

AN ABSTRACT OF THE THESIS OF

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Methods for the detection and measurement of waste materials in water have lagged far behind the many complex problems facing workers in the water pollution field. The present study introduces a new method for the detection and measurement of organic pollution in water. This new method, the persulfate oxidation, is compared with other methods already adopted for the measurement of organic pollution in water.

A wide variety of pure organic compounds that were considered representative of substances found in sewage were analyzed by the persulfate oxidation procedure. Excellent carbon recoveries were obtained for single compound solutions as well as multiple compound mixtures of water-soluble carbohydrates, organic acids, alcohols

and amino acids in dilute solution.

By analyzing dilute glucose solutions and more complex prepared synthetic sewages, as well as raw domestic sewage and trade waste, it was found that the 5-day BOD could be predicted from data obtained from the POC method. It was necessary, however, to derive a different regression coefficient for the raw domestic and trade wastes than was used for the prepared synthetic wastes. A statistical analysis of the data obtained revealed a positive correlation of 0.998 between the POC and the 5-day BOD. In addition, there was only a 3 per cent coefficient of variation for the data obtained by the persulfate method compared to a 10 per cent coefficient of variation for the 5-day BOD.

The predicted 5-day BOD (BOD_C) obtained from the persulfate oxidation was compared with the chemical oxygen demand (COD) and the total carbon (TOC) procedure. It was subsequently determined that the persulfate oxidation measured only a fraction of the carbon oxidized by the COD or TOC methods. In addition, wastes of similar chemical composition exhibited constant and characteristic COD/ BOD_C ratios. There was, however, no evidence to support any relationship between TOC and BOD_C . It was felt significant that the BOD_C based upon the POC levels

provided data equally as useful as that obtained by the classical 5-day BOD.

The identity of persulfate oxidizable carbon was only partially elucidated. It has thus far been determined that the POC fraction comprises a greater carbon fraction than is oxidized during the 5-day BOD, but is considerably less than is measured by either the COD or the TOC procedures. The carbon fraction measured by the persulfate was, however, identified as the carbon fraction oxidized biochemically during first stage aerobic stabilization.

PERSULFATE OXIDIZABLE CARBON AS AN INDEX OF ORGANIC
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TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	2
Biochemical Oxygen Demand	2
Chemical Oxygen Demand	5
Persulfate Oxidation	9
Total Carbon	13
EXPERIMENTAL METHODS	14
Sampling	14
Analytical Procedures	15
The Persulfate Oxidation	15
The Biochemical Oxygen Demand	17
The Chemical Oxygen Demand	18
Persulfate Oxidizable Carbon Recoveries	19
Comparison of POC and 5-day BOD	20
Correlation of POC and 5-day BOD	21
The Total Carbon Determination	22
Comparison of POC, COD and TOC	23
Aerobic Stabilization of POC	24
EXPERIMENTAL RESULTS	28
Carbon Recoveries by Persulfate Oxidation	28
Comparison of POC and 5-day BOD	31
Correlation of POC and 5-day BOD	36
Synthetic Sewage	36
Domestic and Industrial Wastes	40

	Page
Concentrated Composite Waste	41
Comparison of POC, COD and TOC	44
Calibration	44
Domestic and Industrial Wastes	46
Aerobic Stabilization of POC	50
DISCUSSION	57
SUMMARY	63
BIBLIOGRAPHY	64

LIST OF FIGURES

	Page
1. Combustion-diffusion vessels for persulfate oxidation	15a
2. Activated sludge apparatus	25
3. Standard curve for synthetic sewage	37
4. Standard curve for synthetic and domestic sewage	40a

LIST OF TABLES

	Page
1. Persulfate oxidation of water soluble organic substrates	11
2. Reagents used for the persulfate oxidation	16
3. Carbon recoveries by persulfate oxidation of organic compounds with 50 ml combustion flasks	29
4. Carbon recoveries by persulfate oxidation of organic compounds with 125 milliliter combustion flasks.	30
5. Carbon recovered by persulfate oxidation of mixed organic compounds in dilute aqueous solution	32
6. Actual and calculated 5-day BOD for various levels of glucose carbon	34
7. Actual and calculated 5-day BOD for synthetic sewage	35
8. Actual and predicted 5-day BOD for synthetic sewage	38
9. Actual and predicted 5-day BOD for synthetic sewage	39
10. Actual and predicted 5-day BOD of domestic and industrial wastes	42
11. Actual and predicted 5-day BOD of a concentrated composite domestic waste	43
12. Observed carbon recoveries by the COD test	45
13. Comparison of BOD _C , COD and TOD for domestic and industrial wastewaters	47
14. Comparison of BOD _C , COD and TOD for a concentrated composite domestic wastewater	49
15. Activated sludge digestion of a mixed industrial and domestic wastewater	51

	Page
16. Activated sludge digestion of a composite domestic wastewater with added cellulose . . .	53
17. Activated sludge digestion of raw domestic wastewater	55

PERSULFATE OXIDIZABLE CARBON AS AN INDEX OF ORGANIC POLLUTION IN WASTEWATER

INTRODUCTION

Throughout history one of the important factors contributing to the deterioration and eventual fall of great empires has been the abuse and subsequent lack of adequate water supplies. In addition, many of the devastating epidemics that plagued the peoples of past time may be traced to the consumption of polluted water.

Today many parts of the United States are faced by the same water crises known to those of past ages. Many of the streams, lakes and rivers that serve as domestic water supplies are grossly polluted by dangerous levels of domestic and industrial wastes. Methods for the detection and measurement of waste materials in water have lagged far behind the many complex problems facing workers involved in the water pollution field.

Methods for the determination of pollution in water may be broadly classified into two groups, those measuring chemical pollution and those measuring biological pollution. The study presented in this text introduces a new method for the detection and measurement of organic pollution in water. This new method, the persulfate oxidation, is compared with and evaluated in the light of other methods already adopted for the study of organic pollution in water.

HISTORICAL

Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) has become the classical and time honored method for the measurement of organic pollution in water. This procedure is used as the yardstick for the design of sewage treatment processes and the tool by which the efficiency of organic loading rates are determined. As Phelps (24, p. 62) reported, the BOD "has become the most useful single determination in the routine examination of sewage and the effluents of sewage-treatment plants."

The BOD determination was conceived in 1870 by Sir Edward Frankland (30, p. 2-3) who believed that the oxidation of organic materials in streams was a purely chemical reaction. Frankland observed the rate of oxygen loss from polluted waters stored in bottles. It was noted that the oxygen loss progressed in an orderly fashion and that time was an important factor in the purification process. On the basis of these observations Frankland stated, "There is no river in the United Kingdom long enough to effect destruction of sewage by oxidation." A second early worker, Dupré in 1884 (30, p. 3-4) recognized the observed oxygen depletion of stored water samples to be due to the activity of microorganisms, which he termed microphytes. He found

that in the absence of microorganisms little or no oxygen was consumed. In 1927 Theriault (30, p. 2-54) reviewed these early investigations and the subsequent development of the BOD test. Major citations included the works of the British as published in the Reports of the Royal Commission on Sewage Disposal, and in the United States, the Committee Reports of the American Public Health Association. In the United States, Hoover (13, p. 312) reported the use of a permanganate oxygen demand test in conjunction with the BOD for the analysis of pollution in water. In this regard, Hoover has been accredited by Phelps (23, p. 532) as the first investigator to successfully apply the chemical oxygen demand test in America.

Lederer (16, p. 882-888), following extensive studies with the dilution BOD method, concluded that the oxygen demand varied with the dilution and was, therefore, of only limited value. As a result, Lederer (15, p. 482-497; 16, p. 882-888) developed a method that utilized the oxygen of saltpeter during incubation rather than the dissolved oxygen contained in water. It was suggested that the saltpeter BOD might be superior to the dilution method used by the British. He went on to conclude that when proper dilutions were prepared the two methods did not markedly differ. However, Mohlman, Edwards and Swope (17, p. 242) in 1928 pointed out that the variable results obtained by Lederer

with the dilution method were probably due to the use of unsatisfactory dilution water. These workers referred to the work of Theriault and Hommon (29, p. 72-77) who had explained some of the difficulties encountered with the dilution method and had advocated the use of a slightly undersaturated dilution water. Mohlman, Edwards and Swope (17, p. 242-243, 246) also presented data to show that the nitrate method gave lower results than did the dilution BOD, and that the nitrate BOD technique did not indicate demand during the nitrification stage. Furthermore, these investigators explained that the dilution method had become far more accurate with the introduction of improved techniques. The conclusion reached was that the dilution method was quite satisfactory when proper precautions in technique were observed. Thus the use of a standard aerated distilled dilution water with added inorganic salts was suggested.

In 1928 Sierp (28, p. 247) introduced a method that placed nondilute wastes in contact with pure gaseous oxygen. The biochemical oxygen demand was determined by the amount of gas absorbed during a given time at a constant temperature. The oxygen absorption method led to the manometric procedure of Wooldridge and Standfast (34, p. 141-148). In 1936 these investigators studied the purification of sewage by the activated sludge method, but used the Barcroft

micro-respirometer in preference to the classical BOD for the measurement of sewage oxidation rates. The Barcroft method eliminated the necessity of incubating the many dilutions of any one sample required by the BOD test procedure.

At a later date, Caldwell and Langlier (4, p. 202-218) compared the Barcroft differential manometer and the Warburg constant-volume manometer for the measurement of oxygen demand of sewage. Even though the commercial Warburg approach was found to be expensive, it did possess several distinct advantages over and above the standard BOD methods. The oxidation rates were greatly increased in the Warburg method, thus allowing shorter incubation periods. These advances have been adequately reviewed by Gellman and Heukelekian (10, p. 1267-1268).

Chemical Oxygen Demand

A second standard method for the determination of organic pollution in wastewater is the chemical oxygen demand (COD). Several oxidizing agents have been evaluated for use in the COD test procedure. Potassium permanganate, hypochlorites, ceric sulfate, potassium periodate and potassium dichromate have all been proposed as oxidants for the COD procedure. Potassium dichromate appears to be the most popular and has replaced potassium permanganate as the oxidizing agent (21, p. 1297; 1, p. 399-402).

In 1848 Rogers and Rogers (25, p. 353; 26, p. 110) made use of a sulfuric-chromic acid mixture to convert the carbon of graphite and diamond to carbonic acid. Somewhat later, the chromic acid oxidation was applied by Blair (2, p. 223-226) to the analysis of carbon in steel. He prescribed the use of a phosphoric-sulfuric-chromic acid mixture and claimed this method to be more accurate than any other, except for the dry furnace combustion. Cameron and Breazeale (5, p. 29-45) used the Blair procedure for the study of organic content of soils. It was discovered, however, that the chromic acid oxidation yielded results consistently lower than those obtained by the dry combustion method. The oxidizing powers of the chromic-sulfuric-phosphoric acid mixture were applied by Grey (12, p. 2209) and later by Friedemann and Kendall (9, p. 53) for determining the carbon content of aliphatic and other organic compounds. White and Holben (32, p. 83-84) further perfected the technique by boiling the oxidizing mixture and trapping any escaping acid fumes in specially adapted U tubes. Data obtained by using this modified procedure for the analysis of such resistant substances as peat, alfalfa meal, barnyard manure, charcoal and soils compared favorably with the data obtained by dry furnace combustion.

Mohlman and Edwards (18, p. 119) were among the first to adapt the modified chromic acid oxidation for the

determination of carbon content of sewage and trade wastes. These investigators absorbed evolved carbon dioxide in barium hydroxide. The absorbed carbon dioxide was precipitated as barium carbonate. Carbon was determined by titrating the excess barium hydroxide. Mohlman and Edwards believed that a constant ratio existed between organic carbon, as determined by the chromic acid oxidation, and the 5-day BOD. This fact, they felt, supported the theory that the first stage of the oxygen curve was a biochemical carbon oxidation. For raw sewage the ratio $\frac{\text{organic carbon}}{\text{5 day BOD}}$ ranged from 0.38 to 0.74 and for activated sludge effluent from 2.8 to 3.4 (18, p. 121). Mohlman and Edwards (18, p. 110) were, however, unable to establish any relationship between either total carbon and oxygen demand or between total nitrogen and oxygen demand.

In 1949, Moore, Kroner and Ruchhoft (19, p. 953-957) introduced the dichromate reflux method for determination of oxygen consumed during digestion of organic materials. It was found with this method that sugars, cellulose, branched-chain aliphatic acids and alcohols were readily oxidized but that straight chain acids were hardly attacked. Furthermore, when 50% by volume of sulfuric acid was used, chloride concentrations from 250-20,000 parts per million were quantitatively oxidized. With 33% by volume of sulfuric acid, the results obtained were erratic,

depending upon the quantity of 0.25 normal dichromate used.

In 1951 Moore, Ludzack and Ruchhoft (21, p. 1297-1300) compared the many oxidants and procedures proposed for the oxygen consumed determinations. A comparative study of the potassium permanganate method, modifications of the dichromate method and the iodate method was reported. When silver sulfate was added to dichromate mixture as proposed by Moore, Kroner and Ruchhoft (19, p. 953-957), oxidation of straight chain acids and other more resistant compounds was enhanced. In addition, silver sulfate added to the digestion mixture prior to heating prevented the oxidation of chlorides. From this study it was concluded that the Moore dichromate reflux method was superior to all the other procedures tested.

Moore and Ruchhoft (20, p. 711-713) clearly elucidated the relationship existing between the 5-day BOD and COD as follows: "Oxygen consumed methods and the BOD test are two distinctly different parameters indicating chemical and biological requirements which have no a priori intrinsic relationship." Furthermore, "In those wastes containing materials toxic to biological actions, or if the approximate chemical oxidizability of a given waste is desired, an oxygen consumed method can be used advantageously." It was further noted that in domestic wastes in which the settleable solids had been removed, a satisfactory

correlation could be obtained between the COD and the 5-day BOD. In streams receiving domestic wastes the COD-BOD ratio increases as the stream becomes increasingly biologically stable. Thus the Moore dichromate reflux method was accepted by the American Public Health Association and the American Water-Works Association as the standard method for the examinations of water and wastewater (1, p. 399-402).

Persulfate Oxidation

The use of potassium persulfate as an oxidizing agent for the analysis of carbon in organic compounds was first suggested by Franz and Lutze (8, p. 768-770). It was found that water soluble organic substances in dilute aqueous solution could be quantitatively oxidized to carbon dioxide and water. Following the addition of three times the amount of persulfate that theory demands, the mixture was heated to about 75°C and held at that temperature for 10 minutes or longer. Carbon containing substances assayed by the procedure included sodium acetate, adipic acid, sodium benzo-sulfonate, glycerol, starch and gelatin. The results obtained demonstrated good carbon recoveries.

It was not until 1932 that the persulfate oxidation procedure received further attention. At this time Osburn and Werkman (22, p. 421-423) reported having utilized

the persulfate oxidation method for the determination of carbon in fermented liquors. It was pointed out by these workers that the persulfate oxidation method was not seriously affected by the presence of sulfur, nitrogen or chloride compounds. A number of water-soluble organic substances were combusted and the carbon dioxide recoveries computed (Table 1).

In 1954 Katz, Abraham and Baker (14, p. 1503) described the use of a greatly modified and improved combustion-diffusion vessel to be used for the persulfate oxidation. The modified persulfate procedure was employed for the radio-assay of carbon-14-labeled compounds in aqueous solution. The combustion-diffusion vessels were constructed from 50 milliliter Erlenmeyer flasks. The flasks were provided with a center well for the absorption of carbon dioxide. Carbon dioxide was absorbed in five normal sodium hydroxide solution and the carbonate precipitated by the addition of barium chloride. The quantity of carbon recovered was determined by titration of the alkali to the phenolphthalein and methyl orange-methylene blue end points. Katz et al. (14, p. 1503-1504) pointed out that the persulfate method is not limited to the assay of carbon-14-labeled compounds, but may be used for the quantitative analysis of carbon in a variety of water soluble organic compounds. Some of the test substrates combusted which yielded

Table 1
Persulfate oxidation of water soluble organic substrates
(Osburn and Werkman 22, p. 423)

	CO ₂ calculated	CO ₂ found	o/o recovery
acetic acid	176	175	99.4
propionic acid	132	130	98.5
butyric acid	176	173	98.3
chloracetic acid	88	83	94.3
thiourea	44	43	97.7
ethyl alcohol	150	150	100.0
succinic acid	176	173	98.3
dextrose	150	150	100.0
dextrose + NH ₄ Cl ₂	100	99	99.0

95-100% carbon recoveries included glucose, fructose, inositol, glycerol, sodium acetate, lithium lactate, succinic acid, citric acid, benzoic acid, potassium acid phthalate, ethyl acetoacetate, acetaldehyde, glutamic acid, histidine hydrochloride, ethyl alcohol and thymine hydrochloride.

The persulfate oxidation was adapted to the measurement of organic pollution in the water by Gilmour et al. (11, p. 143-149). These investigators established that there was a positive correlation between the persulfate oxidizable carbon (POC) fraction and the 5-day BOD. Domestic wastes as well as a variety of trade wastes were analyzed by both methods and the results compared. For almost every wastewater analyzed the actual 5-day BOD was closely approximated by the predicted BOD value derived from the persulfate carbon determination. It was pointed out that the persulfate oxidizable carbon fraction must be closely related in nature to the carbon fraction oxidized biologically during the 5-day BOD test. Furthermore, in view of the simplicity of the persulfate test it was speculated that the procedure might well have potential value in the water pollution field. Burgess et al. (3, p. 796) extended the findings of Gilmour et al. (11, p. 143-149) by stating, "Water soluble carbon as measured by the persulfate oxidation test is a good measure of organic pollution in water and may be correlated to the 5-day BOD."

Total Carbon

An account by Fleming (7, p. 64-66) described the resistance furnace as giving constant results for the determination of carbon in steel. He was able to process forty-two determinations per hour in a furnace maintained at 1000° C. The combustion tube was constructed of fused silica glazed on the inside. Sample boats were constructed from pure, 22 guage sheet nickel. Dry samples were combusted in an atmosphere of flowing oxygen. Sulfur and water contained in the gases evolved were removed by passage through granular zinc and phosphoric anhydride respectively. Carbon dioxide was absorbed in soda-lime.

Salter (27, p. 637-639) and Winters and Smith (33, p. 202-203) employed the dry combustion method for determining the total carbon content of soils. Winters and Smith (33, p. 202-203) reported that controlled amounts of manganese dioxide enhanced the oxidation of carbonaceous compounds in soil. These workers constructed the gas train of their furnace to effect removal of nitrogen peroxide, sulfur dioxide, sulfur trioxide and water. Because of the ease of handling, anhydrous (potassium perchlorate) was found superior to phosphorous pentoxide for the removal of water. Present combustion methods are patterned after those described by the above early investigators.

EXPERIMENTAL METHODS

Sampling

Samples collected at sewage treatment plants, canneries, pulp and paper mills and plywood plants were immediately iced and held at near freezing temperatures until analyzed. Any one sample was subjected to the test analyses within a 4-hour period. During the early phase of the work all samples were filtered through Whatman #1 filter paper prior to analysis. This procedure was later abandoned and preference was given to the use of settled wastes. Samples which were either highly acid or alkaline were neutralized before analysis. Organic carbonaceous compounds were prepared in dilute aqueous solution. It was found that samples subjected to the persulfate oxidation had to be diluted about ten fold before they could be analyzed by the biochemical oxygen demand test.

Samples for the total carbon analysis almost invariably had to be concentrated to obtain carbon levels great enough to yield accurate results. Concentration was accomplished by use of a rotary-vacuum-evaporator that proved quite efficient at temperatures of 30-50°C.

Analytical Procedures

The Persulfate Oxidation

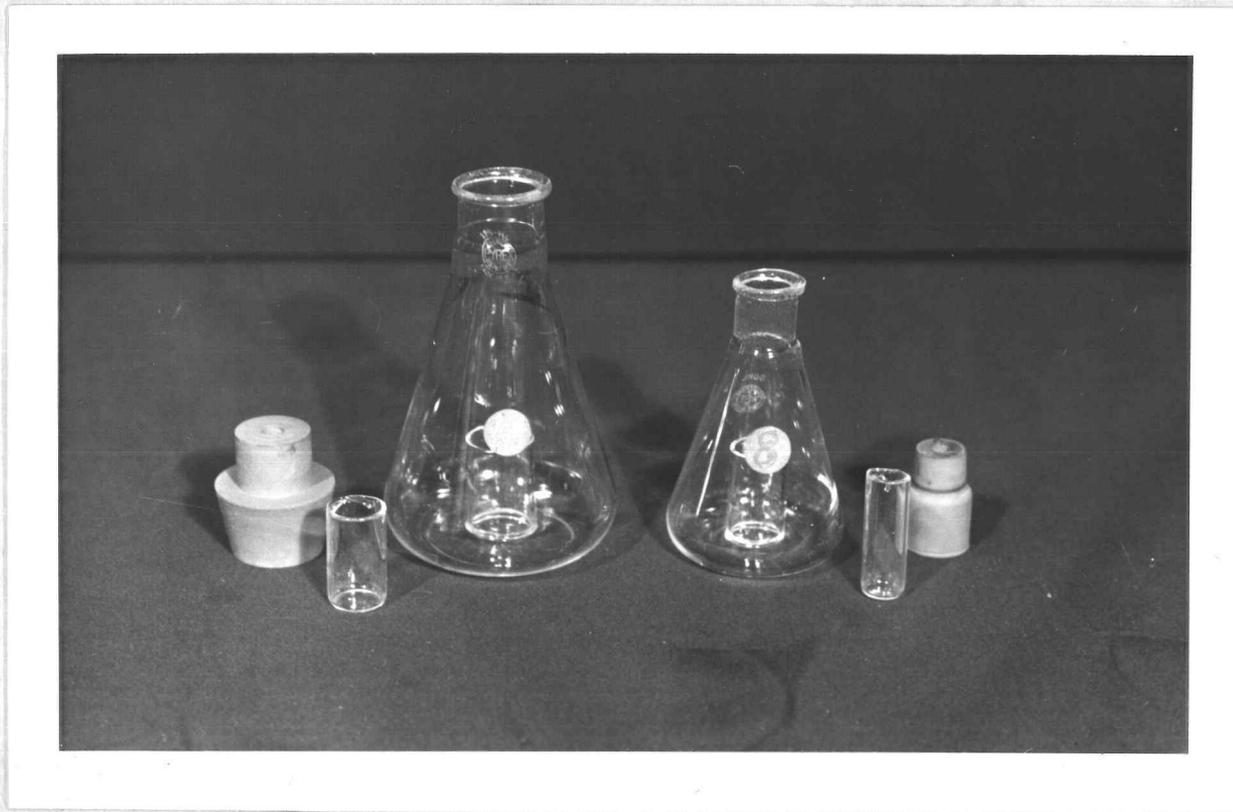
The persulfate oxidation was carried out in combustion-diffusion vessels similar to those suggested by Katz, Abraham and Baker (14, p. 1503). Rather than place the carbon dioxide absorbant directly in the center well, a vial was constructed to contain the absorbant and this vial was then placed in the center well. In addition, vessels were constructed to accomodate a range in sample size from 10 to 50 ml. Combustion diffusion vessels were constructed from either 50 or 125 milliliter Erlenmeyer flasks as shown in Figure 1. Each flask was fitted with a leak-proof center well and the mouth tooled to accommodate a rubber serum bottle stopper.

Samples for analysis were pipetted into the flasks outside of the center well and, when necessary, the volume was adjusted by the addition of distilled water. To the sample was added 5 normal sulfuric acid 4% silver nitrate and potassium persulfate ($K_2S_2O_8$) in the concentrations given in Table 2.

The flasks were swirled to mix the ingredients and to distribute the persulfate. The center-well vial was filled by the addition of CO_2 -free 5 normal sodium hydroxide and lowered by means of a wire hook into the center well of the flask. The rubber serum bottle stopper was slightly wetted with distilled water and fitted tightly into the

Figure 1

Combustion-diffusion vessels for persulfate oxidation



neck of the combustion flask. Just prior to combustion the flasks were evacuated by inserting a hypodermic needle through the serum cap and attaching the same to a water aspirator. The samples were warmed in an oven to 70-75°C for 1-2 hours to bring about combustion. Combustion was complete when the evolution of gases had ceased and the sample had cleared. Usually three to five reagent blanks were prepared for each test series.

Table 2

Reagents used for the persulfate oxidation

Reagent	50 ml Flask	125 ml Flask
5 N H ₂ SO ₄	0.3 ml	1 ml
4% AgNO ₃	1.0 ml	2 ml
K ₂ S ₂ O ₈	0.5-0.6 gm	1-2 gm

Following combustion the flasks were cooled, the vacuum released by inserting the hypodermic needle through the stopper and the stopper removed. The center-well vial was lifted out with a wire hook and the alkaline absorbing solution washed into 125 ml Erlenmeyer flasks with CO₂-free distilled water. The CO₂-free water was prepared by boiling distilled water and providing the container with a trap so that any incoming air was devoid of carbon dioxide.

The absorbed CO_2 was precipitated from the dilute alkaline solution by addition of 7-8 milliliters of precipitating mixture prepared from the following: $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ - 122.2 g; NH_4Cl - 53.0 g made to 1 liter with CO_2 -free water. The resulting barium carbonate (BaCO_3) precipitate was caught in tared medium porosity, sintered-glass filters, washed with CO_2 -free water, dried in the oven at $70-75^\circ\text{C}$ and weighed. After deducting the reagent blank value, the carbon content was calculated from the weight of BaCO_3 obtained.

Compound	Weight
Carbon.....	12.011
Barium carbonate..	197.37

$$\text{mg BaCO}_3 \text{ per mg Carbon} = \frac{197.37}{12.011} = 16.432$$

$$\therefore \text{mg BaCO}_3 \div 16.432$$

The gravimetric method was used during the entire study. It is possible, however, to determine the carbon dioxide absorbed by direct titration of the base through the brom cresol green-methyl red or the thymol blue-brom phenol blue end points.

The Biochemical Oxygen Demand

The biochemical oxygen demand tests were performed as outlined in Standard Methods for the Analysis of Water and Wastewater (1, p. 318-324). Samples for analysis were either properly diluted or pipetted directly

into 300 ml BOD bottles. The sample was then brought to 300 ml with specially prepared dilution water. A raw sewage seed was employed whenever experiments involved analysis of highly concentrated trade wastes or added carbon compounds. Glucose and the other carbon sources were added at predetermined levels along with the seed. Cannery wastes were considered to be self-seeded but the sulfite waste liquor, following neutralization, was seeded with a composite raw domestic sewage. Only those dilutions showing 40-90 percent oxygen depletion were considered valid.

The Chemical Oxygen Demand

The chemical oxygen demand (COD) makes use of a potassium dichromate-sulfuric acid digestion mixture. The procedure employed was essentially that described in 'Standard Methods' (1, p. 399-402). To a 50 ml sample in a 500 ml round bottom flask were added 25 ml of 0.25 N potassium dichromate and 75 ml of concentrated sulfuric acid. Silver sulfate was added to the sulfuric acid at 1 gram per 75 ml in order to effect more complete oxidation of aliphatic and aromatic hydrocarbons and to prevent the oxidation of chlorides. The mixture was refluxed for 2 hours, allowed to cool and washed with distilled water into wide-mouthed 500 ml Erlenmeyer flasks. The excess dichromate was titrated with standardized ferrous ammonium sulfate (FAS) following

addition of a ferrous indicator. The COD values were calculated from:

$$\text{COD} = \frac{(a-b) c \times 8000}{\text{ml sample}}$$

a = milliliters FAS used for blank
b = milliliters FAS used for sample
c = normality FAS

Persulfate Oxidizable Carbon Recoveries

Pure organic compounds that were considered representative of substances found in sewage were prepared at known concentrations in dilute aqueous solution. Before adoption of the persulfate test it was necessary to establish the percentage carbon recovery, the effective recoverable carbon range and the spectrum of organic substances oxidized. Carbohydrates, organic acids, alcohols, amino acids and the salts thereof were subjected to analysis by the persulfate oxidation in single compound solutions as well as multiple compound mixtures. Carbon concentrations used are given in the experimental results section. It was immediately evident that the persulfate oxidation gave excellent carbon recoveries with a wide variety of organic substrates, whether in single compound solutions or complex mixtures. The results of these early experiments encouraged further exploration of the method for the determination of organic pollution in water.

Comparison of POC and 5-day BOD

The first stage biochemical oxygen demand has been recognized as involving the oxidation of carbon. A question of primary importance arose. Would a correlation exist between the persulfate oxidizable carbon (POC) fraction and the 5-day BOD? Phelps (24, p. 65, 69-70) has stated that the 5-day BOD represented only about 68% of the ultimate oxygen demand required for complete stabilization by aerobic decomposition of organic substances. It was hoped that the POC fraction might approximate the carbon fraction oxidized during the first stage of biological stabilization. If this idea held true, the 5-day BOD could be calculated by taking 68% of the oxygen required for complete oxidation of the POC fraction.

In order to test this hypothesis, known amounts of carbon (as glucose) were added to raw filtered sewage. Added carbon ranged in concentration from 0.05-0.5 milligrams per milliliter. These samples were analyzed by 5-day BOD and persulfate oxidation. The BOD value for the sewage seed was deducted from all BOD results obtained by the addition of carbon. Similar experiments were performed using a 15 carbon compound mixture (Table 5) rather than glucose.

Correlation of POC and 5-day BOD

In order to provide a numerical correlation coefficient for expression of the POC, 5-day BOD relationship it was necessary to devise an experiment, the data of which could be analyzed by statistical methods. It was decided to employ the complex synthetic sewage used previously. Samples for analysis by both POC and 5-day BOD were performed in quintuplicate. Statistical analysis of the data provided a correlation from which a standard curve was constructed. However, in order to extend the curve to allow comparison of wastes of greater strength, another experiment was performed that employed analysis of more concentrated synthetic wastes.

In the mathematical description of the BOD process the velocity constant is used as an expression of the rate of aerobic biological degradation of organic materials. The usually accepted value for k is 0.1 for the 5-day BOD incubated at 20°C (24, p. 69-70, 102-105; 1, p. 318). All other factors being constant, k may vary from less than one-half to more than twice the 0.1 value depending upon the chemical and biological nature of the waste. In the light of these findings it was expected that glucose and other readily oxidizable substrates used in the aforementioned experiments would probably exhibit velocity rates

considerably greater than might be observed with domestic or trade wastes (1, p. 321-322). In order to test this theory a number of domestic and trade wastes were collected and analyzed by both the persulfate oxidation and the 5-day BOD procedures. It was found necessary to analyze the data from these and some of the earlier experiments by statistical methods so that better comparisons might be made.

The Total Carbon Determination

Total carbon values were determined by means of a Lindberg type resistance furnace. Samples for analysis were pipetted into nickel barges and evaporated to dryness in an oven kept at 60-70°C. A fan was kept in the oven to promote more rapid evaporation. When necessary, samples were concentrated in a rotary evaporator prior to transfer into barges. The dried material was overlaid with aluminum and combusted in an atmosphere of flowing oxygen at 1220-1260°C for five minutes. Carbon dioxide evolved was trapped in Disorber-C-Cartridges and determined gravimetrically. Carbon was calculated from the weight of CO₂ trapped.

The total carbon procedure was able to detect as little as one milligram of carbon. However, the lowest limit giving accurate results was five milligrams of carbon. Thus samples containing less than five milligrams carbon

were not used. Five milligrams of carbon yielded 18.3 milligrams of CO₂. About 1.2 milligrams appeared to be the maximum weight variation accountable to the CO₂-traps. Therefore, when five milligrams of carbon is oxidized to yield 18.3 mg of CO₂, a 6% error due to weight variation of the CO₂-traps may occur.

For calibration or trial runs to test the combustion apparatus, two or three 50 mg carbon samples were utilized. Usually anhydrous glucose was used as the carbonaceous substrate. Experience taught that samples yielding from 40 to 200 mg of CO₂ were the most dependable.

Comparison of POC, COD and TOC

Following confirmation of the POC, 5-day BOD relationship, it became necessary to compare the persulfate oxidation with other methods used for the analysis of organic materials in water. The object of these studies was twofold:

1. To determine if there existed a significant ratio between the POC and the carbon level as measured by other methods.
2. To further clarify the nature of the POC fraction.

Thus, a number of domestic and industrial wastes were collected and analyzed by persulfate oxidation, COD and the total carbon (TOC) tests. In addition a composite

domestic waste was concentrated to varying carbon levels to represent wastes of different strength but of similar composition. In order to make the results obtained by the different tests compatible, the POC values were converted to calculated 5-day BOD (BOD_c) and the total carbon converted to theoretical oxygen demand (TOD) based on the amount of oxygen required for complete oxidation of the total carbon obtained. In order to compare the data obtained from analysis of the different wastes the COD/BOD_c and TOD/BOD_c ratios were computed.

Aerobic Stabilization of POC

Having developed the COD/BOD_c and TOD/BOD_c ratios from data obtained from the POC, COD and total carbon, it was now possible to follow the step wise oxidation of the organic material in wastes.

These experiments required the construction of a miniature activated sludge apparatus as shown in Figure 2. Air was pulled through bottles filled with water into the 2.5 gallon pyrex solution bottle by means of a water aspirator. In the water bottles and the solution bottle the incoming air was passed through gas dispersion tubes. The incoming air was saturated with moisture prior to entering the sludge digestion chamber to prevent moisture loss by evaporation.

Figure 2

Activated sludge apparatus



The described apparatus was employed for three experiments. For the first experiment a composite domestic and industrial waste was prepared so as to contain a total carbon concentration of about 1.2 mg C/ml. The high carbon level obviated concentration of samples for total carbon analysis.

In the second experiment ground filter paper was added to composite domestic and slaughterhouse waste. The added filter paper cellulose again precluded concentrating samples for the total carbon analysis. From information gained during preliminary work it was possible by blending the correct amounts of raw domestic waste to obtain the level of soluble carbon desired. A composite raw domestic waste from three different sources was used. The raw domestic waste contained about 0.1 mg soluble carbon per ml and about 0.4 mg insoluble carbon per ml as determined by the difference between the POC and TOC tests. A total concentration of 2.5 mgC/ml was used, of which 0.5 mgC/ml was of the water soluble type. Glucose was added at 0.4 mgC/ml to obtain the correct level of soluble carbon. Cellulose in the form of finely ground filter paper was added at 1.5 mgC/ml to gain the calculated insoluble carbon level. The C:N ratio was adjusted to about 17:1 by the addition of urea or ammonium phosphate. Unfortunately several factors contributed to make the two preceding experiments of

limited value. The rate of stabilization was not of a magnitude usually experienced during aerobic decomposition of wastes. The added filter paper cellulose presented major sampling errors and being finely ground was quantitatively oxidized by the persulfate procedure.

A third experiment was planned in which a domestic waste was employed. It was necessary to concentrate samples 10 fold for the total carbon analysis. Removal of residues from the sides of the concentration flask was effected by addition of 2-3 ml of 5N NaOH and 3-5 g of purified quartz sand. The contents of the flask were then actively swirled, shaken and allowed to stand 5-10 minutes. All samples were analyzed for POC, COD and TOC. Data was converted from POC to BOD_c , TOC to TOD to allow comparison with the COD. The COD/BOD_c and TOD/BOD_c ratios and, in some instances, the per cent reduction in oxygen demand was computed for comparison purposes.

EXPERIMENTAL RESULTS

Carbon Recoveries by Persulfate Oxidation

Wastewaters contain a wide variety of soluble carbonaceous substances which contribute to the first stage BOD. A number of compounds that contribute to the 5-day BOD were prepared in dilute aqueous solutions and subjected to persulfate oxidation. In this regard, it was necessary to determine the accuracy of the POC test as well as to establish the optimum range of carbon recovery. Thus some idea as to the spectrum of carbonaceous substances oxidized by persulfate oxidation could be realized.

The data given in Tables 3 and 4 draws attention to the range of recoverable carbon for the two sizes of combustion flasks and to the per cent carbon recovery with various substrates. The optimum carbon range for the 50 ml combustion flasks proved to be 1-10 mg carbon and for the 125 ml flasks 1-25 mg of carbon. The per cent carbon recovery for the various test compounds ranged from 90-114% and averaged 101.4%. The coefficient of variation determined for a portion of the data varied from 0.7 to 5.3% with an average of 3%.

A further experiment employed complex mixtures of carbohydrates, organic acids, alcohols and amino acids prepared in dilute aqueous solution of known concentration. Three

Table 3

Carbon recoveries by persulfate oxidation of organic compounds with 50 ml combustion flasks

Substrate	Added mg Carbon	Recovered mg Carbon	Per Cent Recovery
Glucose	2.00	2.11	105
	5.00	4.95	99
	8.00	8.13	102
	10.00	10.00	100
Butyric Acid	1.00	1.14	114
	3.00	3.13	104
	5.00	4.80	96
Propionic Acid	1.00	1.12	112
	3.00	3.19	106
	5.00	5.19	104
Ethyl Alcohol	1.00	1.06	106
	3.00	3.01	100
	5.00	5.12	102
Acetic Acid	1.00	1.03	103
	3.00	2.73	91
	5.00	4.49	90
Sucrose	1.00	1.12	112
	3.00	3.04	101
	5.00	4.95	99
	8.00	7.99	100
	10.00	10.29	103
Lactose	1.00	1.01	101
	3.00	3.12	104
	5.00	5.00	100
	8.00	7.93	99
	10.00	10.00	100

Table 4

Carbon recoveries by persulfate oxidation
of organic compounds with 125 milliliter
combustion flasks

Substrate	Added mg Carbon	Recovered mg Carbon	Per Cent Recovery
Lactose	1.00	0.97	97
	3.00	2.95	98
	5.00	4.97	99
	8.00	8.00	100
	10.00	10.04	100
	15.00	14.99	100
	25.00	24.89	99

solutions, each containing five different carbonaceous substrates, were oxidized individually and as a fifteen compound mixture. The three solutions were mixed in equal parts in order to simulate a rather complex synthetic sewage of known concentration and composition. As revealed in Table 5, in each case the carbon recovery by persulfate oxidation approached 100%. In the light of these findings it was considered probable that the persulfate oxidation test might be adaptable to the analysis of organic pollution in wastewater. It became necessary, however, to compare compatible data from the persulfate oxidation and the 5-day BOD.

Comparison of POC and 5-day BOD

Specific amounts of the carbonaceous substances tested in the preceding experiments were expected to show definite biochemical oxygen demands when analyzed by the 5-day BOD test. It was pointed out by Phelps (24, p. 54, 69-70) that during the 5-day BOD there occurred only 68% stabilization of organic matter. On this premise, 68% of the theoretical oxygen demand of the carbon measured by the persulfate oxidation test should approximate the 5-day BOD value. In order to test this hypothesis, it was essential to devise experiments to determine the 5-day BOD for known concentrations of persulfate oxidizable carbon. Glucose

Table 5

Carbon recovered by persulfate oxidation of mixed organic compounds in dilute aqueous solution

Substrate	Carbon Added milligrams	Carbon Recovered milligrams	Per cent Recovery
Mixture - A -			
Butyrate			
Propionic Acid			
Ethyl Alcohol	5.00	4.72	94
Acetate			
Glycerol			
Mixture - B -			
Glucose			
Sucrose			
Lactose	5.00	5.14	103
Xylose			
Arabinose			
Mixture - C -			
Leucine			
Asparagine			
Glycine	5.00	4.68	94
Aspartate			
Glutamate			
Mixture of A, B and C	5.00	4.99	100

was chosen as the primary carbon source and was added to filtered raw sewage to yield solutions of known carbon concentration. Aliquots were immediately withdrawn and analyzed by persulfate oxidation and the 5-day BOD test. The calculated BOD values were based on recovered POC and are compared with actual 5-day BOD values in Table 6. The actual 5-day BOD represents only the glucose carbon added, the contribution of the sewage seed having been deducted. Likewise, the POC values were corrected for sewage seed and reagent blanks as well, prior to computing the calculated BOD values.

The data presented in Table 6 calls attention to the observation that 68% of the oxygen required for complete oxidation of persulfate oxidizable carbon approximates quite closely the 5-day BOD obtained. Furthermore, and perhaps of ever greater significance, was the possibility that a usable correlation might exist between the POC and 5-day BOD. This observation was strengthened by data presented in Table 7, wherein a synthetic sewage was subjected to analysis by POC and 5-day BOD. It is quite evident that at least a presumptive positive correlation was indicated between POC levels and the corresponding 5-day BOD. However, more definitive type experiments were needed to establish a numerical correlation.

Table 6

Actual and calculated 5-day BOD for various levels of glucose carbon

Added mg C/ml	Recovered mg C/ml	Calculated 5-day BOD*	Actual 5-day BOD
0.05	0.076	137	150
0.10	0.109	197	195
0.20	0.204	369	382
0.30	0.307	556	540
0.40	0.413	757	735
0.50	0.514	930	885

* 68% of theoretical oxygen demand of persulfate oxidizable carbon

Table 7

Actual and calculated 5-day BOD for synthetic sewage*

Added mg C/ml	POC Recovered mg C/ml	Calculated 5-day BOD	Actual 5-day BOD
0.05	0.050	90	97
0.10	0.102	184	202
0.20	0.193	349	442
0.30	0.292	528	667
0.40	0.398	720	887
0.50	0.498	901	1102

*Synthetic sewage composed of solutions A, B, C shown in Table 5.

Correlation of POC and 5-day BOD

Synthetic Sewage

In order to define the relationship between the POC and 5-day BOD an experiment was conducted that employed the synthetic sewage used previously with analysis of each sample in quintuplicate. The data obtained was analyzed by statistical methods to obtain a regression coefficient, $1807 \text{ X mg C/ml} = 5\text{-day BOD}$, whereby the 5-day BOD could be calculated directly from POC data. Interestingly enough the curve plotted using the derived regression coefficient was identical to that obtained by taking 68% of the theoretical oxygen demand of the POC, as shown in Figure 3.

The predicted 5-day BOD values presented in Table 8 were provided through application of the standard curve and respective regression coefficient. The most striking aspect of the data in Table 8 was the precision with which the BOD values were predicted. For any one carbon level the predicted and actual BOD values were almost identical. A subsequent experiment employed greater carbon concentration in order to extend the range of the standard curve. The soluble carbon range was extended from 0.3 - 1.5 mg C/ml. Carbon recoveries and predicted BOD values were compared with actual 5-day BOD values given in Table 9. Here again, the predicted and actual BOD indices were closely correlated. Calculations using the information

Figure 3
Standard curve for synthetic sewage

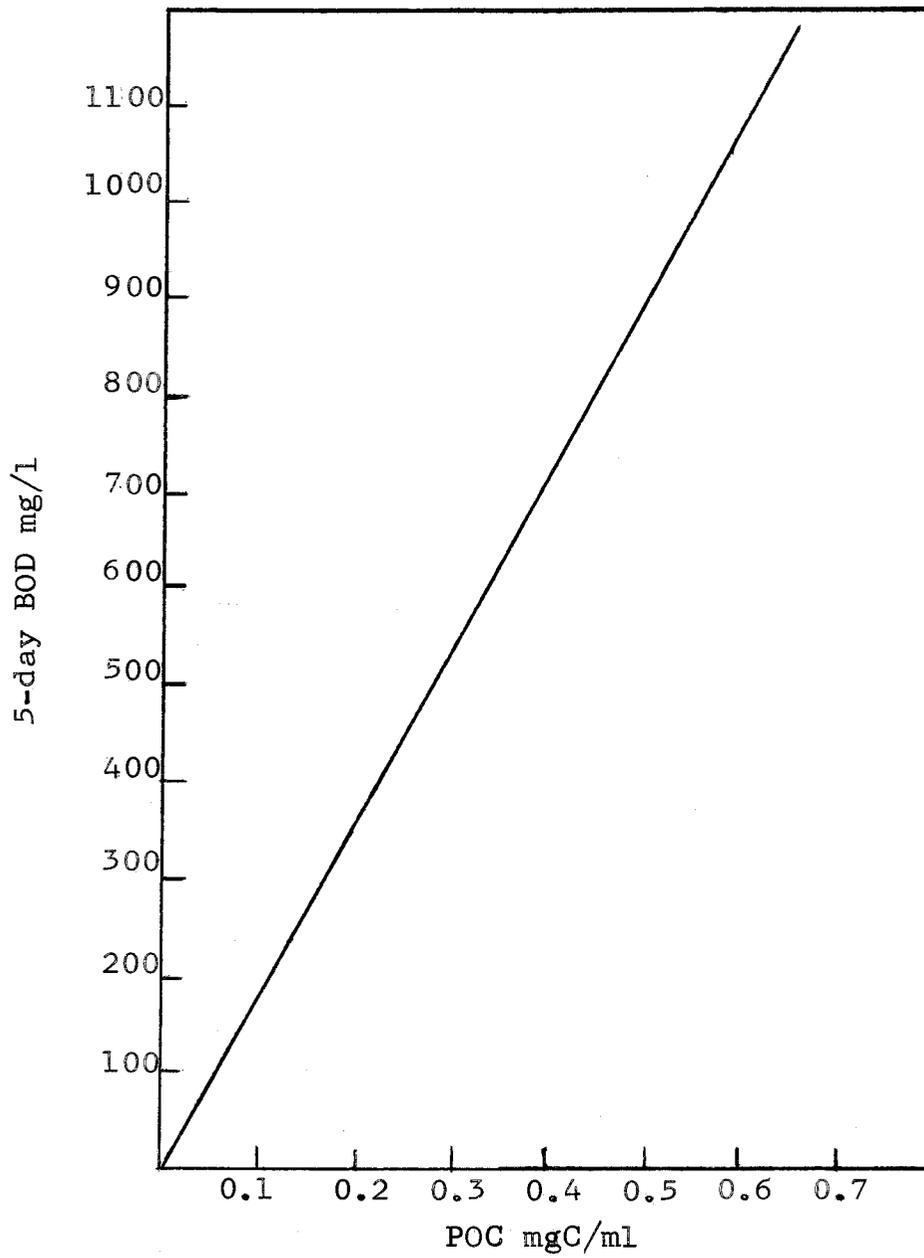


Table 8

Actual and predicted 5-day BOD for synthetic sewage

Added mgC/ml	POC Recovered mgC/ml*1	Predicted 5-day BOD*2	Actual 5-day BOD
0.10	0.940	181	180
0.20	0.204	361	360
0.30	0.295	542	540
0.40	0.397	723	720
0.50	0.499	903	900

*1 average of 5 determinations

*2 derived from regression coefficient
 $1807 \times \text{mgC/ml} = 5\text{-day BOD}$

Table 9

Actual and predicted 5-day BOD for synthetic sewage

Added mgC/ml	POC Recovered mgC/ml*1	Predicted 5-day BOD*2	Actual 5-day BOD
0.30	0.31	560	550
0.60	0.61	1102	1131
0.90	0.92	1662	1759
1.20	1.22	2204	2275
1.50	1.53	2765	2707

*1 average of three determinations

*2 calculated from regression coefficient

 $1807 \bar{X} \text{ mgC/ml} = 5\text{-day BOD}$

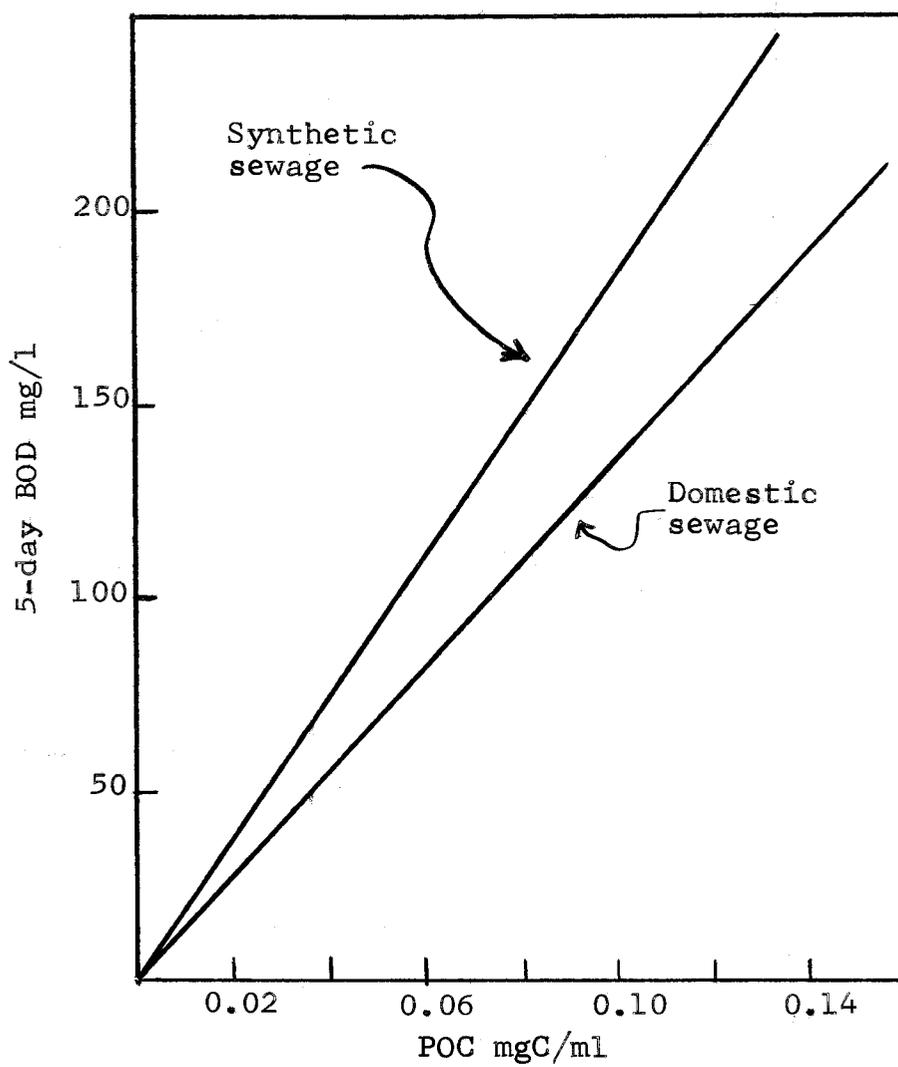
gained from this and the preceding experiment revealed a correlation coefficient of 0.998 between POC and 5-day BOD.

Domestic and Industrial Wastes

Information gained from the preceding experiments allowed further exploration of the persulfate oxidation method for the analysis of domestic and industrial wastes. From the POC data the 5-day BOD could now be predicted. It was hoped, therefore, that the same relationship that was shown for synthetic waste might also apply to raw domestic wastewater and certain trade wastes. It would be expected that POC, 5-day BOD regression coefficients would have to be determined individually for trade wastes of markedly different chemical composition.

A variety of wastewaters were analyzed by POC and 5-day BOD. The predicted 5-day BOD values obtained from calculation using the regression coefficient 1807 were consistently too high. It was discovered graphically and by statistical analysis that the standard curve for raw domestic sewage was proportionally less than that obtained for the synthetic sewage as shown in Figure 4. Statistical analysis of the data revealed that a new regression coefficient of 1383.2 should be used for domestic sewage. Predicted 5-day BOD values derived from both regression coefficients, 1807 and 1383.2, are compared with actual 5-day

Figure 4
Standard curve for synthetic and domestic sewage



BOD values in Table 10. Worthy of particular attention was the accuracy with which the 5-day BOD was predicted, not only for domestic wastes but for a number of trade wastes as well. One notable exception was that of the sulfite waste liquor for which the actual BOD was only about one-half the predicted value. The 5-day BOD test has proven notoriously unreliable for analysis of concentrated wastes of this nature. The predicted BOD based upon POC data probably reflects more nearly the true BOD of these wastes.

Concentrated Composite Waste

A rather unique method was developed for comparison of wastes of different strength but of similar makeup. A composite raw domestic waste was concentrated several fold and aliquots diluted to specific strengths. These wastes were then analyzed by the POC and 5-day BOD and the data compared following conversion of POC values to predicted 5-day BOD. Tabulated in Table 11 are the results obtained from an experiment using a concentrated composite domestic waste. Good agreement was obtained between predicted 5-day BOD based upon the regression coefficient 1383.2 and the actual 5-day BOD. It is evident that the predicted BOD for the 1.0X concentration and the dilute control are the same, but the actual BOD was variable. Throughout the study it was noticed that the variation in actual BOD was of a far

Table 10

Actual and predicted 5-day BOD of domestic and industrial wastes

Waste type	POC mgC/ml	Predicted 5-day BOD		5-day BOD
		1807	1383.2	
Bean waste	0.152	275	210	188
Salem	0.125	226	173	189
Salem domestic	0.099	179	137	146
	0.083	150	115	114
Slaughterhouse	1.708	3090	2362	3076
Albany	2.500	4517	3458	3760
	4.300	7770	5948	4900
Bean waste	0.044	79	61	55
Stayton	0.036	65	50	44
Sulfite liquor	33.4	60,354	46,199	13,110
Salem	34.0	61,438	47,029	22,500
Beet and bean waste				
Corvallis				
Screened	1.64	2963	2268	2100
non-screened	1.73	3126	2393	2130
Domestic & beet				
Corvallis	0.095	172	131	137
Composite	0.084	152	116	135
domestic waste	0.076	137	105	102
	0.070	126	97	64
Corn waste				
Stayton	0.540	976	747	900
Corn waste				
Salem	1.220	2204	1687	1920
Plywood glue				
Corvallis	16.0	28,912	22,130	18,830

Table 11

Actual and predicted 5-day BOD of a concentrated composite domestic waste

Waste Concentration	POC mgC/ml	Predicted 5-day BOD		Actual 5-day BOD
		1807	1383.2	
dilute control	0.113	204	156	133
2.0 X	0.228	412	315	330
1.5 X	0.172	311	238	225
1.3 X	0.147	266	203	169
1.0 X	0.113	204	156	120
0.5 X	0.062	112	86	51

greater magnitude than the data obtained from the POC. According to a statistical analysis of one set of data the coefficient of variation of the 5-day BOD ranged from 5 - 25%. Furthermore, the attitude developed was that the actual 5-day BOD was being put to a test more than was the persulfate oxidation test.

Comparison of POC, COD and TOC

Calibration

At this point in the study it was considered advisable to compare the described persulfate oxidation procedure with other analytical methods. The other tests employed were the chemical oxygen demand (COD) and total carbon by dry combustion (TOC). These tests are described in the experimental methods section of this text.

Both the COD and TOC procedures were subjected to trial analyses prior to experimentation. Known carbonaceous substrates were oxidized by each procedure and the carbon recoveries computed. The formula set forth in "Standard Methods" (1, p. 402) for calculation of chemical oxygen demand was used. The results from a typical calibration experiment determining the COD of weighed amounts of glucose and filter paper cellulose are shown in Table 12. It was found that excellent carbon recoveries ranging from 94-102% were obtained.

Table 12

Observed carbon recoveries by the COD test*

Added mgC/ml	COD	Recovered mgC/ml	Per cent Recovery
Glucose			
0.10	271	0.102	102
0.24	626	0.235	98
0.30	786	0.296	99
Cellulose			
0.240	626	0.235	98
0.110	274	0.103	94
0.282	742	0.279	99

*Computed using constant 50 milliliter sample.

Domestic and Industrial Wastes

A variety of raw domestic and industrial wastes were collected and analyzed by the POC, COD and TOC procedures. Before the data could be compared it was necessary to convert the POC and TOC to values compatible with those of the COD. Having already established that the 5-day BOD can be readily predicted from the POC data, it was decided to convert all the POC data to predicted 5-day BOD values. The predicted 5-day BOD was termed BOD_C . The TOC values were then converted to the theoretical oxygen demand (TOD), or the amount of oxygen in milligrams per liter required for complete oxidation of the total carbon measured. The COD/BOD_C and TOD/BOD_C ratios were computed to provide an easy reference from which to compare the data.

The data obtained from the analysis of the various wastewaters are presented in Table 13. Attention is drawn to the characteristic COD/BOD_C ratio obtained for wastes of presumably similar chemical composition. In the case of domestic wastes, the ratio fell between 2.2 and 2.5, and for bean wastes between 1.4 and 1.5. For trade wastes, however, the COD/BOD_C ratio was found to be unpredictable. No evidence was found to support any relationship between TOD and BOD_C .

Of particular significance was the fact that the BOD_C values based on the POC levels provided data equally as

Table 13

Comparison of BOD_c, COD and TOD for domestic and industrial wastewaters

Waste	BOD _c	COD	TOD	$\frac{\text{COD}}{\text{BOD}_c}$	$\frac{\text{TOD}}{\text{BOD}_c}$
Lebanon domestic	116	256	585	2.2	5.0
Corvallis domestic	100	253	221	2.5	2.2
Albany domestic	113	258	364	2.3	3.2
Salem domestic	217	524	606	2.5	2.9
Stayton bean	115	174	364	1.5	3.2
Salem bean	191	278	266	1.4	1.4
Slaughterhouse	768 667	1580 1708	1748 1564	2.0 2.6	2.3 2.3
Sulfite liquor	87,142	176,400	176,400	2.0	2.0

useful as that obtained by means of the classical 5-day BOD. In this regard, it is interesting to note that the BOD_C constituted approximately 50% of the COD or total oxygen demand. These points attest further to the applicability of the POC 5-day BOD regression coefficient for determination of the actual 5-day BOD.

The COD/ BOD_C ratios shown in Table 13 further illustrate the rather constant relationship that exists between the COD and the 5-day BOD indices. Any extreme variation in this ratio would indicate either a radical change in waste composition or perhaps a procedural error. It is felt that the greater variation observed for the TOD/ BOD_C ratio may be explained by the inconsistent data obtained by the total carbon procedure.

The use of a concentrated composite waste had proven during earlier experiments to be a useful technique. Thus the same technique was employed to prepare wastes of different strength but of similar composition, in order that further testimony might be given to the observation that for similar wastes a common COD/ BOD_C ratio prevailed. Evidence to further support this contention is presented in Table 14. Not only did the COD/ BOD_C ratio remain constant, but also the TOD/ BOD_C ratio. The COD/ BOD_C ratios obtained during this experiment were very near those obtained for domestic wastes as shown previously in Table 13.

Table 14

Comparison of BOD_c , COD and TOD for a concentrated composite domestic wastewater

Waste Concentration	BOD_c	COD	TOD	$\frac{COD}{BOD_c}$	$\frac{TOD}{BOD_c}$
4.0 X	318	747	798	2.3	2.5
2.0 X	176	389	434	2.2	2.5
1.5 X	131	307	343	2.3	2.6

Aerobic Stabilization of POC

In the first phase of experimentation a composite domestic and industrial waste was prepared which contained enough carbon to preclude concentration of samples for the total carbon analysis. The waste mixture contained corn waste, beet waste, domestic waste, slaughterhouse waste and a small quantity of sulfite waste liquor. The intention was to provide a sewage that would be representative of a wide variety of different wastes, realizing that the rate of biochemical oxidation would not be representative for any one component waste alone. The aeration apparatus was kept at room temperature and samples were withdrawn periodically and analyzed by the POC, COD and TOC tests. As in preceding experiments, use was made of the POC and TOC data for calculation of the predicted 5-day BOD (BOD_C) and theoretical oxygen demand (TOD values).

Data obtained from the first experiment are shown in Table 15. During the 204 hour period there was only about 55% reduction in BOD_C . The rate of oxidation of the material was well below that normally expected for raw domestic waste. Initially the COD/ BOD_C ratio for the waste was 1.97, however, as oxidation of the waste proceeded a change in the COD/ BOD_C ratio occurred. During the initial biochemical oxidation only the soluble readily oxidizable substances would be expected to be oxidized. By reference to

Table 15

Activated sludge digestion of a mixed industrial
and domestic wastewater

Time in hours	BOD _C	COD	$\frac{\text{COD}}{\text{BOD}_C}$
0	1978	3902	1.97
16	1300	2857	2.20
36	1217	2825	2.32
60	982	2399	2.44
84	1024	2675	2.61
108	954	2113	2.21
204	899	1737	1.93

the data in Table 15 it is evident from the shift in the COD/BOD_C ratio that the soluble organic moieties measured by the POC are oxidized more rapidly during aerobic stabilization than are those measured by either the COD or the TOC. However, after 108 hours there is a gradual decrease in the COD/BOD_C ratio. This shift may be accounted for by the hydrolysis of the more complex materials to a state whereby they are susceptible to persulfate oxidation.

Data relating to an experiment that employed a composite raw domestic waste are presented in Table 16. Cellulose in the form of finely ground filter paper was added to accentuate the difference between the BOD_C, COD and TOD.

Worthy of attention was the same general trend in the COD/BOD_C ratio that was observed during the previous experiment. The erratic nature of the results of this experiment make it difficult to determine when the peak difference occurred. The most accurate estimate would be that the maximum difference occurred at about 48 hours. Thereafter the ratio slowly declined in the same manner as was experienced previously. The fact that the TOD values were less than the COD has not been explained. Possibly during the drying process a small portion of the waste carbon was lost.

Unfortunately the ground filter-paper cellulose was quantitatively oxidized by the persulfate procedure. However, filter paper in strips was only 10% oxidized. The

Table 16

Activated sludge digestion of a composite domestic wastewater
with added cellulose

Time in hours	BOD _c	COD	TOD	$\frac{\text{COD}}{\text{BOD}_c}$	$\frac{\text{TOD}}{\text{BOD}_c}$
0	2697	6941	6756	2.57	2.50
6	1563	4079	3378	2.61	2.16
12	2656	7020	5746	2.64	2.16
18	1909	6863	3165	3.59	1.66
24	2130	6142	5799	2.88	2.72
48	2130	6575	6065	3.09	2.85
72	2296	6063	5666	2.63	2.47
96	1812	5332	5373	2.89	2.96
120	1604	4380	4522	2.73	2.82

close chemical similarity of cellulose to glycogen, the harsh treatment during manufacture and the highly purified state of the filter paper may in part explain why the weak oxidizing properties of persulfate were able to decompose the cellulose. It was theorized that the grinding exposed terminal glucose units, a readily persulfate oxidizable substrate.

Neither of the foregoing experiments had produced the forthright data expected. During the second experiment major errors in sampling had been brought about by aggregation of the cellulose into slimy chunks that adhered to the sides of the tank and to the air sparger. Furthermore, the rate of stabilization had not approached the expected stability experienced during the usual 5-day BOD. It was hoped, therefore, that a rather weak raw domestic waste might prove more suitable for gaining data, even though samples for total carbon analysis must be concentrated about ten fold. The results of an experiment that employed a raw domestic waste are presented in Table 17.

The most surprising aspect of the data obtained from this experiment was the nearly two-fold increase in the TOD/BOD_C ratio. Furthermore, for the first time, the TOD values were consistently greater than the COD values. This was the only instance in which the TOD data was considered significant. In addition, the 62% reduction in BOD_C was

Table 17

Activated sludge digestion of raw domestic wastewater

Time in hours	BOD _c	COD	TOD	$\frac{\text{COD}}{\text{BOD}_c}$	$\frac{\text{TOD}}{\text{BOD}_c}$
0	104	221	271	2.12	2.61
72	44	106	207	2.41	4.60
120	40	97	165	2.42	4.15

of an expected magnitude. The COD/BOD_C ratio again increased but did not decrease during the entire time period. This result might have been expected since the waste was rather dilute and most of the readily oxidizable organic material was either converted to CO₂ and H₂O or had been assimilated.

At no time during the three activated sludge experiments was the per cent reduction of either the COD or TOD as great as that observed for the BOD_C. Perhaps of greater importance, however, was the observation that the BOD_C fraction decreased at a greater rate than either of the other two fractions. Thus, the carbon fraction measured by the persulfate oxidation was truly a measure of the organic carbon oxidized biochemically during the first stage aerobic stabilization.

DISCUSSION

In the present study the problem of measurement of organic pollution in water was investigated. For many years workers in the water pollution field have depended upon the 5-day BOD and COD indices. These methods, although widely accepted, are subject to certain disadvantages. Both the BOD and COD determine oxygen consumed and, therefore, represent an indirect measure of organic pollution in water. In addition, these tests are subject to a number of inherent errors that often limit the applicability of the results to the study of stream pollution. A method whereby water soluble organic materials contributing to oxygen depletion could be measured directly in terms of concentration per unit volume appeared desirable. The method should be rapid, require a minimum of equipment, be accurate and relatively unaffected by the many ions which usually plague chemical oxidations. Preliminary experiments indicated that the persulfate oxidation appeared to fulfill at least several of the aforementioned requirements.

An initial point of major importance was the question of carbon recoveries by the persulfate oxidation procedure. It was found that a variety of water-soluble organic substances in dilute solution, whether prepared as a single substrate or as complex mixtures were quantitatively oxidized

to carbon dioxide and water by the persulfate method. This finding was in full agreement with results reported by others (8, p. 768-770; 22, p. 421-423; 14, p. 1503-1504). Carbon recoveries computed from the recovered BaCO_3 approached 100 per cent for all the carbon compounds analyzed by the persulfate test.

It was also recognized that should the persulfate method measure organic moieties oxidized biochemically during aerobic stabilization there might exist a correlation between persulfate oxidizable carbon (POC) and the 5-day BOD. By analyzing dilute glucose solutions and more complex prepared synthetic sewages it was found that the 5-day BOD could be predicted from data obtained from the persulfate method. A statistical analysis of the data obtained revealed a positive correlation of 0.998 between POC and the 5-day BOD. Furthermore, there was only a 3% coefficient of variation for data obtained by the persulfate method compared to a 10% coefficient of variation for the 5-day BOD. A regression coefficient ($1807 \text{ X mgC/ml} = 5\text{-day BOD}$) was derived from which the 5-day BOD could be accurately and quickly determined for synthetic wastes.

The question still remained, would the POC correlate with the 5-day BOD when analyzing raw domestic sewage? Data obtained during the investigation revealed that the BOD values predicted on the basis of the regression

coefficient derived for synthetic wastes were too high for use with domestic and industrial wastes. Mathematical analysis of the data revealed a straight line relationship between POC and 5-day BOD for domestic wastes, but it became mandatory to derive a new regression coefficient ($1383.2 \times \text{mgC/ml} = 5\text{-day BOD}$).

The need for a different regression coefficient for domestic sewage may be explained in two ways. First, the velocity constant (k value) may be less for the domestic sewage than for the synthetic sewage. And secondly, a carbonaceous fraction contained in domestic waste may be oxidized by the persulfate oxidation that is not readily oxidized biochemically, or at least not during the 5-day BOD. Either one of these two effects would demand use of a smaller regression coefficient.

As reported by Franz and Lutze (8, p. 768-770) and later by Osburn and Werkman (22, p. 423) the persulfate method was intended for oxidation of soluble organic compounds in dilute aqueous solution. It was further stated by Katz et al. (14, p. 1503) that the method was limited to the analysis of water soluble compounds. In general these findings are in agreement with the results of the present study. One notable exception, however, was the quantitative oxidation of the finely ground filter paper. This observation is unique in that no previous worker employing the

persulfate procedure had reported this finding. The question of the oxidation of filter-paper cellulose may be explained, in part at least, by the very nature of the substrate. The harsh treatment of manufacture and the highly purified state presumably dispose filter paper to oxidation by the persulfate procedure. Compounded upon this was the finely divided state of the material allowing oxidation of terminal glucose units, a readily persulfate oxidizable substrate. As reported by Chen and Lauer (6, p. 1225-1226), insoluble biological materials required special treatment before good carbon recoveries were obtained by the persulfate method. In addition, experiments of a similar nature were conducted during this study in an effort to adapt the persulfate oxidation to a total carbon analysis for sewage materials. The results were fruitless. With the exception of the filter-paper cellulose, it has been repeatedly shown that the slightly acidic solution and the weak oxidizing powers of persulfate limit the method to the analysis of water soluble organic compounds. It was recognized, however, that a chemical oxidation might measure certain organic substances not readily oxidized biologically. It was probably this factor that made necessary a different regression coefficient for domestic sewage than was derived for the synthetic sewage.

The question of the relationship of persulfate

oxidizable carbon to that measured by other methods employed in the water pollution field remained unanswered. It was subsequently determined that the persulfate oxidation measured only a fraction of the carbon oxidized by the COD or the total carbon method. Comparison of the data revealed a relationship between COD and the predicted 5-day BOD for wastes of similar composition. There was, however, no connection between data obtained by the persulfate oxidation and the total carbon procedure or between the COD and the total carbon procedure. The total carbon method proved to be unusually difficult for liquid wastes and the data obtained proved to be of limited value.

The identity of the persulfate oxidizable carbon is as yet only partially elucidated. It has thus far been established that the POC fraction comprises a greater carbon fraction than is measured during the 5-day BOD but is considerably less than that measured by either the COD or the total carbon analysis. The question of the validity of the persulfate method to measure the fraction oxidized biochemically was also raised. Experiments that employed an activated sludge process demonstrated quite clearly that the POC fraction is oxidized biochemically during aerobic stabilization of organic wastes. This fact was exemplified by the change in the COD/BOD_c ratio and by the greater percentage reduction of BOD_c than was recorded for either

the COD or TOD.

A final analysis of the experimental data has given considerable encouragement to the idea that the POC test may prove to be a useful index for the measurement of organic pollution in water. It is expected that further application of the method will undoubtedly serve to establish the method in the water pollution field.

SUMMARY

The following points summarize the principal findings of this study:

1. Excellent carbon recoveries were obtained for a variety of water-soluble organic substrates analyzed by the persulfate oxidation procedure. Compounds analyzed included carbohydrates, amino acids, alcohols and fatty acids.
2. A high positive correlation was established between persulfate oxidizable carbon and the 5-day BOD. A regression coefficient was derived whereby the 5-day BOD of various wastes can be predicted from data obtained from the POC determination.
3. By comparison with other tests employed in the water pollution field, it was possible to identify the persulfate oxidizable carbon fraction as the fraction oxidized during aerobic biochemical stabilization.

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