A "POLLUTION INDEX"

FOR CHARACTERIZING

SEWAGE WATERS

By

ANTON ELBERT GOODWIN

Bachelor of Arts
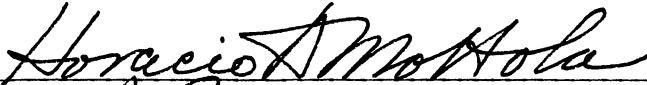
Phillips University

Enid, Oklahoma

1958

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
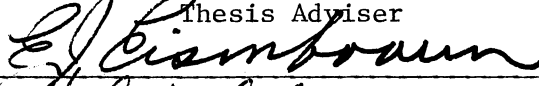for the Degree of
MASTER OF SCIENCE
July, 1975

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Thesis Approved:

Horacio A Mottola
Thesis Adviser

E J Eisenbraun

H. R. Gearhart II

N N Durham
Dean of the Graduate College

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CHAPTER I

INTRODUCTION

For over a hundred years man has been interested in the oxygen consumed by natural and waste waters. The interest in determining the periods of time and the amounts of oxygen necessary to stabilize polluted water was responsible for the initial studies of consumed oxygen. Forchamer (1) was first to measure the chemical oxidation of industrial waters in 1849 and Frankland (2) was measuring the decrease in oxygen content of the Thames River as early as 1870. The Biochemical Oxygen Demand Test (BOD) has evolved from these early studies (3). It is performed by measuring the dissolved oxygen content of the sample using the modified Winkler or iodometric method, incubating the sample in the dark at 20° centigrade for 5 days and again measuring the dissolved oxygen content. The difference in oxygen contents is expressed as mg/l BOD.

The discussion section of the Standard BOD method states: "The test is of limited value in measuring the actual oxygen demand of surface water" (3). But in spite of this shortcoming the BOD is used by industries and treatment plants and this continued use only points out the desire to have a measure of the oxygen needed to stabilize a water. Because five days are required to make a BOD determination, chemical methods were developed for estimating it.

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As will be shown in Chapter II, these methods give only limited estimates of the BOD. The most widely accepted chemical method is the Standard Chemical Oxygen Demand Method (COD) (4). This method determines the "oxygen equivalent of that portion of organic matter of a sample that is susceptible to oxidation by a strong oxidant" (4). Potassium dichromate in a 50 percent solution of boiling sulfuric acid is used to oxidize the organic material and the test result is expressed as mg/l COD. Because this test is reproducible it has become an index of the amount of organic material in the water.

At this point it can be said that basically there are two methods available for assessing the degree of pollution of a water. In this work pollution is defined as organic material in water that undergoes biochemical oxidation. The Standard BOD method which gives an estimate of the amount of oxygen needed to stabilize the organic material in the sample and the Standard COD method which is a measure of the organic material that is chemically oxidized. Even with these two methods the search continues for other methods and modifications to estimate the degree of pollution. This points to either the need for a more refined chemical or biological method or an entirely different parameter for characterizing pollution. The work reported here is an attempt to develop a new approach to characterize the organic pollution in water.

In developing this new approach it is important to recognize that a problem common to waste water treatment plant personnel and others concerned with water pollution has been the assessing of the pollution load on a receiving stream. Gaudy and Gaudy (5) state

that in assessing the "pollution load" it is the "potential deple-
tion of the DO (dissolved oxygen) resource in the receiving stream"
that is most important. The interest is not to determine the amount
of organic material present, but to determine the amount of dissolved
oxygen that is necessary to stabilize a discharge containing this
organic material. A deduction is that the rate of biochemical oxida-
tion is as important as the amount of dissolved oxygen needed. The
presence of a compound with a slow rate of oxidation places a smaller
pollution load on a receiving stream than does the presence of a
compound with a high rate of oxidation. If the oxidation rate is
slow enough, then oxygen can be replaced naturally without depletion.

The different kinds of organic material found in water contri-
bute to the pollution load in varying degrees. For example, organic
material such as ethanol, benzoic acid, and o-cresol undergo bio-
chemical oxidation readily (6), and therefore place a greater pollu-
tion load on the resource of dissolved oxygen than more resistant
materials such as tertiary-butanol, diethylene glycol, and toluene.
Heukelekian (7) has tabulated a considerable number of biodegradable
compounds and their BOD.

If the rate of biochemical oxidation is an important parameter,
then it logically follows that the rate of chemical oxidation would
be a useful parameter when assessing the pollution load by chemical
methods. This premise is the basis for the development of a new
index for characterizing water pollution.

CHAPTER II

A SURVEY OF CHEMICAL OXYGEN DEMAND METHODS

Chemists and engineers are looking for quicker and easier
methods to obtain information about the degree of pollution. If
one must wait 5 days for a BOD analysis to indicate the degree of
pollution, then there is much to be desired in that action to reduce
the oxygen demand cannot be initiated before the dissolved oxygen may
be depleted. The literature shows investigators using chemical oxida-
tion methods in attempts to gather results in shorter periods of time.
Permanganate was one of the earlier oxidizing agents used (8-26).
Dichromate (2, 27-50), hypochlorite (51-58), sulfuric acid (59),
ceric sulfate (60-64), iodate (65-66), hydrogen peroxide (67), ferrate
(68), and peroxydisulfate (69-77) have also been used as oxidizing
agents in studies of organic materials in water. Results from these
methods were difficult to compare, simply because each investigator
employed different concentrations of reagents, different reaction
temperatures, different digestion times, and different volumes of
reagents and samples.

Standard COD Method

In 1949 W. A. Moore et al. (2) reported the dichromate reflux
method. In a study using 30 organic compounds it was shown that this

method gave reproducible results though some compounds such as benzene, acetic acid, alanine, and pyridine were not totally oxidized. Moore et al. (38) next made a comparative study of five different methods. They were the standard permanganate method (9), iodate methods of Dzyadzio (65) and of Ingols (78), and dichromate methods of Madison (79) and of Moore (2). He pointed out his method did not suffer from shortcomings of the other tests. For example, the permanganate test results were not uniform because of the effects of heating, agitation of sample, and fading of endpoint when titrating. The digestion period of the Madison method required very close attention to determine when the sulfuric acid and phosphoric acid mixture had fumed for exactly 4 minutes. The results of Ingols' method were not to be found reproducible. Other investigators have reported similar results when comparing methods (1, 63, 65, 80-82). Presently the dichromate method is considered by some as being the best COD method available (83).

When using Ag_2SO_4 as a catalyst as suggested by Muers (84), Moore et al. (2) showed that his method gave higher COD values for some compounds such as acetic acid, alanine, ethyl alcohol, and chlorobenzene and therefore concluded the catalyst extended the usefulness of the test. Previous investigators used silver catalyst in the form of silver dichromate (85) and silver nitrate (30). A number of metals have also been studied for their catalytic property in the dichromate method. Simon (27, 85) conducted oxidation experiments using lead, cobalt, nickel, mercury, copper, iron, zinc, and magnesium chromates. Moore et al. (2) studied selenium, copper, nickel, and platinum as catalysts in his method and recently Palaty (86-88) has investigated

the catalytic effects of inorganic salts such as nickel sulfate, cobalt sulfate, manganese sulfate, ceric sulfate, mercuric sulfate, ammonium molybdate and others.

Using silver sulfate (84) catalyst and mercuric sulfate (89, 90) as a complexing agent for chlorides, the Moore method has become the established Standard Method for American Public Health Association, American Water Works Association, and Water Pollution Control Federation for determining the "oxygen consumed" or more commonly known as the Chemical Oxygen Demand (COD) (4). The test is run for a period of two hours under the conditions of high sulfuric acid content, high reflux temperatures and with a catalyst. It is recognized that adherence to the use of catalyst, to the specified volumes for sample and oxidants, and to reflux time is necessary if results are to be reproduced. This is because some compounds such as glycine, lactic acid, and glutamic acid (39) are not oxidized as readily as glucose, tartaric acid and cellulose (2).

Modifications to the Standard COD Method

Modifications to the Standard COD Method (45-50, 91-97) have been proposed for the purposes of shortening the time of the test, of reducing the cost of the test and for checking for correlation of COD with BOD. Other modifications have been made so automated measurement of COD can be performed (98-104). Two recent, rapid COD methods are the Oxygen Demand Index (ODI) test of Westerhold (46) and the Rapid COD method of Jeris (47). In the ODI test the sample and reagents are placed into a one inch test tube, reacted in boiling

water bath for twenty minutes, cooled and the percent transmission
determined at 600 nm wavelength by a spectrometer. A calibration
curve that is generated using glucose as the standard compound is
used to convert the percent transmission to a BOD value of a standard
glucose solution (97). The Jeris Rapid COD method calls for the
reaction to be carried on until a temperature of 165°C is reached,
to quench the reaction with water and then to determine the COD by
titration. A critical look at papers written by investigators
serves: 1) to illustrate that rates of oxidation were a affecting
the reactions and 2) to point out the attempts to correlate COD with
BOD.

Shriver and Young (105) studied the precision with which ODI
measurements could be made and the dependability of using the ODI
test as a measure of the BOD of waste water samples. The reaction
time of 20 minutes was not investigated to determine whether or not
any slow reacting species were present. One cannot criticize its
use because the reaction time of 2 hours as specified by the Standard
COD Method is not sufficient for complete oxidation of all organic
material such as glutamic acid. The presence of large quantities of
slow reacting material would seriously affect the outcome of the test.
The use of a calibration curve to convert the quantity of reacted
material to BOD is the same as using a constant correlation factor to
convert COD to BOD. This should not be done for it is known that
only when stable conditions exist in a waste water can such a corre-
lation be made. The test samples were raw waste water, primary
effluent, filter effluent, and final effluent from two different

waste water treatment plants. After presenting plots of their data, Shriver and Young concluded that the precision was as good as that reported for other COD tests and that limited correlation existed between ODI values and BOD. Here again, one can conclude that rates of reaction were affecting the ODI test and that attempts were made to correlate a chemical oxygen demand test with BOD.

W. N. Wells (106) made an evaluation of the Jeris Rapid COD test. The test was to be employed on a routine day-to-day basis for the analysis of waste waters that vary little in their composition. He recognized three variables: temperature, time of digestion, and sample volume, as influencing the COD values. An attempt was made to determine their effect by carrying out a series of experiments using glucose and glutamic acid as test samples. Wells concluded that standing time and digestion time had little or no effect on the COD values. This is a true statement for glucose and glutamic acid. What would his conclusion have been if glycine (used by Jeris (47) and by Moore (2)) with a slower rate of oxidation had been used such that the organic material was not completely oxidized?

Another effect studied by Wells was temperature in the range of 50°C to 205°C. He found that temperature had an effect on the COD values and recognized the differences in rates of oxidation for glucose and glutamic acid, but failed to consider the possibility of slower reacting compounds such as glycine, alanine, or sodium stearate that may be present in sewage samples. This is a weakness in the design of his study.

The effect of sample volume on COD values was also studied by

Wells. Because there was no trend in COD values of the test series,
he stated his results were inconclusive and therefore speculated that
changes in sample size may result in differences in rates and the
extent of oxidation of organic compounds. A change in sample size
brings about a change in concentration of the reaction species. A
change in concentration results in change of rate. Foulds and
Lunsford (1) using a sewage sample and Jeris (107) using sewage
samples from two locations concluded that sample size did effect the
COD value. Here again is seen the effect that changes in concentra-
tion have on the rate of oxidation. Wells realized the possibility of
different rates of oxidation and the times necessary for the system
to come to equilibrium, but he did not investigate this question.

Finally, Wells undertook a series of tests on untreated and
treated waste water to determine if a correlation existed between
Jeris Rapid Method COD and BOD. He found a correlation between
COD and BOD for each waste water studied providing there were little
changes in organic content of the system. The two facts that are
apparent are: rates of reaction were affecting the results of the
Jeris Rapid Method and that only limited correlation between COD
and BOD can be made.

Carbon Analyzer Instruments

Over the years, the main criterion for adopting a new chemical
method or modification has been - "it produces higher results." The
higher results mean the COD values are nearer the 100% theoretical
value for complete conversion of the compounds to carbon dioxide

and water. Because some organic materials are not completely oxidized in the chemical oxygen demand tests, there were techniques developed to determine the total amounts of carbonaceous material in water samples. These methods employ high temperature combustion tubes (108-114). Because different catalysts such as nickel, platinum or copper oxide are used and because different reaction atmospheres such as hydrogen, carbon dioxide or helium are used, there are different products formed such as methane, carbon monoxide or carbon dioxide. Consequently, either a flame ionization detector or infrared analyzer is used to monitor the products formed in the analysis. The amounts of products formed are a measure of the total organic carbon (TOC) in the samples. Schaffer et al. (115) showed in a study that results from a carbon analyzer were both accurate and precise and that corre-lations of the TOC with BOD and COD existed for waste water of "some consistency in character." That is, as long as the type of material remains constant then a correlation would exist between TOC and BOD. This is the same conclusion reached by Jones (116), Shriver and Young (106), and Jones in Jennelle (117). The fact to be drawn from this discussion about TOC is that correlations between carbon analyzer results and BOD are no better than correlations between COD and BOD.

From the review presented in this section, two points emerge. The first is that the investigators were experiencing the effects of rates of oxidation in their studies. This emphasizes the need to consider the use of a rate factor in developing a new index to char-acterize pollution. The second point is that the investigators were able to make only a limited correlation at best between COD and BOD.

Obviously, an understanding of the changes that take place during the degradation of organic material by a biological process would be helpful in developing a new method for indexing pollution.

Limited Correlation Between COD and BOD

An idea always present with investigators was the development of a rapid chemically based test that would serve to estimate the oxygen needed to stabilize a waste water (91, 92, 118-129). Even Moore et al. looked for a correlation between BOD values by his method and the Standard BOD test values on natural stream samples. They concluded that a correlation was not feasible because of seasonal changes, changing biological activity, changing stream flows and changing industrial activities (39, 129).

An insight into the biological process occurring during the degradation of organic material can be obtained through an understanding of the Rapid Biochemical Oxygen Demand test developed by Hiser and Busch (130). Their technique employs a different approach in that the disappearance of the soluble biodegradable organic material during an eight-hour time interval is measured by using a COD test, while the BOD test measures the oxygen utilized by microorganisms during a 5-day period to effect disappearance of the organic material. (Mullis and Schroeder (131) extended this technique to include particulate organic material found in waste water that can be solubilized by microorganisms.) Mullis and Schroeder presented a typical graph obtained from the Hiser and Busch method for determining the total biological oxygen demand (T_bOD) of a soluble waste. Figure 1
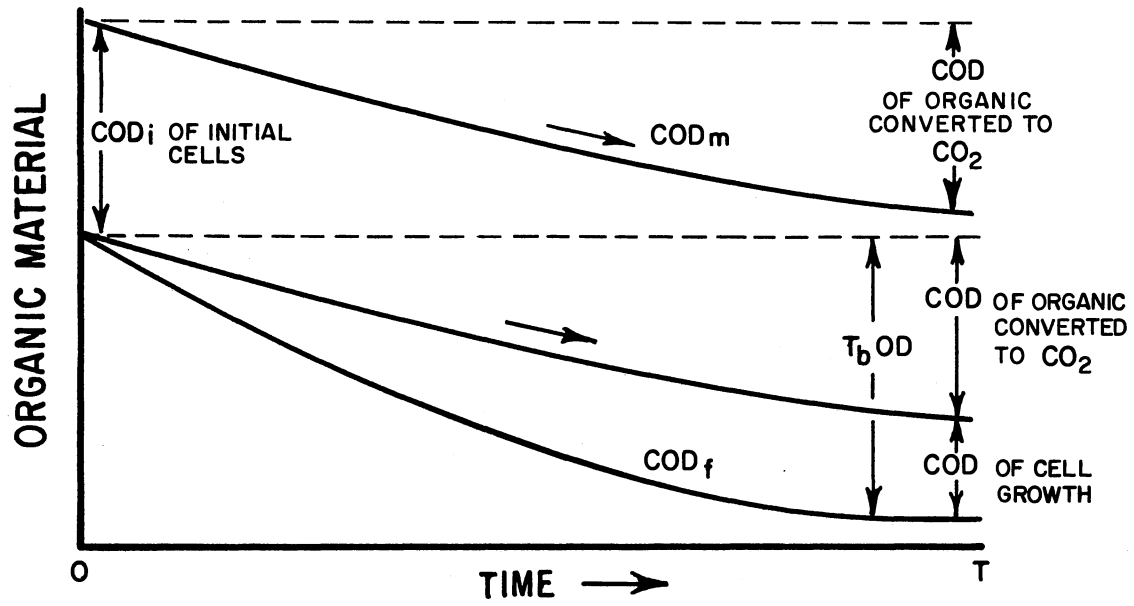
Figure 1. Biological System Changes

illustrates the changes the biological system undergoes and how these changes are measured.

The COD_m is the mixed liquor COD. The mixed liquor is the combination of the soluble substrate and the acclimated bacterial culture. The COD_f is the COD of the filtrate passing thru a 45 μm filter. The filtrate is assumed to contain only soluble substrate. The decrease in COD_m is a measure of the organic material converted to CO_2. The decrease in COD_f is a measure of the decrease in substrate. The final COD_f is a measure of non-biodegradable organic material. At time t=0, the difference between COD_m and COD_f is a measure of the initial cell COD_i. At time t=T when all biodegradable organic substrate has been utilized, the COD due to cell growth can be obtained from the following equation:

$$COD \text{ of cell growth} = COD_m - COD_f - COD_i$$

Therefore, the COD of cell growth plus the COD due to the conversion of organic to CO_2 give the total change in COD which is equal to the total biological oxygen demand. The important thing to note here is that the COD test was used to monitor the change in organic material. Providing the fraction of biodegradable organic material present in the waste remains constant, then a correlation exists between COD value and T_bOD value.

This understanding of the changes that are occurring when a mixture of biodegradable and non-biodegradable compounds is utilized shows that the COD method cannot differentiate between the two types of compounds whereas the BOD test can.

CHAPTER III

A WAY TO CHARACTERIZE WATER POLLUTION

In the first two sections of this report, two points about rates
of chemical oxidation were brought out. These were: 1) rates were
not being considered during the evaluations of various COD methods
and 2) rates would be a useful parameter in characterizing a polluted
water sample. This section develops the rationale for its use.

General Considerations

It is known that different compounds have different rates of
chemical oxidation. The presence of a compound that is easily
oxidized is more likely to contribute to the pollution load than a
compound such as elemental carbon. This suggests that the degree
of pollution can be indexed by measuring the rate of oxidation of
the organic pollution in the water.

To illustrate the idea that the rate of chemical oxidation is
a useful parameter, Figure 2 is presented.

Consider four water samples that have identical COD values, but
each contains a different compound with a different rate of chemical
oxidation that ranges from a slow rate for sample 1 to a fast rate
for sample 4. The four samples in the illustration cannot be dis-
tinguished using the COD values alone, since they are all equal.
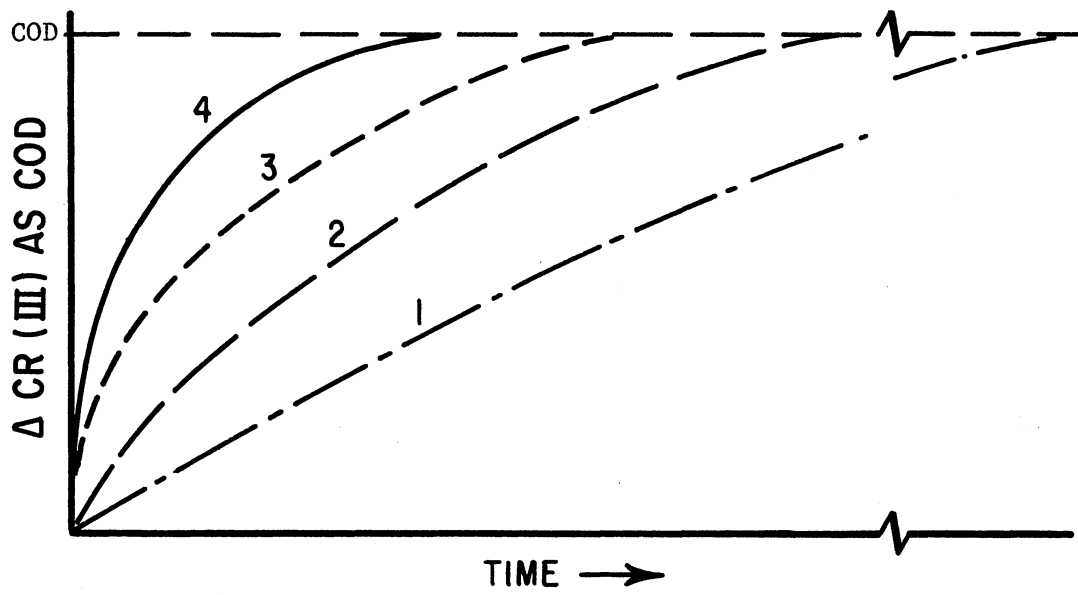
Figure 2.   Illustration of Rate Profile of
Samples With Equal COD

But when considering the rates of chemical oxidation it is possible to order the samples in the following manner: Sample 4>3>2>1.

A literature search shows that little use had been made of rates of chemical oxidation of wastewater.   It appears that most investigative efforts were directed towards chemical methods that would estimate the quantity of organic material present.   Ivekovic and Gertner (132) used rate data in the form of a ratio of the permanganate COD at 30 minutes to the permanganate COD at 15 minutes to distinguish differences in the composition of organic matter in water.   This ratio, which they called "relation of oxidizability," indicates recent pollution as its value approaches unity.

Another consideration should be given to the quantity of material present.   It is important to know if the rate of oxidation is due to a small quantity of rapidly oxidized material or due to a large quantity of slowly oxidized material.   Figure 3 illustrates this idea.

Consider four water samples where each contains a different compound at such a concentration that the initial rates of oxidation are identical.   By measuring the quantity of material present, the four samples can be ordered as follows: Sample 1>2>3>4.   This shows the need to consider the quantity of material present when indexing a water sample.

Instantaneous Rate Term

The rate of oxidation is dependent on the concentrations of reacting species and on the reaction temperature.   The relationship
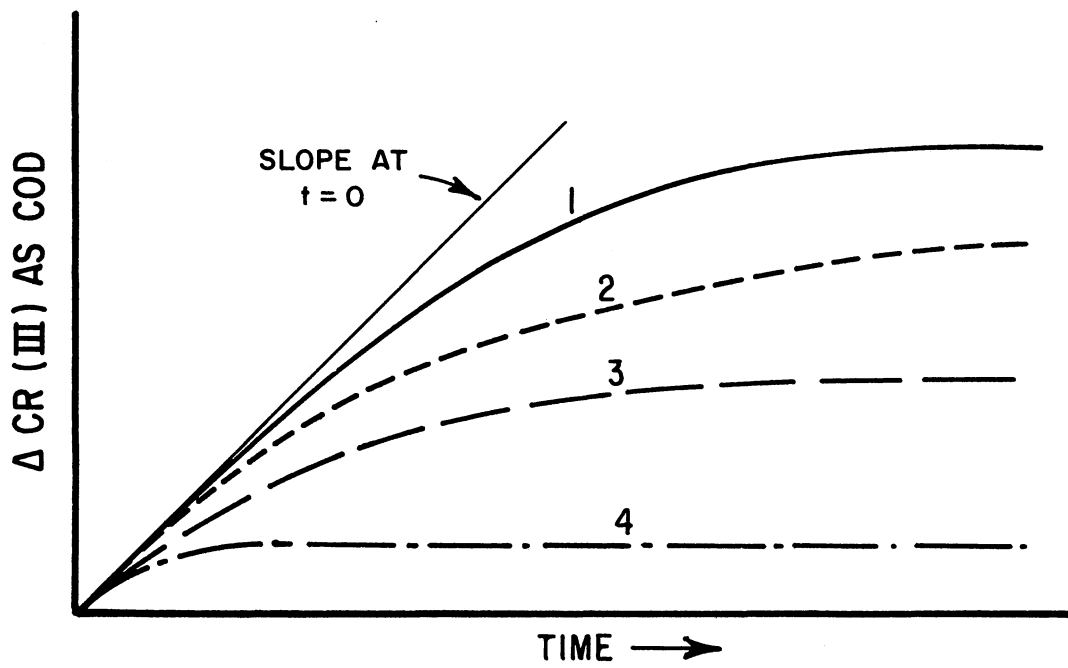
Figure 3. Illustration of Rate Profile of
Samples With Equal Initial Rates

for these factors can be given by a rate equation which has the general form:

Rate = k(T) x function of concentration of reactants.

The k(T) term expresses the dependence of temperature while the concentration function gives the dependence on the concentrations of sulfuric acid, potassium dichromate and an organic compound. When the solution of the rate equation is possible there is information that would be useful in describing the pollution. For example, the k(T) would measure the oxidizability of the organic material present and would remain constant as long as the material remained unchanged. A change in k(T) would indicate a change in the character of the material which would be useful information.

But a sewage plant water contains a mixture of many types of compounds and neither a k(T) term nor a concentration function can be easily determined. Each compound present would have its own k(T) term and so there could be no unique k(T) term for the mixture that makes up sewage. With no k(T) term then only the instantaneous rate of chemical oxidation can be used as an index of pollution. Though the instantaneous rate changes during the course of the reaction, its maximum value at the beginning of the reaction will be effected by all compounds and therefore it is information about the organic material present.

Quantity Term

It is recognized that different compounds are oxidized at different rates and so rates cannot be used as a direct measure of

quantity of a mixture of organic materials. At first glance the rate
parameter seems to offer less as an index to pollution than measure-
ments of quantity such as COD and TOC. If this were the only purpose
for a rate factor as a pollution index, then nothing would be gained
in using it. The advantage of the rate factor comes when considera-
tion of both rate and quantity of material is made. For example, if
a small amount of material is present and there is a high rate of
chemical oxidation then the pollution is caused by a highly oxidiz-
able compound. Or if a high rate of oxidation is obtained when a
very large quantity of material is present, then the pollution can
be characterized as being caused by large amounts of slowly oxidiz-
able material. These characterizations are not presently made in
the current methods of chemical measurements of pollution. Thus,
the advantage of using rates as a measure of the degree of pollution
is obvious and shows the need for a quantity term when indexing
pollution.

Fast Reacting Species Term

Linearity was found when second order plots were made for
eighteen of the thirty compounds included in this study. Eleven
other compounds gave second order plots that have the appearance
of simultaneous reaction of two organic species while pyridine under-
went no reaction.

The appearance of two organic species undergoing reaction can
be explained by assuming the compound was cleaved or oxidized rapidly
to compounds which were further oxidized at a slower rate. For

example, ethanol is probably oxidized to acetic acid which is oxidized very slowly.

Second order plots of the simultaneous reaction of two organic species can be graphically solved by a logarithmic extrapolation method to give the percent of fast reacting species (133). This technique is used in this work to determine the percent of the reaction that undergoes fast chemical oxidation. This result is the third term of the PI and is called the Percent of Fast Reacting Species (%FRS) for the lack of a better denomination. To know that fraction of sample that is undergoing faster chemical oxidation helps to characterize the sample.

Pollution Index

By using: 1) the rate of oxidation as a measure of oxidizability, 2) the total concentration of organic species, and 3) the logarithmic extrapolation technique to determine the fraction of fast reacting species, the organic material of a water sample can now be better described. We propose to call this three term combination the Pollution Index (PI). For example a water sample with the following PI (0.01, 370,35%) would indicate this sample undergoes a chemical oxidation at a maximum determined rate of 0.01 COD per sec, it has a total concentration of 370 COD units and there is a 35% of fast reacting species present. It is my contention that this Pollution Index is useful and meaningful for describing pollution and examples are given in Chapter V.

CHAPTER IV

EXPERIMENTAL

The reagents for the oxidation system, the compounds investi-
gated, the configuration of the equipment, and the procedure for
gathering the data that are needed to determine a Pollution Index
(PI) are described in this chapter.

Reagents for Oxidation System

Sulfuric Acid - (E. I. DuPont de Nemours & Company, Wilmington, Del.)
Reagent grade was used without further purification.

Potassium Dichromate - (J. T. Baker Chemical Company, Phillipsburg,
N. J.) Reagent grade was used without further purification. A 0.25N
solution was prepared by diluting 12.259 grams to 1 liter volume.

Water - The water used in this work was deionized water drawn from
inhouse system.

Formaldehyde Solution - (Mallinckrodt Chemical Works, St. Louis, Mo.)
Reagent grade.

100% T Solution - This solution was prepared by mixing the following:

    333 milliliters of 0.25N potassium dichromate

    667 milliliters of water

    1000 milliliters of concentrated sulfuric acid.

1000 COD Solution - This solution was prepared by adding formaldehyde
to the 100% T Solution until all dichromate was reduced to the Cr(III)
specie.

Organic Compounds Studied

  All compounds were purchased and used without further purification.

α-D-Glucose – (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

Lactose – (Baltimore Biological Laboratory, Baltimore, Md.) Chemical pure.

Acetic Acid – (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

Citric Acid – (J. T. Baker Chemical Company, Phillipsburg, N. Y.) Reagent grade.

t-Tartaric Acid – (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

Malic Acid – (Chem. Service, Inc., Media, Pa.) Purity unknown.

Furoic Acid – (Chem. Service, Inc., Media, Pa.) Purity unknown.

Benzoic Acid – (U.S. Department of Commerce, National Bureau of Standards, Washington, D.C.) Standard Sample 39f.

Salicylic Acid – Source and purity were unknown.

p-Hydroxybenzoic Acid – (Chem. Service, Inc., Media, Pa.) Purity unknown.

Glycine – (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

β-Alanine – (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

DL Trosine – (Nutritional Biochemicals Corporation, Cleveland, Ohio) Purity was highest commercially available, NBC control number 7482.

Valine – (Matheson, Coleman and Bell, Milwaukee, Wisconsin) Fine chemical grade.

α-Amino-isobutyric Acid – (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

Glutamic Acid - (Fisher Scientific Company, Fair Lawn, N. J.) Reagent grade.

Isopropyl Alcohol - (Mallinckrodt Chemical Works, St. Louis, Mo.) Reagent grade.

Ethyl Alcohol - (U.S. Industrial Chemicals Co., New York, N. Y.) Reagent grade.

Catechol - (Chem. Service, Inc., Media, Pa.) Purity not known

5-Me-2-isopropyl Phenol (thymol) - (Mallinckrodt Chemical Works, St. Louis, Mo.) U.S. P XIII crystals.

o-Cresol - (Chem. Service, Inc., Media, Pa.) Purity not known.

m-Cresol - (Chem. Service, Inc., Media, Pa.) Purity not known.

2,4,6-trinitrophenol - (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

2-Naphthol - (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

Benzene - (Mallinckrodt Chemical Works, St. Louis, Mo.) Reagent grade.

Pyridine - (Eastman Kodak Company, Rochester, N. Y.) Reagent grade.

Toluene - (Mallinckrodt Chemical Works, St. Louis, Mo.) Reagent grade.

Cellulose - (W&R Balston Limited, England) No. 1 Whatman filter paper.

Nitrilotriacetic Acid - (J. T. Baker Chemical Company, Phillipsburg, N. J.) Reagent grade.

Demand Reference Sample No. 2 - (United States Environmental Protection Agency, National Environmental Research Center, Method & Performance Evaluation, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268). See Appendix A for further documentation.

Instrumentation

This section describes the instrumentation used to collect the rate data. It is logical to divide the various components into three groups. These are called: 1) the reaction group, 2) the sample transport and monitor group, and 3) the data processing group.

The Reaction Group

The reaction vessel was a 250 ml round-bottom flask with three 24/40 ground glass necks. The first neck contained a 300 mm water jacketed condenser with 24/40 ground glass joint. The second neck contained a -10 to 360°C thermometer with a ground glass collar and the appropriate ground glass reducers that positioned the thermometer bulb just above the stirring bar. The third neck contained either the 24/40 ground glass plug during the addition of the concentrated sulfuric acid or the high temperature sampler during the two-hour reaction period. A 140 watt heating mantle (Glas-Col Apparatus Co.) was used to maintain the reaction mixture at the reflux temperature of 144°C. A magnetic stirrer was used to turn a 3/4 inch glass encased stirring bar.

The Sample Transport and Monitor Group

The high temperature sampler (see Figure 4 for dimensions) was fabricated in the Continental Oil Company glass shop. The sampler performed three functions during the reaction: 1) to continually sample the 50% sulfuric acid solution in the reaction vessel, 2) to cool the reaction solution to room temperature, and 3) to inject air segments
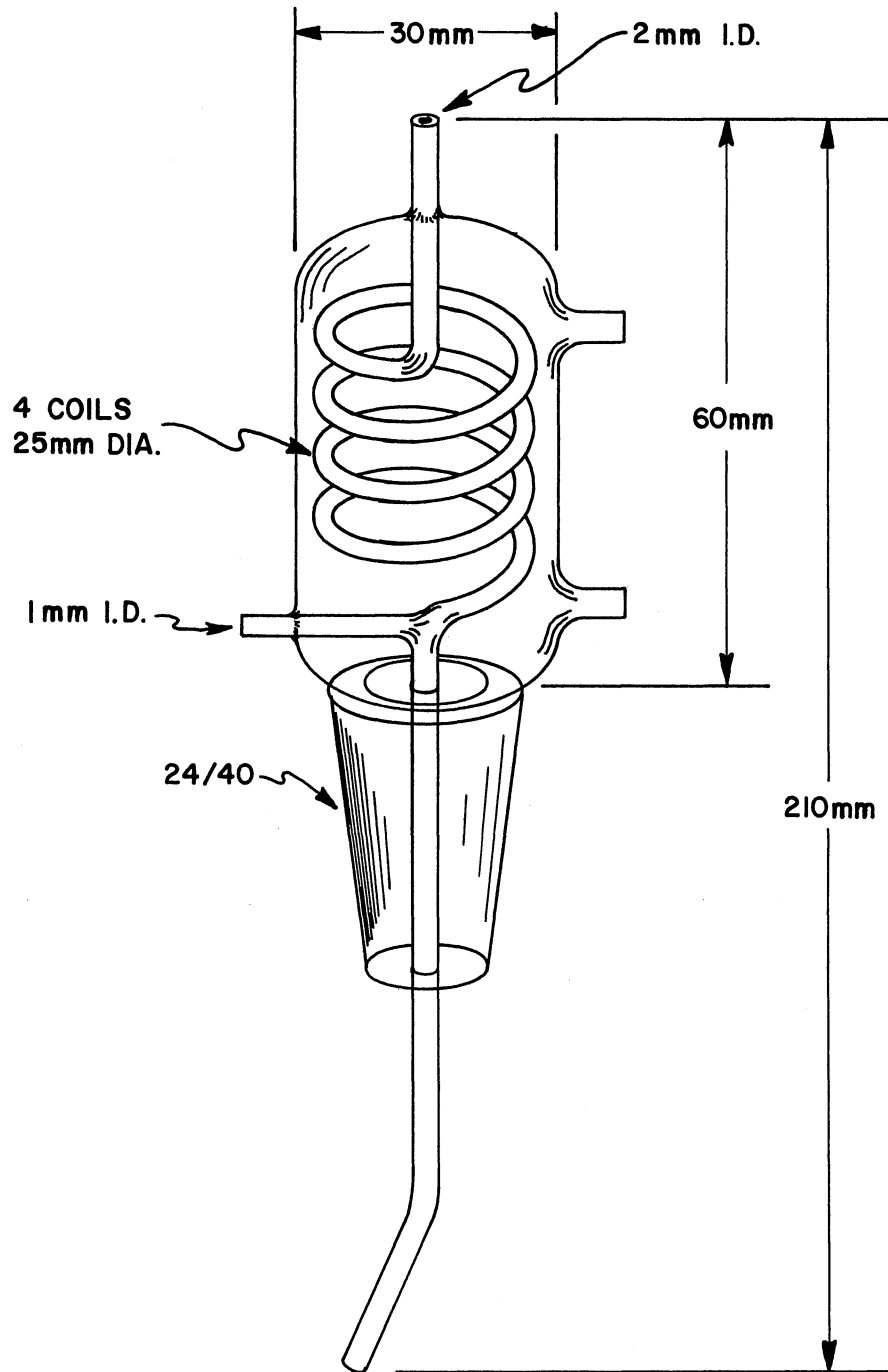
Figure 4. High Temperature Sampler

into the sample stream to form "anti-diffusion air barriers" and "to

provide continual 'wiping' of the tubular system" (134).

A two-speed proportioning pump (Technicon Instruments Corporation,

Part No. 105-A201-01 60 Hz) was used to continually withdraw sample

from the reaction vessel, to inject air into the sample stream, and

to pump the sample through a colorimeter. The flow scheme and the

tube sizes are given in Figure 5. A standard Debubbler T fitting

#C4 (Technicon Instruments Corporation) was used to remove the air

before the sample enters the flow cell of the colorimeter. A tubular

Flow Cell Colorimeter (Technicon Part No. 112-A000-02 15 mm Flow cell)

with 620 mm filters was used to monitor the absorbance changes. A

single channel of a Bristol Double Pen Recorder (Model No. (TC) 64A-

T-2Ph 2 x 570-51) was used to record the analog signal. A scan of

the visible spectrum on a Perkin-Elmer 202 spectrophotometer showed

the wavelength maximum at 610 nm for the Cr(III) specie. Since this

is a broad band, a 620 nm filter was used in the colorimeter for these

experiments.

The Data Processing Group

A general purpose laboratory computer system at Continental Oil

Company was used to handle and calculate data. (See Figure 6 - Block

Diagram of General Purpose Laboratory Computer System.) An analog

signal was generated by a slave potentiometer that was attached to

the balancing mechanism shaft of the Bristol recorder. This signal

was digitized and used by the computer system for further operation.

The components of the computer system used in this investigation
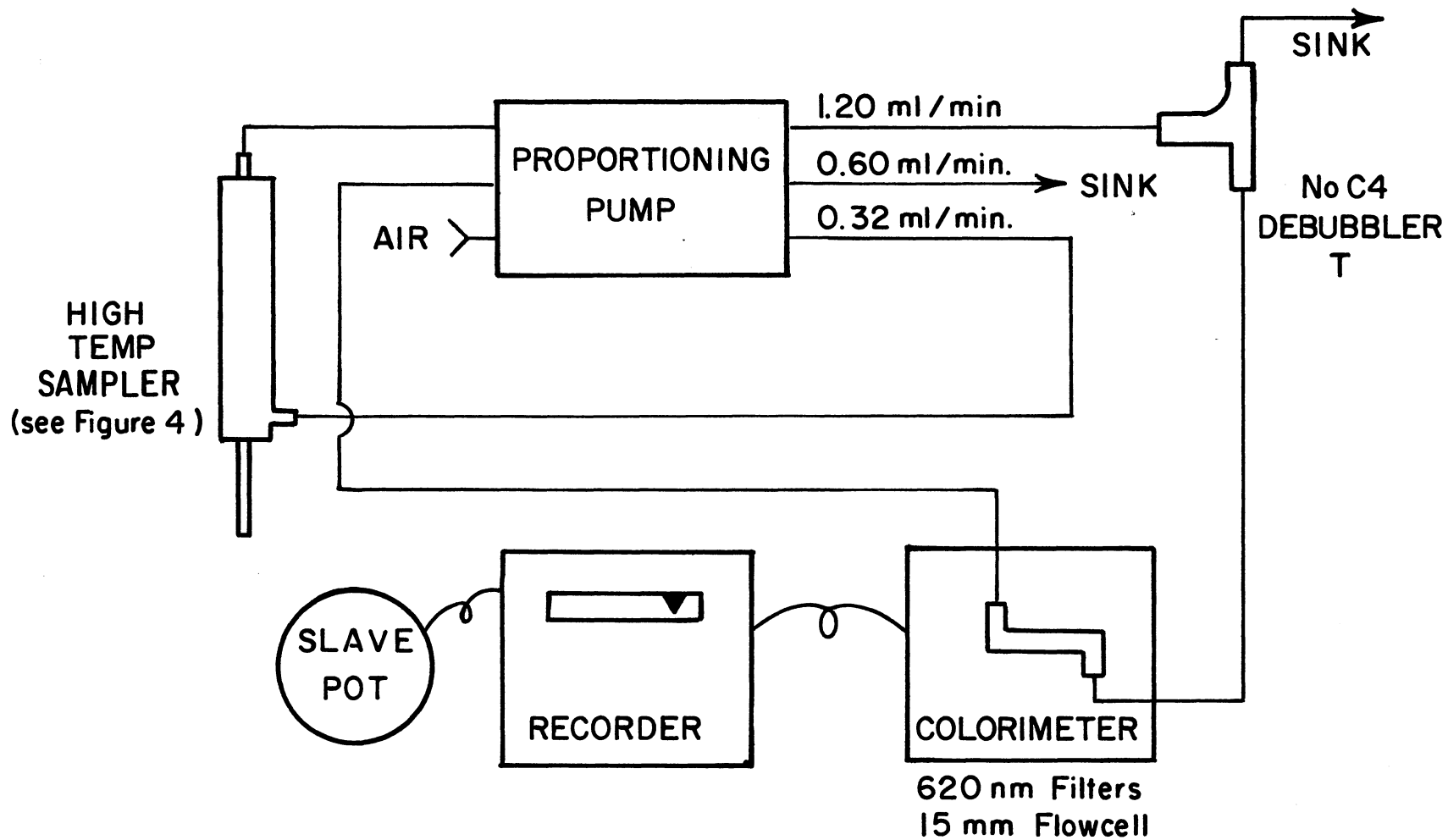
Figure 5. Flow Diagram for Transport and Monitor Group
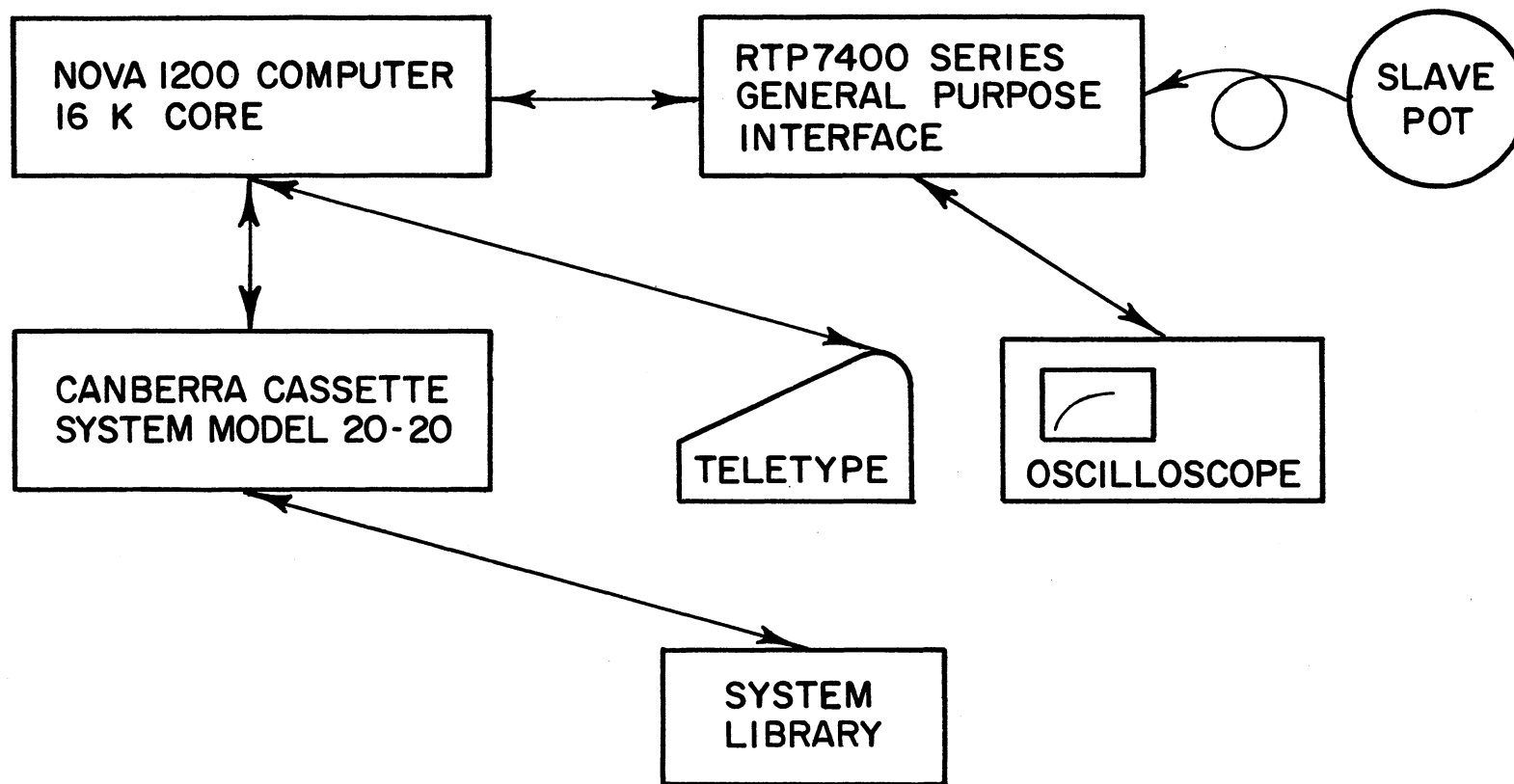
Figure 6.   Block Diagram of General Purpose Laboratory
Computer System

consist of:

1. A Nova 1200 minicomputer with 16 K of core memory. (Data General
    Corporation of Southboro, Massachusetts)

2. The teletypewriter - Model 33TZ (Teletype Corporation, Skokie,
    Illinois)

3. A general purpose interface system - RTP7400 Series Real-Time
    Peripheral Devices (Computer Products of Ft. Lauderdale, Florida)

4. The oscilloscope - 5103N Oscilloscope System (Tektronic, Inc.,
    Beaverton, Oregon)

5. A three-deck cassette storage system Model 2020 (Canberra Indus-
    tries, Meriden, Connecticut)

6. The computer system library (Chemical Analysis Group of Continental
    Oil Company, Ponca City, Oklahoma). This library consists of a
    series of assembler language subroutines designed to service all
    peripheral equipment performing data acquisition and other func-
    tions that are necessary for kinetic measurements. These sub-
    routines and a series of BASIC subroutines are called by BASIC
    programs to perform data collection and processing. These sub-
    soutines and programs are stored on cassette tapes for easy access
    and use.

The following is a description of the operations performed by the
computer system during a test run:

The computer system sampled 234 data points during the first 10 minutes
of the experimental run and then sampled 22 data points at 5 minute
intervals for the balance of the 2 hour oxidation period. Each of
the first 234 points was the result of a single A/D conversion and

each of the remaining 22 points was an average of 256 points taken at 1 millisecond intervals. Each data point as sampled was displayed on the oscilloscope as a transmittance vs. time curve.

After all the data had been collected, a rate plot of absorbance vs. time could be displayed fullscale on the oscilloscope. From this display two points on the rate curve could be selected by using the teletype. Then a least squares linear-fit was calculated using all data between the two selected points. The slope and intercept of this line were printed out along with the absorbance values that were determined at the 5 minute intervals. Finally, the computer system stored all run data on a cassette tape for future recall.

Procedure for Running Sample

The procedure for an oxidation run was as follows: Thirty milliliters of 0.25N potassium dichromate, fifteen milliliters of the 1000 COD stock solution of the compound being studied and 45 milliliters of distilled water were pipetted into the reaction vessel. A glass cap was inserted into the position where the high temperature sampler will be placed after the addition of acid. The heating mantle was positioned and turned on, and the magnetic stirrer was placed into motion. At that time, 90 mls of concentrated sulfuric acid was added by slowly pouring it down the barrel of the reflux condenser. The rate of addition of acid was controlled such that no violent bumping took place within the reaction vessel. The time required for this step varied from 40 to 90 seconds and the temperature of the system reached 135 to 140°C at the end of the addition. The heating mantle

brought the solution to reflux temperature of 144°C.

At the end of the acid addition the high temperature sampler was inserted into the position where the glass plug had been. It was necessary to combine all reagents before insertion of the sampler, since the change in viscosity due to the addition of sulfuric acid creates an unstable baseline. This condition continued until all the acid had been added. Since the colorimeter signal cannot be used until it has stabilized, the sample was inserted after all the reactants have been added.

With the high temperature sampler in position a command was given to the computer to begin data collection. The time for monitoring the reaction was set for two hours with the computer taking 234 data points during the first ten minutes, and 22 data points at five minute intervals thereafter. When the last data point was taken, the slope of the rate curve was determined and was printed out along with the absorbance values of the last 22 data points taken. Either turnaround of the system to process another sample or shutdown of the Reaction Group and Sample Transport and Monitor Group was made to end the run.

CHAPTER V

RESULTS AND DISCUSSION

Selection of Oxidation System

In the selection of an oxidation system the only restriction was
that the reaction must be amenable to monitoring by a spectropho-
tometer. This restriction permits the use of available equipment that
simplifies data collection and handling. Glucose, glutamic acid and
alanine were selected as model compounds that were used in screening
different systems. These compounds were selected because the litera-
ture search indicated differences in their rates of chemical oxidation
in the dichromate system and because glucose and glutamic acid are
used as standards in pollution control work. In initial screening
studies a Coleman 124 Double Beam Spectrometer was employed to follow
the reactions in 1 cm cell while a strip chart recorder was used to
collect the data.

The oxidation system considered and comments regarding short-
comings are given in Table I. The system selected for this work was
sulfuric acid-dichromate, the same one used by W. A. Moore et al. (2).
Its selection came about because of the following reasons: 1) this
oxidation system is familiar to many people because it is part of the
Standard COD Method, 2) it is stable at high temperatures, 3) it reacts
with the three test compounds, and 4) the oxidation reaction is

TABLE I

OXIDATION SYSTEMS

System	Comments
Nitric acid-ceric ammonium nitrate	Contains chromogenic species
Perchloric acid-ceric ammonium nitrate	Does not oxidize all model compounds
Sulfuric acid-ceric sulfate	Does not oxidize all model compounds
Sulfuric acid-potassium dichromate	Oxidizes model compounds at high temp.
Sulfuric acid-potassium permanganate	Undergoes auto-oxidation

colorimetric measurements in the COD test by monitoring the Cr(III)

ion at wavelengths of 586, 600, and 610 nm or monitoring the Cr(VI)

ion at 410 nm (46, 96-98, 100, 104, 135).

<div align="center">

Selection of Organic Compounds

and the COD Quantity

</div>

It was of interest to determine the rate of oxidation of a number

of organic compounds that are typical of those found in sewage waters

(see Table II). All of the compounds selected by W. A. Moore et al.

(2) except for p-cumyl phenol were used in this study. Nitrilotri-

acetic acid was added to the list because of controversial interest as

a substitute for phosphate in detergent formulation (136). The Envi-

ronmental Protection Agency's Demand Sample 2 (High Level) was run

because it was available.

Solutions of each compound were prepared at concentrations equiva-

lent to a theoretical value of 250 mg/liter COD, with the exception of

the EPA Demand Sample 2 which was 370 mg/1 COD as received. In calcu-

lating the amount of material required to produce a 250 mg/liter COD

solution, the assumption was made that the oxidation products of the

organic compound are carbon dioxide, water and ammonia. The two

exceptions are the compounds picric acid and pyridine where the assump-

tion was made that nitric acid is a reaction product instead of ammonia.

It was assumed that the $-NO_2$ functional groups of picric acid are

cleaved to form nitric acid. No rationalization can be given for

pyridine except to say it did not undergo reaction.

A typical sample of a calculation to determine the amount of

compound required for a 250 mg/1 COD is the following for glutamic

TABLE II

DATA FOR COMPOUNDS STUDIED

	Theoretical Concentration of 250 mg/1 COD					
Compound	Maximum Determined Rate dx/dt (COD/Sec)	Standard Method COD	% Fast Species	COD w/o Cat.	TOC as COD	AquaRator COD
Salicylic Acid	4.65	253	100	256	266	251
Lactose	3.75	226	100	231	249	219
Malic Acid	3.60	244	100	273	355	220
Cellulose	3.37	249	100	247	---	---
2-Naphthol	3.24	246	100	260	216	241
+ Tartaric Acid	3.19	235	100	262	389	230
Thymol	3.07	235	100	229	200	262
Tyrosine	2.61	248	100	252	235	234
Catechol	2.53	234	100	238	247	252
Citric Acid	2.48	250	100	262	333	235
Methylhydroxybenzoic Acid	2.47	284	100	268	296	277
Furoic Acid	2.37	266	82	250	310	231
o-Cresol	2.32	235	100	238	242	251
Glucose	1.9	239	100	255	261	219
Isopropanol	1.26	254	64	194	157	228
m-Cresol	1.34	251	87	236	238	282

TABLE II (CONTINUED)

Compound	Maximum Determined Rate dx/dt (COD/Sec)	Standard Method COD	% Fast Species	COD w/o Cat.	TOC as COD	AquaRator COD
Nitrilotriacetic Acid	1.11	216	79	239	357	248
Benzoic Acid	0.79	251	100	270	240	252
Lactic Acid	0.66	214	38	120	255	226
Ethanol	0.64	218	30	88	157	233
Toluene	0.60	214	51	138	294	238
Benzene	0.55	145	43	112	204	238
Picric Acid	0.44	260	100	289	240	126
Valine	0.44	195	72	190	237	298
Glutamic Acid	0.21	234	30	183	277	288
Glycine	0.19	257	14	264	374	371
Methylalanine	0.13	168	30	207	253	325
Alanine	0.01	147	100	98	230	272
Acetic Acid	<0.01	224	100	31	246	236
Pyridine	<0.01	2	100	2	163	195
EPA-2 (370 COD)	0.11	364	61	300	410	345

(Values for COD w/o Cat., TOC as COD, and AquaRator COD are discussed later in this thesis.)

acid. Glutamic acid has the formula $C_5H_9NO_4$ and a molecular weight of 147.13. The oxidation reaction is written as;

$$C_5H_9NO_4 + 4.5O_2 \rightarrow 5CO_2 + 3H_2O + NH_3.$$
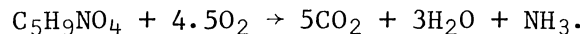
The ratios of the amounts of reactants to their molecular weights can be equated to give the relationship;

$$\frac{Compound\ Wt}{147.13} = \frac{250\ mg/1\ oxygen.}{4.5\ x\ 32}$$

Solution of this algebraic equation yields the compound weight of 0.2554 grams of glutamic acid per liter as the needed quantity.

Analysis of Rate Data

Profile Curves

The first observations show the thirty test compounds can be placed into one of the following categories because of their known concentrations and the extent of reaction after 120 minutes. Either the compound; 1) has reacted to give the theoretical COD value, 2) has reacted to give a value less than theoretical COD, 3) was still undergoing reaction at the end of two hours, or 4) did not react. Table III gives groupings of compounds using this classification. This designation of compounds is interesting but leaves much to be desired in that this classification depends on knowledge of both its concentration and its chemical formula. Therefore, this classification cannot be extended to unknown compounds or systems containing mixtures.

For the purpose of this study a reaction is said to have gone to

TABLE III

CLASSIFICATION BY EXTENT OF REACTION AFTER 120 MINUTES

Completely Reacted	Partially Reacted	Being Reacted	Not Reacted
Salicylic Acid	Benzene	Acetic Acid	Pyridine
Lactose	Valine	Alanine	
Malic Acid	Isopropyl Alcohol	Glycine	
Cellulose	Toluene	Glutamic Acid	
2-Naphthol		Nitrilotriacetic Acid	
+ Tartaric Acid		Methylalanine	
Thymol		Lactic Acid	
Tyrosine		Ethanol	
Catechol			
Citric Acid			
Methylhydroxybenzoic Acid			
o-Cresol			
m-Cresol			
Glucose			
Benzoic Acid			
Picric			

completion when the rate of oxidation was less than 1.1×10^{-3} COD/second. This value was determined by selecting thritten compounds that had completely reacted to their theoretical COD in less than 30 minutes and performing a statistical analysis on their rates of oxidation at time 30 minutes. The 90% confidence interval was found to be $0.9 \pm 0.2 \times 10^{-3}$ COD/sec. The upper limit of this interval was arbitrarily selected to define the condition when no reaction was taking place. It must be pointed out that some compounds such as benzene and acetic acid are undergoing reaction at rates less than 1.1×10^{-3} COD/sec. because when the reactions are catalyzed as in the Standard COD Method higher COD results are obtained (see Table II).

The oxidation reactions of this study were not catalyzed with silver sulfate as specified in the Standard Methods COD test. The catalyst was omitted in order to slow down the faster reactions of compounds such as glucose, 2-naphthol and salicylic acid so that their reactions could be followed over a longer period of time.

Since the rates could not be monitored at the beginning of the reaction because of changing viscosity, initial rates could not be determined. Hence, maximum determined rates were measured at approximately 60 seconds. To determine the reproducibility of the maximum rates, five compounds were selected and rerun. Table IV lists these compounds, the number of runs, the 90 percent confidence interval and the standard deviation of their maximum rates. It should be pointed out that replicate runs were not made on the same day so that day-to-day variations are reflected in the statistics.

TABLE IV

ANALYSIS OF FIVE SELECTED COMPOUNDS

Compound	No. of Runs	Maximum Determined dx/dt (COD/Sec)		% Fast Reacting Species	
		90% Confidence Interval	s	90% Confidence Interval	s
Glucose	3	1.9 ± 0.3	0.20	(100% by definition)	---
Benzoic Acid	3	0.79 ± 0.05	0.028	(100% by definition)	---
Lactic Acid	3	0.66 ± 0.06	0.033	38.4 ± 3.2	1.9
Benzene	3	0.55 ± 0.14	0.075	42.7 ± 8.0	4.7
Glutamic Acid	6	0.21 ± 0.02	0.028	30.4 ± 3.2	1.2

Rate Data Points

In the analysis of the rate data the first twenty-five data

points (covering approximately 60 seconds of time) were not used.

Several rate profile curves for fast reacting compounds appeared to

have a kink during this interval of time (see point b in Figure 7).

The occurrence of this kink can be explained when it is recalled

that the reaction was not being monitored during the addition

of sulfuric acid. This addition required approximately 60 seconds

during which time reaction products were being formed. When the

high temperature sampler was finally inserted, a period of time was

necessary for the constant pump to come to equilibrium. This kink

appears to mark that point in time when the reaction is being moni-

tored at its real rate.

When analyzing the absorbance data several relationships such

as $\ln(x)$, $\ln(a-x)$, $\ln(\frac{1}{a-x})$, and $\ln \frac{b(a-x)}{a(b-x)}$ were plotted against time.

In these natural logrithmic relationships $\underline{a}$ is the concentration of

the compound, $\underline{b}$ is the concentration of potassium dichromate, and $\underline{x}$

is the amount of reacted species. At times greater than 60 seconds,

plots of $\ln \frac{b(a-x)}{a(b-x)}$ vs time are linear and this is indicative of a

second order reaction. When considering that the concentration of

potassium dichromate is 1000 mg/1 COD and that the concentrations of

compounds under study are 250 COD, then second order reactions are

expected. Because second order plots of data are linear, then second

order plots are used in characterizing the organic material.
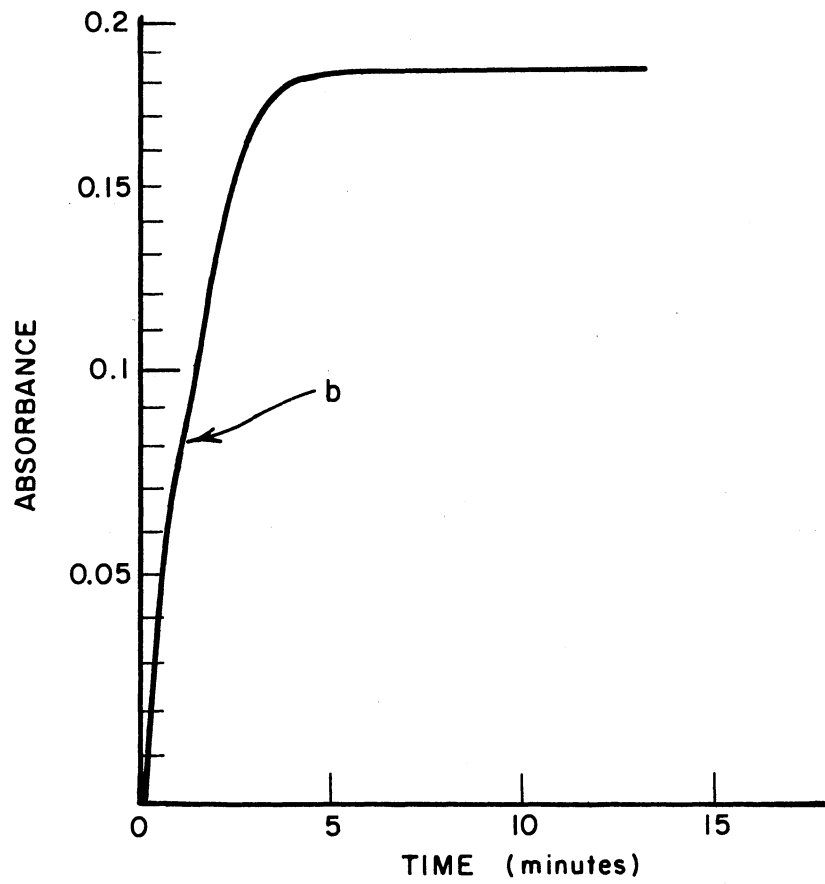
Figure 7.   Rate Profile of Glucose

Measurement of Quantity of Organic Material

From the beginning of this work it was realized that only a few organic materials would be chemically oxidized to yield their theoretical COD values. This fact has caused some confusion to an already complex problem of characterizing a water sample such as sewage water. Therefore in the interpretation of data the choice of COD value to use when making a calculation was most important. Several techniques were available for measuring the quantity of organic material in the prepared solutions. These were Standard COD Method, the Beckman Model 15 Total Organic Carbon Analyzer, the Precision Scientific Company AquaRator, and the COD as determined from absorbance data collected during a sample run. The COD value that is determined from run data is a Standard Method COD without silver catalyst and is designated as COD (w/o cat). Table II gives the values from the various techniques mentioned above for the compounds that were studied.

The column TOC as COD contains total organic carbon data (mg C/l) that was determined on the Beckman TOC Analyzer and then converted to mg/l COD. (The conversion factor used was 2.67 which is the ratio of molecular weights of diatomic oxygen to carbon.) The column AquaRator COD contains data determined on the AquaRator. Since results can be obtained from these instruments in a few minutes, either seemed to be an ideal technique to obtain a quick measurement of quantity of organic material. But statistical analysis of each column of thirty data points shows that for samples with a theoretical COD concentration of 250 mg/l, one can only be 90% confident that their mean

result will fall in the following intervals. For the Beckman TOC Analyzer 259 ± 19 mg/l COD and for the AquaRator 248 ± 13 mg/l COD. The standard deviations were 59.4 for the former and 42.5 mg/l COD for the latter technique. A Variance Ratio test shows that the data obtained on the two carbon analyzer instruments are from different sample population than the COD data. Therefore, their data should not be used as a measure of the term in the PI.

The choice for the COD value when studying known compounds was made in the following manner. The COD (w/o cat) value was used when the compound was completely oxidized and in all other cases the theoretical COD value was used. A compound that is completely oxidized during the sample run has both the Standard Method COD and the COD (w/o cat) values that are equal to the theoretical COD value. To check this definition a statistical analysis of COD values was made for fifteen compounds that were completely oxidized and that had a theoretical COD of 250. The 90% confidence intervals were 248 ± 7.1 mg/l COD for the Standard Method COD values and 225 ± 7.6 mg/l COD for the COD (w/o cat) values. The standard deviations were 15.5 and 16.7 mg/l COD respectively. The results of a student's t test indicate the two means came from the same sample population.

The choice for COD value when studying unknown samples such as sewage water was chosen in the following manner. The COD (w/o cat) value would be used when it was equal to or greater than the Standard COD value. The Standard COD value would be used in all other cases.

Use of Plots to Determine the Percent of

Fast Reacting Species

When second order plots of the absorbance data are made it
appears that the compounds fall into two groups. The first group
appear to be the oxidation of a single organic species and are
arbitrarily designated as having 100 percent fast reacting species
(see Table II). (Pyridine is the only compound in this work that
does not undergo reaction and is arbitrarily placed into this group.)
Figure 8 is a second order plot for glucose and illustrates a com-
pound of this group.

The second group of compounds appear to be the oxidation of two
organic species that have different rates. Figure 9 is a second
order plot for glutamic acid that is used to illustrate a compound
of this group. At reaction times when all the first reacting species
have been consumed only one remains and a straight line is obtained.
This line is extrapolated to the ordinate axis at time t=0 and the
intercept value is used to determine the percent of fast reacting
species. In Appendix B a typical calculation is given for the deter-
mination of the percent of fast reacting species of glutamic acid
is given. Table IV gives the 90 percent confidence intervals and the
standard deviations for the percent of fast reacting species for three
compounds. It is pointed out that day-to-day variations are included
in these statistics. With the first group of compounds defined as
having 100 percent fast reacting species then a group classification
can be dropped. The term for percent of fast reacting species now
describes the organic material.
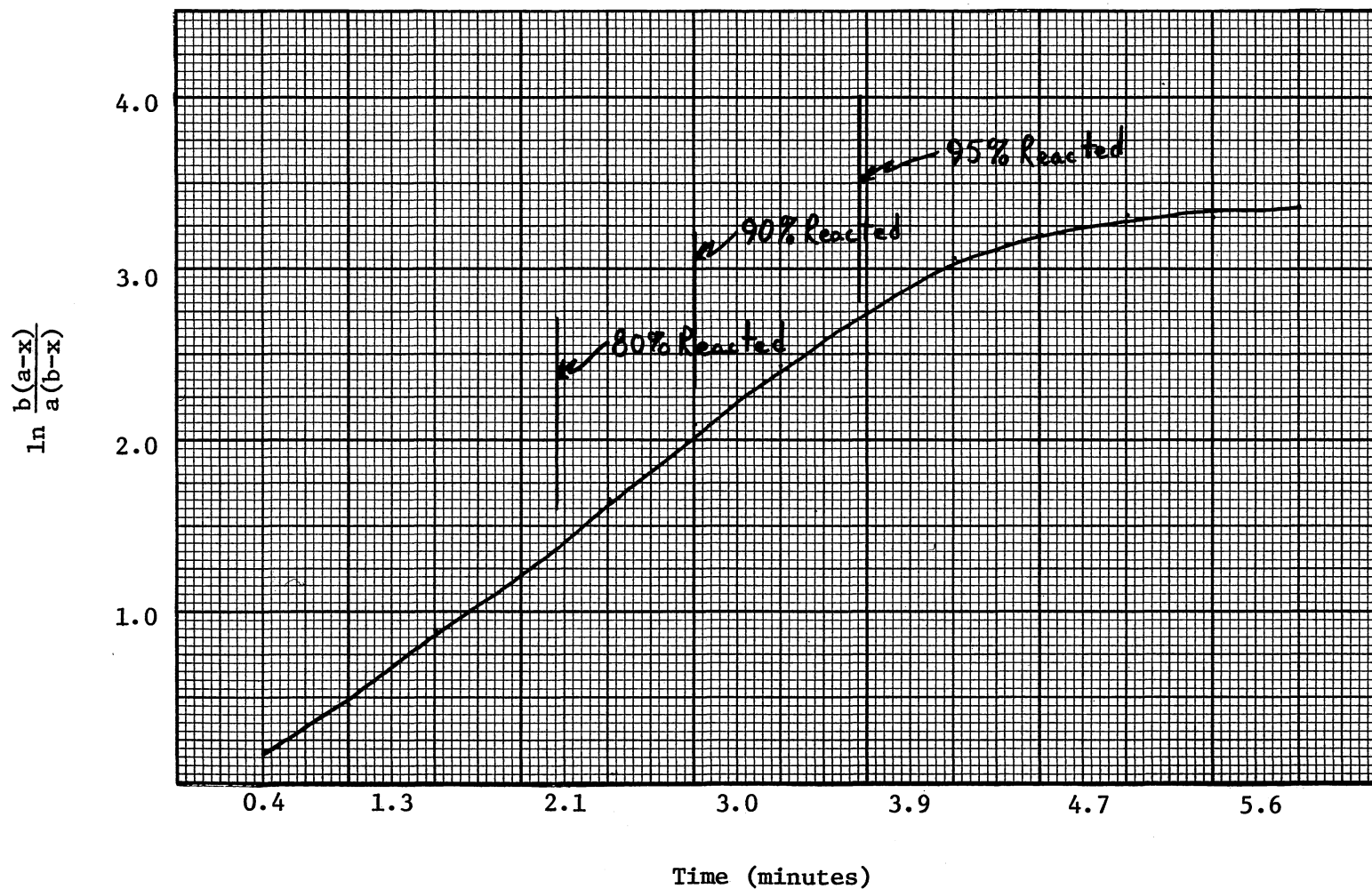
Figure 8. Second Order Plot of Glucose
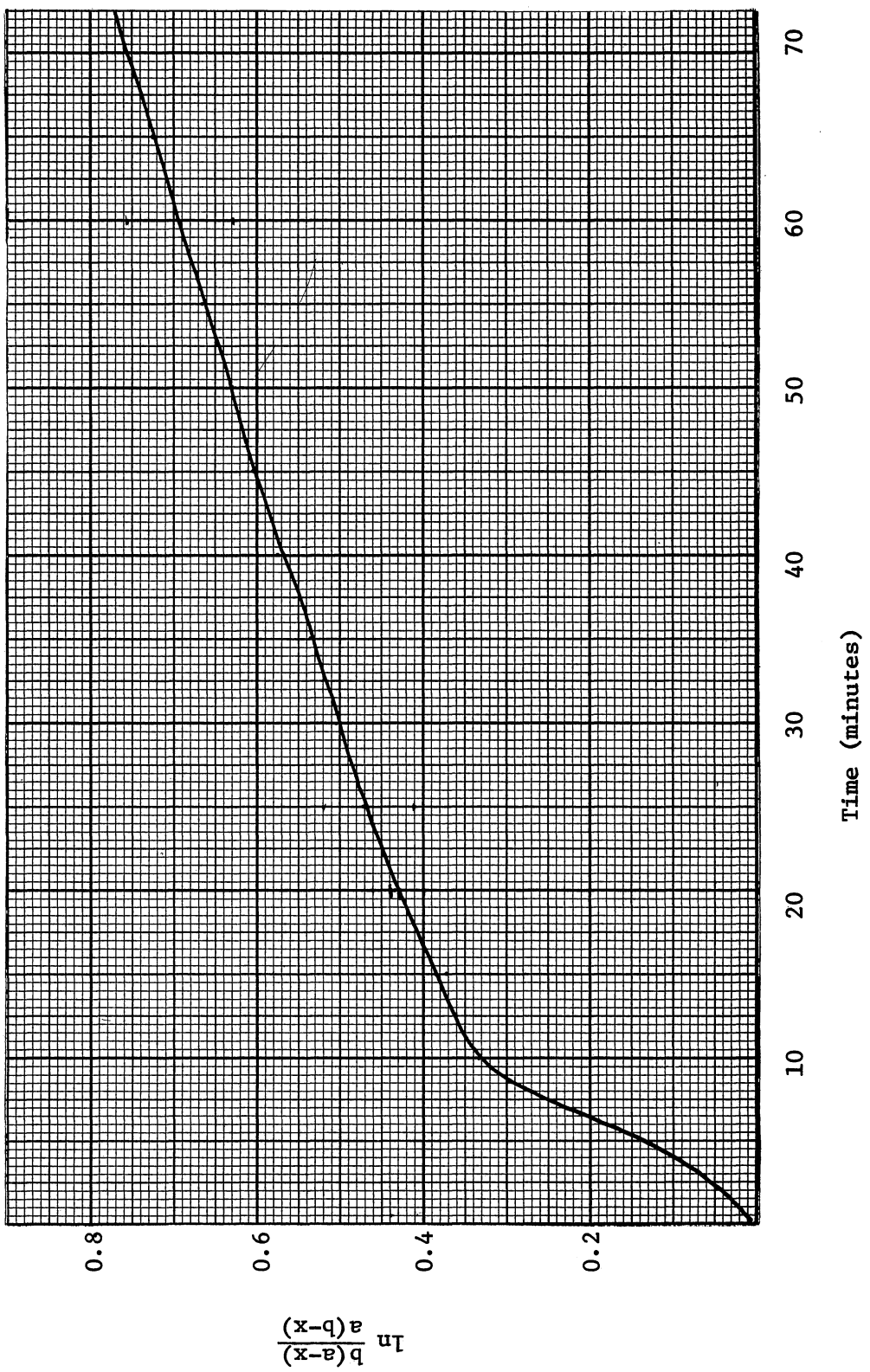
Figure 9. Second Order Plot of Glutamic Acid

Pollution Index

The first three columns of data in Table II are the values for
the three terms that are used to describe the organic pollution of a
water sample. For example, in this work glutamic acid would have a
Pollution Index (PI) of (0.21, 234, 30%). An unknown water sample
with this PI is characterized as a mixture that undergoes dichromate
oxidation at a maximum rate of 0.21 COD per second, the total concen-
tration of material is 234 mg/l COD and a 30% fast reacting species
is present.

For a system being continuously monitored, a change in the PI
could be used to qualitatively characterize the nature of the change.
To illustrate the usefulness of the PI in indicating a change in the
type of material an experiment using salicylic acid and glycine was
conducted and the results are given in Table V. The concentration
for the various mixtures of these compounds was 500 mg/l COD. Inspec-
tion of the results shows that neither COD values nor Biochemical
Oxidation Demand (BOD) values can distinguish differences. Only the
terms of rate of chemical oxidation and of the percent of fast reacting
species can show that real differences exist in these systems. This
shows the ability of the PI to detect changes in the type of organic
material that can be taking place, changes not detected by present
chemical and biological methods.

Pollution Index of Sewage Samples

It was of interest to extend the concept of the Pollution Index
to unknown mixtures. The rate and quantity terms can be determined

TABLE V

POLLUTION INDEXES OF MIXTURES

Theoretical Concentration of 500 mg/1 COD		
Ratio Glycine to Salicylic Acid	PI	Standard Method BOD
1:0	(0.27, 505, 16%)	339
4:1	(1.15, 517, 32%)	303
1:1	(2.55, 519, 54%)	354
1:4	(4.27, 529, 81%)	309
0:1	(6.26, 539, 97%)	315

for unknown samples and so success depended on the determination of the third term. Primary Reactor Effluent and Final Reactor Effluent samples that were taken at the Pollution Control Center, Ponca City, Oklahoma, on each of two days were used as test samples.

Even though sewage waters contain a mixture of compounds, the second order plots of the reaction did give the appearance of two reacting species being present. Figures 10 and 11 are plots for a Primary Reactor Effluent and Final Reactor Effluent waters and the flags on the plots indicate the extent of the reaction. For example, "80%" indicates that 80 percent of the reaction has been completed at that time. Another run of sewage samples that were taken another time give similar plots. Since the second order plots appear linear for 80 to 90 percent of the reaction, then a percent of fast reacting species can be determined. Therefore a Pollution Index for sewage samples can be written. The results for these samples are given in Table VI.

<h2 style="text-align:center">Summary</h2>

An attempt has been made to develop a new approach to describe the nature of pollution in sewage waters. This three term designation is called a Pollution Index (PI) and consists of the maximum determined rate of oxidation (COD/sec), a measure of the quantity of material present (COD), and the percent of fast reacting species. The rate term is the maximum slope of a rate profile curve that is determined by continuously monitoring an uncatalyzed sulfuric acid-dichromate reflux oxidation. The quantity of organic material is
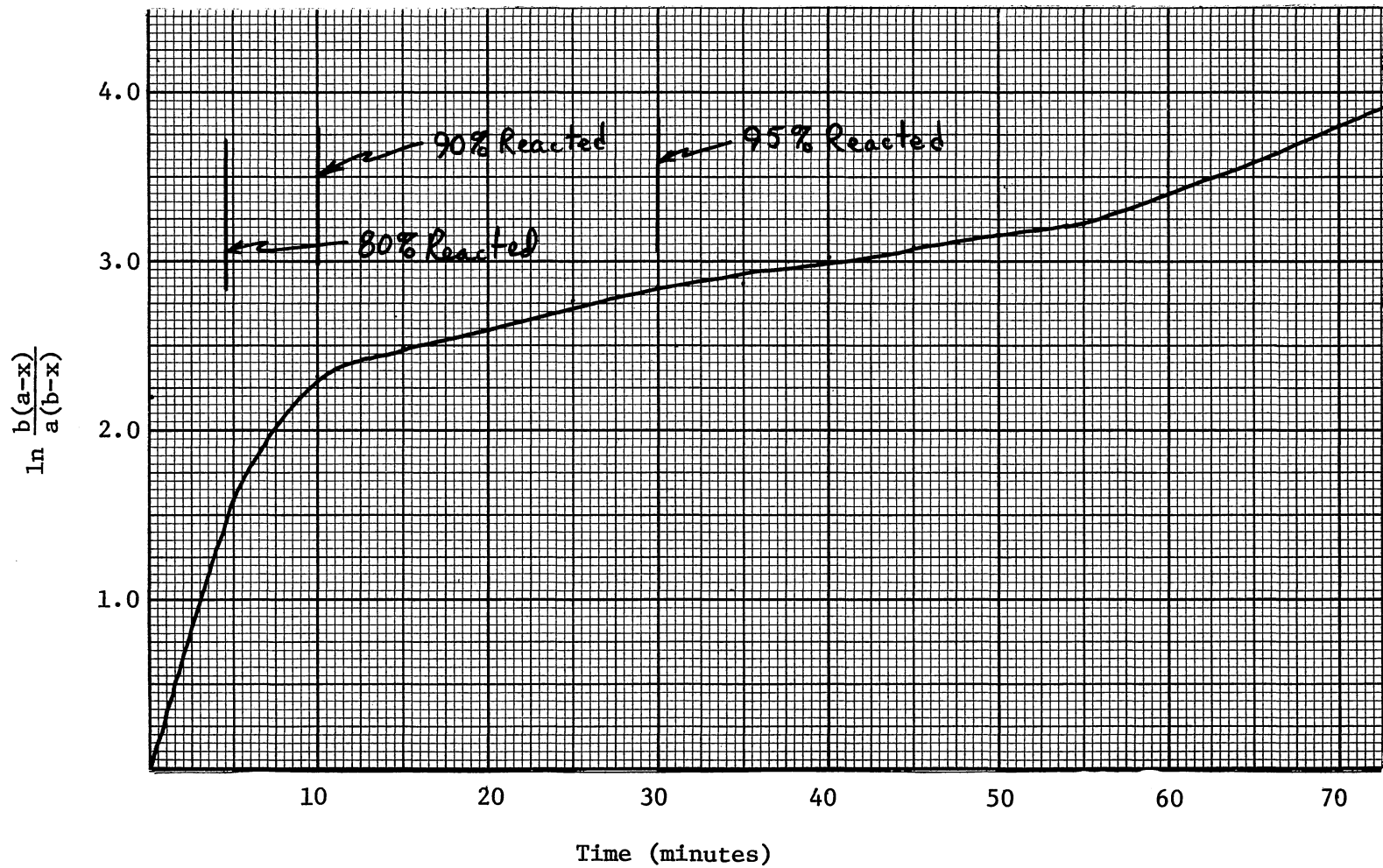
Figure 10. Second Order Plot of Primary Reactor Effluent
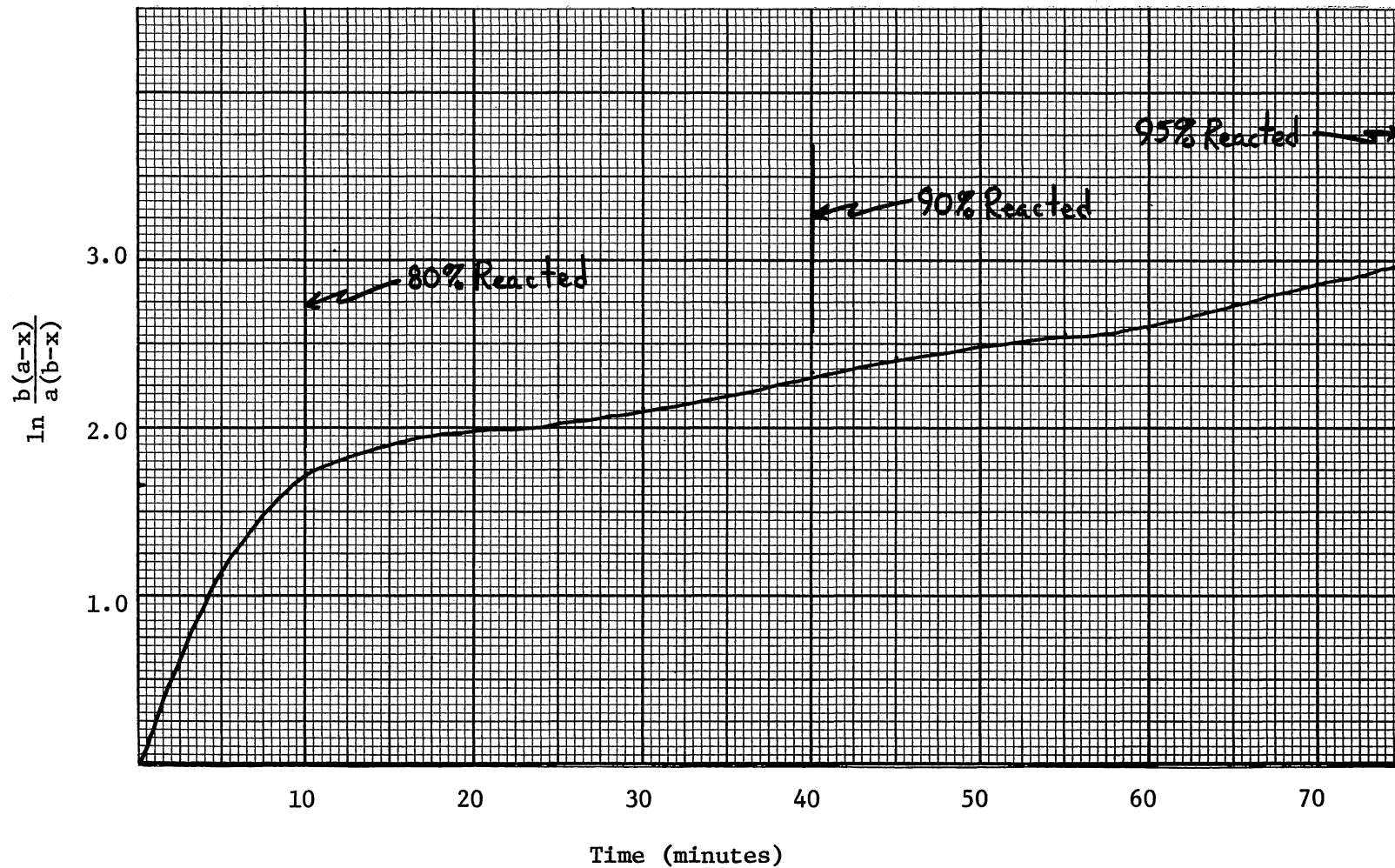
Figure 11. Second Order Plot of Final Reactor Effluent

TABLE VI

POLLUTION INDEXES OF SEWAGE SAMPLES

Sample	PI	Standard Method COD
Primary Reactor Effluent		
27 Feb	(0.81, 169, 91%)	---
1 Mar	(0.48, 129, 64%)	160
Final Reactor Effluent		
27 Feb	(0.26, 61, 82%)	---
1 Mar	(0.36, 68, 68%)	62

measured by the Standard COD Method. The last term is determined by a graphical logarithmic extrapolation method and gives that fraction of material that is oxidized at a fast rate. By considering the rate of chemical oxidation and the quantity of material present then the nature of the pollution can be described, such as being highly oxidizable or slowly oxidizable. Further characterization can be made by knowing the percent of material that undergoes fast reaction.

Recommendations for Future Work

Further investigations are needed to determine whether or not pseudo-first order reactions can be achieved by increasing the concentration of potassium dichromate. If this can be done, then the mathematical analysis of data would be greatly simplified which would generate wider interest.

Another recommendation is to develop instrumentation to monitor the initial stage of the reaction. Equipment used in this work was slow in that; 1) before any sampling of the system was made, 40 to 60 seconds were needed for the addition of sulfuric acid and 2) a time of approximately 2 minutes and 40 seconds was needed to transport the sample to the colorimeter for absorbance measurements. Equipment designed to reduce this time could bring a time window in which pseudo-first order reaction may be occurring at the presently used concentration of potassium dichromate.

The ultimate goal would be a "proportionality constant" to characterize, independently of concentration, the normal effluent to a sewage plant. If this can be realized then a change in the

proportionality constant above would be indicative of a change in the character of material.

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APPENDIX A

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
National Environmental Research Center
Method & Performance Evaluation
Analytical Quality Control Laboratory
Cincinnati, Ohio 45268

Demand REFERENCE SAMPLES

True Values, mg/liter

Parameter	Sample 1	Sample 2
Organic Carbon[1]	4.0	145
Chemical Oxygen Demand[2]	10.3	370
Biochemical Oxygen Demand[3]	3.1	186

[1] The calculated theoretical levels of organic carbon produced in these samples by dissolving the weighed amounts of high purity reagents in distilled water.

[2] The calculated theoretical COD values obtained by complete oxidation of the samples to carbon dioxide, water, and ammonia. In actual practice, the theoretical values are very difficult to attain.

[3] The concentrations given for BOD are theoretical demands based on reported values in *Standard Methods* using river water as seed. These values may or may not be reproducible in a specific laboratory because of natural variability of the seed organisms from sample to sample.

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INSTRUCTIONS FOR *Demand* REFERENCE SAMPLES

CAUTION: Read Instructions Carefully Before Opening Ampuls

The requested set(s) of two water sample concentrates are enclosed in this package. The concentrates were prepared by dissolving known amounts of analytical reagent-grade glucose and glutamic acid in distilled water. Each concentrate can be analyzed for biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC).

When diluted according to instructions, the organic carbon values will be in the range of normal surface water, and domestic sewage, respectively.

The concentrates were preserved by autoclaving the sealed ampuls. Repeated analyses over a period of weeks verify that the concentrations are correct and that the samples are stable. However, the concentrates must be diluted and analyzed immediately after the ampuls are opened to avoid degradation of the compounds.

When you are ready to begin the analyses, open each ampul by snapping the top off at the break area on the neck and dilute the concentrates as follows:

Sample 1 (Low Level)

Biochemical Oxygen Demand - Dilute 8 ml of Concentrate 1 to volume in a 2-liter volumetric flask using a natural surface water. If the natural water BOD is expected to exceed 4 mg/liter, dilute the natural water 1:1 with distilled water before preparing samples. This constitutes the sample now ready for analysis.

Chemical Oxygen Demand and Total Organic Carbon - Dilute 5 ml of Concentrate 1 to volume in a 500 ml volumetric flask with distilled water.

Sample 2 (High Level)

Biochemical Oxygen Demand - Dilute 5 ml of Concentrate 2 to volume in a 250 ml volumetric flask using distilled water. This constitutes the sample now ready for analysis. Dilute as required. Use a natural surface water or domestic sewage as seed.

Chemical Oxygen Demand and Total Organic Carbon - Dilute 15 ml of Concentrate 2 to volume in a 500 ml volumetric flask with distilled water.

Be sure to determine the BOD's of a dilution series of the seeding material so that the proper seed correction can be made (See *Standard Methods*).

$$* \quad * \quad * \quad * \quad * \quad * \quad *$$

The primary function of this sample series is to provide a quality control service to the analyst. No statistical evaluation nor formal report is planned. The analyst is not required to submit results but we encourage the return of analytical data to the M&PE Activity as a continuing check on long-term stability of samples.

A sealed envelope containing the statement of true values is enclosed with these instructions for use as you desire. If there are any questions or problems, please contact:

John A. Winter or Harold A. Clements
Method & Performance Evaluation Activity
Environmental Protection Agency, NERC
Analytical Quality Control Laboratory
Cincinnati, Ohio 45268

Phone: Area Code 513, 684-2917
                           684-2983

APPENDIX B

DETERMINATION OF PERCENT OF FAST REACTING SPECIES

To determine the percent of fast reacting species the following two steps were taken: 1) the construction of a second order plot for the determination of an intercept value and 2) the solution of an algebraic equation to give the fraction of fast reacting species.

Construction of Second Order Plot

A second order plot of $\ln \frac{b(a-x)}{a(b-x)}$ vs time was made using absorbance units for concentration values. The absorbance value for $\underline{a}$ was equal to 0.394 and is equivalent to the amount of dichromate (1000 mg/l COD) in a reaction solution. This is an average value determined by reducing all the Cr(VI) species to Cr(III) and measuring its absorbance. The value for $\underline{b}$ was the absorbance value equal to the concentration of the organic material. Its value was either a maximum absorbance or an absorbance value calculated from the COD value and was selected in one of two ways as defined in the section Measurement of Quantity of Organic Material in Chapter V. The values for $\underline{x}$ were the various absorbance values measured during the course of the reaction.

A computer program LNPLT2 (see Appendix C) was used to calculate and to print out the $\ln \frac{b(a-x)}{a(b-x)}$ values and coded times. These values were plotted on graph paper using the abscissa axis for time and the ordinate axis for the natural logarithmic term. The

straight line that was formed during the time period of the slow

reacting species was extrapolated back to time t=0 (see Figure 10

for a typical plot). The intercept determined was used in calcula-

ting the percent of fast reacting species.

Solution of the Algebraic Equation

The following algebraic equation;

$$INT. = \ln \frac{b(a-F)}{a(b-F)} \qquad (1)$$

and its theory can be found in textbooks that deal with kinetics of

chemical reaction (133). In this equation, INT. is equal to inter-

cept value, a and b are defined in the section above, and F is

equal to that fraction of b that is the fast reacting component.

By solving for F and evaluating the following equation;

$$\% \ FRS = (F/b) \times 100 \qquad (2)$$

the percent of fast reacting species is found. As an example, the

intercept value in Figure 10 for glutamic acid is 0.31. The a value

is equal to 0.394 and b is equal to 0.099. In solving equation 1,

F is found to equal 0.032 absorbance units. Therefore, solving

equation 2 yields % FRS = 32.6.

APPENDIX C

COMPUTER PROGRAM TO CALCULATE
LOGARITHMIC TERM

```
100   REM        2 APR 75 AEG
105   REM        LØGPLT---TØ CALCULATE DATA FØR 2ND ØRDER PLØT
110   DIM A[255],B[255]
111   FØR R=1 TØ 5
112     PRINT
113   NEXT R
115   PRINT "  INPUT RUN NUMBER FØR CALCULATIØN"
120   INPUT X1
125   IF X1>130 GØTØ  115
130   CALL 6,3,10, 0,A[ 0]
135   IF X1= 0 GØTØ  115
140   CALL 6,3,10,1,A[ 0]
145   CALL 6,3,255,1,B[ 0]
150   IF A[ 0]=999 GØTØ  270
155   IF A[ 0]<>X1 GØTØ  140
160   PRINT
165   PRINT A[ 0]
166   PRINT
167   LET C= 0
168   FØR I= 0 TØ 255
169     IF C>B[I] GØTØ  171
170     LET C=B[I]
171   NEXT I
172   PRINT "  MAX ABSØRB IS ";C,I
173   PRINT
174   PRINT " DØ YØU WANT TØ USE STD CØD?"
175   PRINT " 1 = YES, 0 = NØ"
176   INPUT Y
177   IF Y= 0 GØTØ  190
178   PRINT
179   PRINT " INPUT STD CØD"
180   INPUT C
185   LET C=C*.3945/1000
190   LET D=.8*C
195   LET I= 0
199   IF I>255 GØTØ  271
200   IF D<B[I] GØTØ  211
205   LET I=I+1
210   GØTØ  199
211   PRINT
212   PRINT "  .8*MAX ABSØRB IS  ",I,B[I]
213   GØTØ  400
215   PRINT
216   IF I<235 GØTØ  228
217   GØTØ  275
220   PRINT
225   PRINT
226   GØTØ  232
```

```
228    LET M=I/14
229    LET E= INT (M)
230    IF E>1 GOTO  232
231    LET E=1
232    LET P=20
233    FOR N=1 TO P
234      LET J= INT (N*M+.5)
235      LET A=.3945-B[J]
240      LET B=C-B[J]
245      LET L= LOG ((C/.3945)*(A/B))
250      PRINT J,L
255    NEXT N
265    GOTO  301
270    STOP
271    PRINT
272    PRINT " 0.8*MAX ABSORB>>B(256)"
274    PRINT
275    LET I=117
276    PRINT I, LOG ((C/.3945)*((.3945-B[I])/(C-B[I])))
277    FOR J=234 TO 254
280      LET A=.3945-B[J]
285      LET B=C-B[J]
290      LET L= LOG ((A/B)*(C/.3945))
295      PRINT J,L
300    NEXT J
301    PRINT
302    PRINT " RECALCULATE? YES=1,NO=0"
303    INPUT T
304    FOR R=1 TO 5
305      PRINT
306    NEXT R
307    IF T=1 GOTO  165
308    PRINT
309    PRINT " STOP AND GOTO 320"
310    LET X1=X1+1
311    GOTO  140
315    STOP
320    PRINT " INPUT RUN NUMBER"
325    INPUT X1
330    GOTO  135
335    STOP
400    LET U=.9*C
405    LET V=.95*C
410    LET W= 0
415    IF U<B[W] GOTO  430
420    LET W=W+1
425    GOTO  415
430    PRINT " .9*MAX ABSORB IS "W,B[W]
431    LET W= 0
435    IF V<B[W] GOTO  450
440    LET W=W+1
445    GOTO  435
450    PRINT " .95*MAX ABSORBIS "W,B[W]
455    GOTO  215
```

VITA $\mathcal{2}$

Anton Elbert Goodwin

Candidate for the Degree of

Master of Science

Thesis: A "POLLUTION INDEX" FOR CHARACTERIZING SEWAGE WATERS

Major Field: Chemistry

Biographical:

   Personal Data: Born in Kingfisher, Oklahoma, November 16,
        1935, the son of Anton Eble and Mary Lucile Goodwin.

   Education: Attended grade school in Wichita, Kansas and
        Enid, Oklahoma; graduated from Enid High School in
        1954; received the Bachelor of Arts degree from
        Phillips University, with majors in Mathematics and
        Chemistry in June, 1958; completed requirements for
        Master of Science degree via Talk-Back Television in
        July, 1975.

   Professional Experience: Member of the American Chemical
        Society; worked three years as analytical chemist for
        Doughnut Corporation of America, Hillsdale, Michigan;
        worked six years as analytical and refinery chemist in
        Manufacturing Department of Continental Oil Company;
        worked the past six years as analytical chemist in
        Research Services Division, Research and Development
        Department of Continental Oil Company, Ponca City,
        Oklahoma.