
							2	2	
							3	5	
							4	10	
							5	15	
							6	20	
							7	30	

Table 25

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE COMPOSITE - 1*   ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/1	Total mg/1	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-Mg/1
1		3.13	3.36	7.15		Before aeration			
2	0	2.46		7.60	7.4	After aeration			
3	2	1.96	1.92			Tracer added	1	0	1.96
4	9	1.12					2	2	0.75
5	16	0.76				*5 mg/1 of	3	5	0.51
6	23	0.45				organic added	4	10	0.23
7	30	0.32		7.60			5	15	0.11
8	37	0.16					6	20	0.066
9	42	0.09					7	30	0.033
							8	45	0.052
							9	60	0.019
							10	90	0.043

Table 26

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE COMPOSITE - 1*   ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/1	Total mg/1	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/1
1		1.07	1.49	7.10		Before aeration			
2	0	0.80		7.65	7.75	After aeration			
3	3	0.50	0.56			Tracer added	1	0	0.560
4	6	0.20					2	3	0.147
5	9	0.05				*5 mg/1 of	3	5	0.089
6	12	0.03				organic added	4	10	0.023
7	15	0.0		7.60			5	15	0.019
							6	20	0.021
							7	30	0.022
							8	45	0.024
							9	60	0.013
							10	90	0.019

Table 27

IRON OXIDATION IN ATWOOD, ILLINOIS, WATER

ADDITIVE COMPOSITE - 2*

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		3.30	3.36	7.20		Before aeration			
2	0	2.45		7.50	7.4	After aeration			
3	2	1.18	1.92			Tracer added	1	0	1.92
4	9	0.96					2	2	0.710
5	16	0.50				*25 mg/l of	3	5	0.580
6	22	0.36		7.55		organic added	4	10	0.230
7	29	0.17					5	15	0.086
8	36	0.08					6	20	0.042
							7	30	0.018
							8	45	0.036
							9	120	0.018

Table 28

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE COMPOSITE - 2*

ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.22	1.51	7.10		Before aeration			
2	0	1.09		6.75	8.35	After aeration			
3	2	0.93	1.43			Tracer added	1	0	1.431
4	7	0.81					2	2	0.938
5	12	0.60				*25 mg/l of	3	5	0.641
6	17	0.45				organic added	4	10	0.269
7	22	0.30					5	15	0.066
8	27	0.22					6	20	0.047
9	32	0.17					7	30	0.034
10	37	0.13					8	45	0.048
11	42	0.03					9	60	0.037
12	47	0.0		7.10			10	90	0.043

Table 29

IRON OXIDATION IN CLINTON, ILLINOIS, WATER

ADDITIVE TARTARIC ACID* ALKALINITY Not measured

							Tracer Study		
No.	Time min.	Fe++ mg/l	Total mg/l	pH	D.O.	Remarks	No.	Time min.	Soluble Iron-mg/l
1		1.95	1.88	7.61		Before aeration			
2	0	1.25		7.82	6.7	After aeration			
3	3	0.78	1.84			Tracer added	1	0	1.840
4	10	0.22					2	1	1.600
5	18	0.17				*5 mg/l of	3	5	0.820
6	28	0.06				organic added	4	10	0.420
7	38	0.10		7.82			5	15	0.190
							6	20	0.100
							7	25	0.078
							8	30	0.047
							9	40	0.021

APPENDIX C

Sample Radioactive Counting Table

No.	Minutes	Count[1]	Count-Blank	CPM	Iron-mg/l
B	Blank[2]	1,500	0	0	0
T	Total	11,500	10,000	2,000	2.00[3]
1	1	9,500	8,000	1,600	1.60
2	5	6,500	5,000	1,000	1.00
3	10	4,500	3,000	600	0.60
4	15	3,000	1,500	300	0.30
5	20	2,000	500	100	0.10
6	30	1,500	0	0	0.00

[1] Five-minute counts were taken to minimize the count per minute error.

[2] The samples were counted against a 10 ml distilled water blank which was used to measure the background activity.

[3] The first iron value would come from the reference sample taken at the time the tracer was added. The succeeding values are in proportion to the count.