

STUDIES IN THE FIELD OF  
CHEMICAL OXYGEN DEMAND ANALYSIS

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## ABSTRACT

Cerium(IV) was substituted for dichromate as the oxidant in the chemical oxygen demand test. To assess the conditions for optimal oxidation, the effects of total volume, substrate concentration, acid type, and catalyst were studied on the oxidation of ten organic compounds. Under the oxidative conditions studied, cerium(IV) proved in the main to be a much less effective oxidant than dichromate.

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## I. INTRODUCTION

The rapid growth of production facilities to parallel world demand, has in many cases, led to land, air, and water pollution. As a result man is confronted with states of ecological imbalance.

Water pollution is the result of discharging large volumes of untreated inorganic and organic waste materials directly into natural bodies of water. Man is realizing therefore, that if a continuing source of clean water is to be available for his physiological, social, and aesthetic needs, stricter controls must be imposed on effluents released into the environment.

To assess the water quality of such effluents, analytical procedures have been devised to measure such parameters as dissolved oxygen, alkalinity, hardness, color, turbidity, total dissolved solids, sulphate and chloride ions, trace metals, coliform bacteria, and biochemical and chemical oxygen demand.

The biochemical and chemical oxygen demand procedures were developed specifically for use in wastewater analysis. These tests yield important parameters necessary for estimating the oxygen demand that organic material would exert on the total oxygen assets of a receiving stream. Prevention of the release of effluents known to have extremely high oxygen demands avoids depletion of the oxygen assets of the receiving

stream and the consequent death of fish and green plant life.

The biochemical oxygen demand or B.O.D. attempts to simulate under controlled laboratory conditions, the manner in which organic material is oxidized in a receiving stream. In effect, it measures the weight of dissolved oxygen utilized by microorganisms, as carbonaceous and nitrogenous materials are metabolized.

The chemical oxygen demand or C.O.D. provides a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant(39).

The C.O.D. test was developed to overcome two inherent difficulties with the B.O.D test. The latter test cannot be used with wastes containing toxic materials nor can it provide information regarding a waste in a short period of time. Thus, Moore, Kroner, and Ruchhoft(31) developed the C.O.D. test utilizing potassium dichromate as the oxidant.

As dichromate fails to completely oxidize certain aromatic and long chain aliphatic compounds, this study was undertaken to assess the oxidizing power of ceric ion on the oxidation of organic compounds. Ceric ion was chosen as the oxidizing agent, as it has a higher potential than that of dichromate, especially when in contact with perchloric acid. To determine the optimal

conditions for oxidation, the effects of variations of total volume, substrate concentration, acid type, and catalyst were studied. Ten organic compounds were used as substrates for these studies.

## II. LITERATURE REVIEW

### 2.1 Biochemical Oxygen Demand

The biochemical oxygen demand is defined as "the amount of oxygen that would be demanded by organic material in the course of complete biochemical oxidation"(33). The present B.O.D. test was developed from the initial work of Frankland(as quoted in reference 33), who believed that the oxidation of organic material in a closed system was a purely chemical reaction. Later Dupre(as quoted in reference 33) recognized that the observed oxygen depletion of a stored sample of bottled water was due to the activity of microorganisms and that without this form of life little or no oxygen was consumed.

Adeney and McGowan(as quoted in ref. 33) utilized the oxygen depletion values as measures of pollution. Samples of effluent were examined for dissolved oxygen. Duplicate samples were incubated for five days at 65° F and the residual oxygen then determined.

Theriault and Hommon(as quoted in reference 33) realized that details such as the nature of the dilution water, tightness of seal, and the dilution factor required improvement and standardization before reliable and comparable results could be expected. The technique that evolved from their systematic studies was adopted in a Standard Method(as quoted in reference 33) in 1936.

In 1937, Lea and Nichols(25) found that in order to achieve the high oxygen demand of glucose, it was necessary to add to the dilution water small quantities of mineral salts containing ammonia, potassium, sodium, calcium, magnesium, phosphorus, and sulphur. Thus modifications were made to the previous Standard Method and a new revised Standard Method(as quoted in reference 33) appeared in 1946.

With the introduction of a Standard Method, further work was carried out on the rate of reaction occurring in the B.O.D. bottle. Streeter and Phelps(as quoted in reference 33) found that the rate of biochemical oxidation of organic matter was proportional to the remaining concentration of unoxidized substance, measured in terms of oxidizability. This statement suggested that the B.O.D. was a reaction of the first order. When time was taken in days, Streeter and Phelps found that the velocity rate constant had a value of 0.1. With this value, the five-day B.O.D. would oxidize 68% of the total carbonaceous material present. Studies in recent years have shown however, that the velocity constant rarely has a value of 0.1, but may vary from less than one half to more than twice this value(38). This variance makes it impossible to calculate the ultimate carbonaceous demand of a sample unless the "k" value has been determined on the sewage, waste or stream

under consideration.

Schroeder(35) found that the time period during which the sample was incubated was meaningless and that only the plateau B.O.D. values were significant in the determination. Schroeder noted that the plateau could occur at any time depending upon the number and physiological state of the bacteria initially present. The plateau B.O.D. value was found to be reproducible and to have a definite stoichiometric significance.

Carbonaceous organic material, nitrogenous material and chemical reducing compounds are three classes of material that can exert an oxygen demand during the B.O.D. test. Carbonaceous and nitrogenous materials are usable as an energy source by aerobic microorganisms, while reducing compounds react with dissolved oxygen. Reducing compounds are not measured by the test unless the immediate oxygen demand is calculated and this value added to the oxygen demand value obtained from the five day B.O.D.

The distinction made between the oxygen demand exerted by the carbonaceous or nitrogenous compounds is important in evaluating the results of the test. Winogradski and Jordan(as quoted in reference 33) and Heukelekian(20) found carbohydrate material tended to inhibit the functioning of the nitrifying organisms. Phelps(33) noted that nitrification began between

the tenth and twentieth day of incubation. Thus in most cases nitrification is not included in the B.O.D. result. However, when dealing with biologically treated effluents which are low in carbonaceous matter, the nitrification stage occurs sooner and is included in the test. Such results may be misleading if considered solely in terms of the demand such a waste may place on the oxygen assets of a receiving stream. Although an oxygen demand is exerted by the nitrogenous material, nitrite oxygen is still available as an oxygen source. Phelps has stated that by lowering the dissolved oxygen supply of a stream, nitrification can stimulate reaeration and can actually increase the total oxygen resources of the stream.

Selection of the proper seed is a very important parameter in B.O.D. determinations. Standard Methods(38) indicates that with food processing wastes, a satisfactory seed(inoculum) may be obtained by using the supernatant liquor from domestic sewage. However, industrial wastes may contain compounds not amenable to oxidation by domestic sewage seed. Therefore, seed may be prepared from soil, acclimated against specific substrates in the laboratory, or collected at a point several miles below the point of discharge of the waste.

With regard to toxicity and the B.O.D., Coburn(8) found that mercuric chloride levels beyond 0.2 ppm brought about a sharp drop in B.O.D. until at 2 ppm there



was complete bacteriostasis. Presence of chromic and chromate ions were also found to have similar but less drastic effects on the B.O.D. at concentrations of 10 ppm.

Gannon(17) has shown that the dilution factor can also have a significant influence on the results of the test. On 100% and 50% dilutions of river effluent, Gannon found that the 50% dilution gave lower results than the 100% dilution.

From the literature cited it is evident that the B.O.D. test has many limitations. It can be affected by toxic materials, seed, the dilution factor, and fails to indicate the ultimate carbonaceous demand. The five day delay also makes the test unacceptable in cases where results are required quickly. To quote Hoover(21), "The B.O.D. test is paradoxical. It is the basis of all regulatory actions and is used routinely in almost all control and research studies on sewage and industrial waste treatment. It has been the subject of a tremendous amount of research, yet no one appears to consider it adequately understood or well adapted to his own work."

## 2.2 Chemical Oxygen Demand

The aforementioned problems associated with the B.O.D. necessitated the development of a new test, the chemical oxygen demand, or C.O.D. The chemical oxygen demand determination provides a measure of the oxygen

equivalent of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant(39).

The first chemical oxygen demand determination utilized potassium permanganate as the oxidizing agent. The basis of the test was developed by Forehamer(as quoted in reference 16) in 1849. Various modifications to Forehamer's original method were introduced by Woods(as quoted in reference 16) in 1869 and Miller(as quoted in reference 16) in 1865. Woods suggested that the sample be heated to 60° C before the addition of permanganate. Miller suggested the use of potassium iodide to decompose the excess permanganate, followed by titration of the iodine set free with sodium thiosulphate. Miller also stipulated that the allotted time for the action of the permanganate on the oxidizable substances in the water be three hours.

In 1867, Kubel(as quoted in reference 16) introduced a method which differed from those previously devised in that the solution was boiled for five minutes after the addition of the permanganate. The excess permanganate was determined by titration with oxalic acid.

In 1901, Weems(as quoted in reference 16) suggested that the permanganate should be allowed to act on the sample for twelve to twenty-four hours. Stamm(37)

carried out the oxidation with permanganate in an alkaline solution, and prevented the reaction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  by the addition of a barium salt which allowed a better end point to be obtained. In determining the pollution in sea water, Benson and Hicks(4) found that the application of the Zimmerman-Reinhardt procedure in titrating the excess permanganate gave more reproducible results. The purpose of the Zimmerman-Reinhardt solution(a mixture of manganous sulphate, sulphuric and phosphoric acids) was to reduce the potential of the permanganate so that chlorides would not be oxidized to chlorine. This drop in potential also led to a decrease in oxidation of the organic material present.

Matubara(27) found that increased oxidation could be obtained by increasing the boiling time and the concentration of potassium permanganate used, saponifying fats or oils and neutralizing water-soluble fatty acids. Lovett(26) observed that totally different values were obtained depending upon whether 0.125N or 0.0125N potassium permanganate was used. Kashkin and Karasik(as quoted in reference 31) added an initial excess of potassium permanganate calculated to be equivalent to 0.3 to 0.5 mg of oxygen and determined the final excess by titration with oxalic acid at boiling temperature. Shutkovskaya(36) compared the color of the potassium permanganate solution after heating against colored glass

plates to assess the oxygen demand. Standard Methods (as quoted in reference 16) proposed a C.O.D. method where the oxygen consumed from permanganate was that amount used by the sample when digested for 30 minutes in a boiling water bath with a definite strength of acid or alkaline solution.

The research carried out on the permanganate method demonstrated that it was not entirely satisfactory for the determination of oxygen consumed values. The effect of agitation on the sample was important as manganese dioxide tended to precipitate out of solution. Thus if the sample was not agitated frequently, variable results were obtained. The manganese dioxide that did precipitate was difficult to redissolve before the sample was titrated. Permanganate gave a definite end point but as the permanganate color faded slowly, the titration had to be conducted slowly and carefully to obtain a permanent end point. Different analysts who followed the same methods of manipulation produced appreciably varying results. It was also found that the sample size chosen was significant and that the best reproducible results were obtained when the substrate consumed 50% of the oxidizing agent(32).

In 1938, Dzyadzio(12) used potassium iodate in a 65% to 85% sulphuric acid solution as the oxidizing agent. The sample and oxidant were heated to 200° C and

the excess iodate determined iodometrically. Johnson, Tsuchiy, and Halvorson (as quoted in reference 31) modified the method by refluxing the mixture if the sample were high in volatile acids. Although this method gave very reproducible results for different sample volumes, the method required more time, equipment and manipulation than was necessary with the permanganate method (32).

Adeney and Dawson (2) were among the first to use dichromate in the presence of sulphuric acid to detect organic matter in water. The sample and oxidant were heated to  $110^{\circ}$  C for two hours and the excess dichromate was titrated with ferrous sulphate using an outside indicator. Rhame (34) also used dichromate as the oxidizing agent but used the iodometric procedure for determination of the excess dichromate. Ingols and Murray (22) modified Rhame's procedure by refluxing the sample and oxidant for 60 minutes at about  $140^{\circ}$  C. The excess dichromate was then determined iodometrically.

In 1948, Madison (as quoted in reference 32) proposed a method whereby a sample was digested in a mixture of sulphuric and phosphoric acids using dichromate as the oxidant. The digestion period was terminated when the concentrated acids had fumed for exactly four minutes. The test was not satisfactory, for if the sample was fumed too long the oxidizing agent was

decomposed. Blank determinations also gave poor agreement due to the difficulty of stopping the digestion at the right point. The indicator used, sodium diphenylamine sulphonate, was unsatisfactory as it required a lapse of time before there was any noticeable change in the color of the indicator. As a result, back-titration was frequently necessary (32).

In 1949, Moore, Kroner, and Ruchhoft (31) proposed a method in which a sample was subjected to oxidation by a 0.25N potassium dichromate-sulphuric acid mixture. It was found that optimal oxidation occurred if the proportion of sulphuric acid was 50% by volume. Higher acid ratios led to decomposition of the dichromate. At a 50% acid ratio it was also observed that chlorides were quantitatively oxidized. This factor constituted a serious error in the method. It was also found that many straight-chain acids and alcohols were incompletely oxidized and that in many cases the iodate method proposed by Johnson, Tsuchiya, and Halvorson (as quoted in reference 31) gave higher results. The method proposed by Moore et al. differed from previous methods that used dichromate in that 1,10 phenanthroline ferrous complex was used as an indicator and ferrous ammonium sulphate was used as titrant.

In 1951, Moore, Ludzack, and Ruchhoft (32) modified their method by adding silver sulphate as a

catalyst. It was found that this catalyst greatly increased the oxidation of long chain acids and alcohols. However, certain compounds tended to precipitate the silver and either nullified its effects or resulted in a lower oxygen consumed value than the method without catalyst. The latter conditions were especially prevalent when the sample had a high concentration of chlorides. The precipitated silver also caused difficulty in determining the end point, owing to turbidity effects. The authors stated that if work was done on a given type of waste it would be beneficial to use both the regular and catalyzed method and select the one giving the better results.

Dobbs and Williams(11) developed a method to eliminate the chloride interference in the C.O.D. method originally proposed by Moore, Kroner, and Ruchhoft. The chloride interference was attributed to the reduction of dichromate by the chloramine cycle, a cycle which could convert chloride to chlorine in the presence of nitrogenous organic material. Medalia(29) had reported that the chloride interference could be prevented by adding mercuric nitrate. However, Dobbs and Williams found that the nitrate ion oxidized the reduced form of the indicator, shifting the end point of the titration beyond the equivalence point. To overcome this effect, mercuric sulphate was substituted, since large quantities

of sulphate ion were already present in the digestion mixture. Cripps and Jenkins(9) found that chlorides were complexed completely if a mercuric sulphate:chloride ratio of 10:1 were maintained.

Burns and Marshall(6) found that even with a 10:1 ratio of mercuric sulphate to chloride, chlorides were oxidized to chlorine. Upon the introduction of a correction factor for this oxidation, the authors found that on two tested compounds(acetic acid and phthalic anhydride) the results were only about 83% of the theoretical values. This deficiency remained constant over a wide range of chloride concentrations. Therefore the authors introduced a multiplication factor to compensate for this difference.

Nitrite nitrogen was found to be another source of interference in the test. Standard Methods(39) states that a C.O.D. of 1.14 mg is exerted per mg of nitrite nitrogen. Subrahmanyam, Sastry, and Pillai(41) found that the addition of sulfamic acid would destroy the nitrite. A sulfamic acid:nitrite N ratio of 10:1 has been found to be satisfactory for the destruction of nitrite nitrogen(39).

Jeris(23) developed a rapid C.O.D. test which involved heating a sample in the presence of dichromate and sulphuric and phosphoric acids to 165° C. The samples were heated in an open flask without a reflux condenser.



Results from this test indicated that all substrates studied (excluding pyridine and glycine) were oxidized to a satisfactory level when compared to the Standard Methods (39) procedure. However the Department of Food Science at the University of Manitoba found that the Jeris method gave low results compared with the Standard Method when duplicate samples of the same potato processing wastes were being examined (7).

El-Dib and Ramadan (14) studied the oxidation of some organic substrates with ceric ion. These workers found that without the addition of a catalyst, ceric ion gave approximately 70% of the theoretical C.O.D. value for a given compound. They also found that a combined chromium-silver catalyst gave substantial increases in oxidation.

### 2.3 Instrumentation

Instrumentation entered the oxygen demand test when Stenger and Van Hall (40) developed a method that could determine the oxygen demand of a sample two minutes after homogenization or dilution. In the generalized equation for oxidation  $C_a H_b N_c O_d + n/2 O_2$  yields  $a CO_2 + b/2 H_2O + c/2 N_2$ . Although the amount of  $CO_2$  could be measured by an infra-red analyzer the result could not be correlated exactly with oxygen demand because the values "b" and "d" in the equation were unknown. Stenger and Hall replaced the oxidizing gas  $O_2$  with that of  $CO_2$  so