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 occuring 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 $MnO_4^=$ to 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, Tsuchiyn, 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° 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° 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 expecially 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. Subrahmanyan, 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

that the equation for oxidation became: $C_a H_b N_c O_d$ + m CO_2 yielding (m + a) CO + b/2 H_2O + c/2 N_2. By balancing both equations with respect to oxygen, n=m + a, or the number of moles of carbon monoxide produced in the second equation was equivalent to the number of oxygen atoms required for oxidation in the first equation. Using this principle, organic material was combusted in the presence of carbon dioxide and the amount of carbon monoxide produced measured by an infra-red analyzer.

Goldstein, Katz, Meller, and Murdoch(19) have also developed an instrument which is based on combustion of an organic sample. A sample is injected into an electric furnace with a flowing stream of nitrogen gas and a small oxygen component. At the surface of a platinum catalyst the impurities are oxidized by depleting the oxygen on the platinum surface. The oxygen equilibrium on the catalyst surface is then restored by the oxygen in the gas stream. This results in a momentary depletion of oxygen in the gas stream which is measured in a silver-lead fuel cell and is a function of the oxygen demand of the sample.

Unfortunately, the platinum catalyst used in the latter system can be subject to catalyst poisoning by heavy metals. Both instrumental methods are also somewhat limited by the fact that the injected sample must have an oxygen demand in the range of 10 to 300 ppm.

The accuracy of the former system also is limited by the fact that the presence of sulphate and nitrate ions in the sample can lead to substantial decreases in the oxygen demand values.

III. EXPERIMENTAL METHODS

3.1 Experiment 1 Ceric Oxidations

3.1.1 Introduction

To assess the conditions for optimal oxidation using cerium(IV) as the oxidant in the C.O.D. test, the effects of total volume(V), substrate concentration(S), acid type(A), and catalyst(C) were studied on the oxidation of ten organic compounds. A 3x2x2x4 factorial experiment was designed which utilized three levels of factor V, two levels of factor S, two levels of factor A, and four levels of factor C.

Total volume was selected as a factor as Moore, Kroner, and Ruchhoft(31) had shown this to be an extremely important parameter in dichromate oxidations. Total volumes of 30 ml(V1),35 ml(V2) and 45 ml(V3) were used in the first experiment.

Substrate concentration was shown to be an important parameter in permanganate oxidations. Therefore its effect on ceric oxidations was noted using substrate concentrations of 1 g/l(S1) and 0.25 g/l(S2).

As the potential of cerium(IV) can vary from 1.70 volts to 1.30 volts depending upon the acid environment, the oxidation was carried out in the absence(A1) or presence(A2) of 2M perchloric acid.

The exclusion of catalyst(C1), silver catalyst(C2), manganese catalyst(C3), and a combined

silver and manganese catalyst(C4) were chosen as the levels of factor four.

Silver catalyst was chosen as its effectiveness had been demonstrated in dichromate oxidations, while McCurdy and Guilbault(28) had shown that manganese catalyst was effective(in combination with perchloric acid) in increasing the oxidation rate of mercury(I) to mercury(II) when using ceric ion as the oxidizing agent.

Ten organic compounds were chosen from three major classifications of compounds to be oxidized. Glucose, maltose, and starch were tested as representatives of the carbohydrates. Alanine, phenylalanine, tryptophan, and casein were chosen to represent amino acids and proteins. Phenylalanine and tryptophan were particularly chosen to note the effect of ring structure on oxidation. Glycerol, butyric acid, and glycerol tributyrate(G.T.B.) were chosen as representatives of the lipids.

Preliminary work revealed that ceric ammonium sulphate was the best reagent to use for the preparation of cerium(IV) solutions. It was found that the ceric solution should be approximately 2M with respect to sulphuric acid to facilitate the dissolution of the cerium salt. Ceric sulphate was also found to be satisfactory for the preparation of cerium solutions although the latter solution remained a "milky yellow"

color until it was diluted with distilled water. The third reagent tested was the tetra-hydrate form of ceric sulphate. It cannot be recommended for the preparation of cerium solutions as it was very hard to dissolve. As large quantities of the cerium reagent were required for this study, the salt ceric ammonium sulphate was utilized because of market availability and cost factors.

3.1.2 Sample Preparation

The two substrate concentrations, S1 and S2, were respectively 1 g/l and 0.25 g/l. In the majority of cases solutions of these concentrations were prepared by dissolving the appropriate substrate in distilled water and making up to 1000 ml in a volumetric flask.

In the cases of alanine and phenylalanine it was necessary to heat the solution to dissolve the substrates. Tryptophan and casein were dissolved in a very dilute sodium hydroxide solution(0.30 g/l) instead of distilled water.

The insolubility of glycerol tributyrate presented difficulties. The triglyceride was shaken vigorously with the required volume of water. The suspension was rapidly transferred to a beaker provided with a magnetic stirrer, and it was stirred continuously during sampling.

For convenience, volume measurements rather than weight measurements were used for butyric acid.

Concentrations of 1 ml/l and 0.25 ml/l were used.

The substrates were reagent grade chemicals obtained from BDH(Canada) Ltd.

3.1.2.1 Reagents

1. Ceric Ammonium Sulphate Solution(0.1N-0M Perchloric acid): 126.5 g of hydrated ceric ammonium sulphate were added to a mixture of 350 ml of distilled water and 60 ml of concentrated sulphuric acid. This mixture was heated to near boiling and was stirred constantly. After heating for 30 minutes the mixture was cooled and the supernatant transferred to a 2000 ml volumetric flask. Distilled water(350 ml) and concentrated sulphuric acid(140 ml) were added to the insoluble portion. The mixture was heated until the remaining ceric salt dissolved. After cooling, the solution was added to the 2000 ml volumetric flask and the contents made up to volume with distilled water.

2. Ceric Ammonium Sulphate Solution(0.1N-2M Perchloric acid): This solution was prepared in the same manner as the preceding solution except that 330 ml of 72% perchloric acid was added before bringing the contents of the 2000 ml flask up to volume with distilled water.

3. Ferrous Ammonium Sulphate Solutions(0.05N-0.10N): Ferrous ammonium sulphate (39g-78g) was dissolved in 600 ml of distilled water.

Concentrated sulphuric acid(40 ml) was added to this solution. The solution was transferred to a 2000 ml volumetric flask and the contents brought up to volume with distilled water.

4. Potassium Dichromate Solutions(0.1N-0.25N): Potassium dichromate was dried in an oven at 103 C for two hours. After cooling in a desiccator, potassium dichromate(9.8072 g-23.5180 g) was weighed out and dissolved in 600 ml of distilled water. The solution was transferred to a 2000 ml volumetric flask and the contents brought up to the mark with distilled water.

5. Sulphuric acid-silver sulphate solution: Silver sulphate(22 g) was mixed with concentrated sulphuric acid(4.08kg) and the mixture allowed to stand for two days.

6. Manganous sulphate solution: 2.12 g of hydrated manganous sulphate were dissolved volumetrically in 500 ml of distilled water.

7. Ferroin indicator: A solution of 1,10-phenanthroline ferrous sulphate was obtained commercially from British Drug Houses.

3.1.2.2 Method

A 10 ml aliquot of ceric ammonium sulphate solution(OM perchloric acid) or (2M perchloric acid) was transferred to a 250 ml flat-bottomed boiling flask. To this mixture was added a 5 ml aliquot of substrate(1 g/l

or 0.25 g/l). Distilled water was then added to bring the sample to one of the standard total volumes, ie. 30,35, or 45 ml. The following catalyst treatments were used:

(1) C1: 10 ml of concentrated sulphuric acid, no catalyst.

(2) C2: 10 ml of silver sulphate-concentrated sulphuric acid solution.

(3) C3: 1 ml of manganous sulphate solution plus 10 ml of concentrated sulphuric acid.

(4) C4: 10 ml of silver sulphate-concentrated sulphuric acid solution plus 1 ml of manganous sulphate solution.

Blank determinations were carried out for each treatment combination by substituting distilled water for substrate. Following sample preparation the flasks were swirled to ensure uniform mixing. Anti-bumping granules (BDH) were then added to each flask. The samples were then refluxed for two hours using Corning hot plates and Liebig and coil condensers having standard 24/40 ground glass joints. After refluxing and cooling, the condensers were washed down with distilled water to make a final volume of approximately 100 ml in the boiling flasks. Four drops of ferroin indicator were added and then each flask was titrated with 0.1N ferrous ammonium sulphate solution to a reddish-orange end-point. The ferrous ammonium sulphate solution was standardized daily

against a 0.1N potassium dichromate solution.

3.1.2.3 Standardization of Ferrous Ammonium Sulphate Solution

A 10 ml aliquot of 0.1N potassium dichromate solution was transferred to a 250 ml Erlenmeyer flask. Fifty millilitres of distilled water were added to the flask followed by the addition of 30 ml of concentrated sulphuric acid. The solution was swirled and then cooled. Four drops of ferroin indicator were added and the solution was titrated with ferrous ammonium sulphate solution to a reddish-brown end point.

3.1.2.4 Calculation of C.O.D.

The C.O.D. was calculated using the equation $(V1-V2)x\ N\ x\ 8000/V3$ where V1 is ml of ferrous ammonium sulphate solution used for the blank, V2 is the ml of ferrous ammonium sulphate solution used for the sample, V3 is the ml of substrate solution, and N is the normality of the ferrous ammonium sulphate solution used(39). The constant, 8000, is introduced to convert millequivalents of oxidant consumed in the oxidation of a given volume(in millilitres) of solution to milligrams of oxygen required to oxidize one litre of the same solution. All the calculations were adjusted so that the C.O.D. figure for each treatment combination was based on a substrate concentration of 1 g/l.

3.2 Experiment 2 Dichromate Oxidations

3.2.1 Introduction

To serve as a comparison for the ceric oxidations, treatment combinations involving total sample volumes of 30 ml(V1) and 35 ml(V2), substrate concentrations of 1 g/l(S1) and 0.25 g/l(S2), 0M perchloric acid(A1), and catalysts, silver(C2), manganese(C3), and no catalyst(C1) were subjected to oxidation using a 0.1N dichromate solution.

As a further comparison, all compounds were oxidized by the Standard Methods(39) procedure. Four replications were used in the latter two procedures.

3.2.2 Sample Preparation

Sample preparation was identical with that described in section 3.1.2.

3.2.2.1 Reagents

Reagents used were the same as those described in section 3.1.2.1.

3.2.2.2 Modified Dichromate Method

The method used to prepare the treatment combinations involving total volume, substrate concentration, acid type, and catalyst was identical with that of section 3.1.2.2 except for the substitution of a 0.1N potassium dichromate solution for the ceric ammonium sulphate solution, and a reduced number of levels for total volume, acid type, and catalyst as described in the

introduction.

3.2.2.3 Standard Method

A 10 ml aliquot of a 0.25N potassium dichromate solution was placed in a 250 ml flat-bottomed boiling flask. To this solution was added a 20 ml aliquot of substrate solution(0.25 g/l) and 30 ml of the sulphuric acid-silver sulphate solution. The flask was swirled thoroughly and a few anti-bumping granules added. Blank determinations were carried out by replacing the 20 ml aliquot of substrate solution with 20 ml of distilled water. After refluxing and cooling, sufficient distilled water was added to make a total volume of approximately 100 ml in the boiling flasks. Four drops of ferroin indicator were added to each flask, followed by titration with a 0.1N ferrous ammonium sulphate solution. The C.O.D. was calculated in the manner previously described in section 3.1.2.4.

3.3 Experiment 3 Oxidation Rate Curves

3.3.1 Introduction

Rate curves were plotted using a total sample volume of 30 ml, a substrate concentration of 0.25 g/l, silver catalyst, and 0.1N solutions of ceric ammonium sulphate(OM perchloric acid) and potassium dichromate. These were the conditions that gave optimal oxidation in the latter two experiments.

3.3.2 Sample Preparation

The method of sample preparation was identical

with that described in section 3.1.2.

3.3.2.1 Reagents

The reagents used were the same as those described in section 3.1.2.1.

3.3.2.2 Method

A 10 ml aliquot of 0.1N ceric ammonium sulphate solution(0M perchloric acid) or 0.1N potassium dichromate solution was placed in a flat-bottomed boiling flask. A 5 ml aliquot of substrate solution(0.25 g/l) was added, followed by the addition of 5 ml of distilled water and 10 ml of sulphuric acid-silver sulphate solution. The flasks were thoroughly swirled. Duplicate samples were then refluxed for 0,15,30,45,60,90, and 120 minutes. Blank determinations were conducted by replacing the 5 ml aliquot of substrate solution with 5 ml of distilled water. Blank determinations were refluxed for 2 hours. After refluxing, the condensers were washed down with distilled water to make a total volume of 100 ml in the boiling flasks. Upon thorough cooling, four drops of ferroin indicator were added and the samples titrated with 0.05N ferrous ammonium sulphate solution to a reddish-orange end point(ceric ion) or a brownish-red end point(dichromate). The C.O.D. was calculated in the same manner as described in section 3.1.2.4.

3.4 Experiment 4 Chloride Interference

3.4.1 Introduction

The interfering effect of chloride ion on the

standard C.O.D. determination received comment in the literature survey. It was of obvious importance to determine whether a similar effect occurred when chlorides were present in oxidation mixtures containing ceric ion. Using the procedures already described, 0.1N ceric ammonium sulphate(0M perchloric acid) in the presence of silver catalyst was treated with 5 ml aliquots of 0.05% and 1.0% sodium chloride solutions. The mixtures were refluxed as before and the extent of reduction of ceric ion was determined by titration. The effect of adding mercuric sulphate to complex the chloride ion was also tested.

3.4.2 Sample Preparation

In this experiment no organic test solutions were used.

3.4.2.1 Reagents

The reagents used were the same as those described in section 3.1.2.1 with the following additional reagents:

1. Sodium Chloride Solution: 0.05 g of Analar sodium chloride was dissolved in water and made up to volume in a 100 ml volumetric flask.

2. Sodium Chloride Solution: 1 g of Analar sodium chloride was dissolved in water and made up to volume in a 100 ml volumetric flask.

3. Mercuric Sulphate, Analar.

3.4.2.2 Method

A 10 ml aliquot of 0.1N ceric ammonium sulphate solution(0M perchloric acid) was placed in a flat-bottomed boiling flask. A 5 ml aliquot of one of the sodium chloride solutions was added followed by the addition of 5 ml of distilled water to make a total sample volume of 30 ml. Ten millilitres of sulphuric acid-silver sulphate solution was added and the flask thoroughly swirled. Duplicate samples were then refluxed for 2 hours. The procedure was then repeated using 10:1 mercuric sulphate to chloride ratios. Blank determinations were conducted by replacing the 5 ml aliquot of sodium chloride solution with 5 ml of distilled water. After refluxing, the condensers were washed down with distilled water to make a total volume of 100 ml in the boiling flasks. Upon thorough cooling, 4 drops of ferroin indicator were added and the samples titrated with 0.05N ferrous ammonium sulphate solution to a reddish-orange end point. The C.O.D. was calculated in the same manner as described in section 3.1.2.4.

Experiment 5 Catalysis of Ceric Oxidation by Chromic Ion

3.5.1 Introduction

As reported in the literature survey, El-Dib and Ramadan(14) used a catalyst containing silver(as silver sulphate) and chromium(as chromic sulphate) for ceric

oxidations with good results. In view of the results obtained by the latter workers, it was of interest to determine whether the chromic ion was truly catalytic or whether it was oxidized to dichromate, which then actually accomplished the oxidation.

The experiment was an exercise in spectrophotometry employing tandem cuvettes. In one compartment of the tandem cell, ceric ammonium sulphate solution was placed, while in the other compartment there was a solution of chromic sulphate. The spectrum between 200 and 450 nm was determined using a water blank. The experiment was repeated using a refluxed mixture of ceric and chromic sulphates in both compartments of the tandem cell.

3.5.2 Sample Preparation

This is described in section 3.5.2.3.

3.5.2.1 Reagents

The reagents used were the same as those described in section 3.1.2.1 with the addition of the following reagent:

1. Chromic Sulphate Solution: Three grams of chromic sulphate were dissolved in distilled water and made up to volume with distilled water in a 100 ml volumetric flask.

3.5.2.2 Special Apparatus

1. A pair of Hellma No. 250 tandem cuvettes.

Each chamber had a light path of approximately 4.375 mm and the cells had the following overall dimensions: 45 mm high, 12.5 mm wide, 12.5 mm deep and the windows were 125 mm thick.

2. A Unicam SP 800 double-beam recording spectrophotometer.

3.5.2.3 Method

Solutions of ceric ammonium sulphate, chromic sulphate and potassium dichromate were used in the manner shown in the following table:

Solution	Sulphuric Acid (Conc.)	Potassium Dichromate (0.25N)	Ceric Ammonium Sulphate (0.1N)	Chromic Sulphate (3%)
A	5 ml	---	2 ml	---
B	5 ml	---	---	2 ml
C	5 ml	0.8 ml	---	---
D	5 ml	---	2 ml	2 ml

The solutions were made up to a total volume of 30 ml and refluxed for 15 minutes. After cooling the samples were made up to volume in a 1000 ml volumetric flask. The following spectra were determined:

(a) Solution A in one compartment of the tandem, and solution B in the other compartment. Henceforth, this shall be referred to as solution E.

(b) Solution D in both compartments of the tandem.

(c) Solution A in one compartment and solution D in the other compartment of the tandem.

(d) Solution A in both compartments of the tandem.

(e) Solution B in both compartments of the tandem.

Spectra were determined between 200 and 450 nm against a distilled water blank.

IV. RESULTS AND DISCUSSION

4.1 Data and Thesis Compilation

The data analysis was carried out on the University of Manitoba's IBM 360/65 system. All the calculations were done in single precision arithmetic using either Statistical Package 13, factorial experiments in randomized complete blocks, or specially written programs in Fortran(10).

Tables were printed out by channeling the output of a program to an IBM 2741 communications terminal, utilizing the Manitoba University Monitor(MUM) programs "PRINT" and "LIST"(1).

The thesis itself was compiled and typed by an IBM 2741 typewriter terminal utilizing the "MUM" programs "TEXT" and "ETEXT"(1).

4.2 Discussion of Experimental Results

4.2.1 Experiment 1 Ceric Oxidations

Table I illustrates the effects of total volume, substrate concentration, acid type and catalyst on the oxidation of the organic compounds tested. Total volume, or acid ratio, had a marked effect on ceric oxidation, especially for the amino acid-lipid compounds tested. Alanine, in particular, had its C.O.D. value reduced by over 50% when the acid ratio was reduced by only 4%.

Excluding the carbohydrate compounds tested, a decrease in substrate concentration brought about a

TABLE I
MEANS OF THE MAIN EFFECTS FOR CERIC OXIDATION
(EXPRESSED AS Mg OXYGEN/G SUBSTRATE)

FACTOR:	VOLUME*			SUBSTRATE CONC.*		ACID TYPE*		CATALYST*			
LEVEL :	1	2	3	1	2	1	2	1	2	3	4
SUBSTRATE											
GLUCOSE	616.	583.	513.	589.	552.	567.	574.	488.	642.	518.	634.
MALTOSE	653.	600.	536.	617.	576.	591.	602.	517.	643.	537.	689.
STARCH	648.	604.	537.	625.	567.	590.	603.	525.	657.	544.	660.
PHENYLALANINE	1478.	1283.	1079.	1161.	1399.	1269.	1291.	1285.	1316.	1217.	1302.
ALANINE	186.	75.	30.	69.	125.	88.	106.	8.	149.	34.	198.
TRYPTOPHAN	1433.	1393.	1333.	1379.	1393.	1381.	1392.	1367.	1396.	1388.	1394.
CASEIN	776.	661.	575.	641.	700.	650.	691.	490.	771.	666.	754.
GLYCEROL	790.	744.	682.	717.	760.	734.	743.	675.	759.	724.	796.
BUTYRIC ACID	824.	564.	375.	431.	744.	379.	816.	367.	789.	800.	450.
G.T.B.	771.	537.	406.	498.	645.	527.	616.	389.	733.	431.	733.

*WHERE: TOTAL VOLUME: V1=30 ML V2=35 ML V3=45 ML

SUBSTRATE CONCENTRATION: S1=.1% S2=.025%

ACID TYPE: A1=0M PERCHLORIC ACID A2=2M PERCHLORIC ACID

CATALYST: C1=NO CATALYST C2=Ag CATALYST

C3=Mn CATALYST C4=Ag+Mn CATALYST

decrease in substrate concentration brought about a corresponding increase in the C.O.D. value. The effect of substrate concentration was most evident in the cases of alanine and butyric acid where the 1 g/l sample had a mean C.O.D. value 45% below that obtained when a 0.25 g/l sample was used.

The presence of 2M perchloric acid in the oxidation mixture brought about only slight increases in oxidation for nine of the ten compounds tested. Butyric acid however, had its C.O.D. value increased by over 50% with the inclusion of perchloric acid in the oxidation mixture.

The means of the main effects for the catalyst treatments indicate that silver had the most pronounced effect on oxidation. Manganese in the main, gave only slight increases in oxidation except with casein and butyric acid, where oxidation increased over the no catalyst treatment by about 30% and 50% respectively. The combined catalyst gave little increase or in some cases a decrease in oxidation over the C.O.D. values obtained using silver catalyst.

Appendix III lists the analysis of variance tables for the organic compounds tested. In all cases, the main effects were shown to be highly significant at the 1% significance level. Catalyst, total volume, substrate concentration, and acid type were the order of

the descending "F" values for the main effects of glucose, maltose, starch, and casein. With alanine, glycerol and glycerol tributyrate the order of the "F" values for the main effects were total volume, catalyst, substrate concentration, and acid type. The "F" values of the main effects of phenylalanine and butyric acid were ordered in terms of substrate concentration, and acid type while those for tryptophan were ordered in terms of total volume, substrate concentration, catalyst and acid type. Replications were found to be non-significant except in the cases of phenylalanine, butyric acid, and glycerol tributyrate. The deviation for phenylalanine cannot be explained, although in the latter two cases, variance could be explained by the volatility of the butyric acid sample and the difficulty encountered in obtaining a uniform sample of glycerol tributyrate.

4.2.2 Experiment 2 Dichromate Oxidations

Table II illustrates the means of the main effects for dichromate oxidation of the ten organic compounds tested.

An increase in total volume, that is, a decrease in the acid ratio, led to a decrease in oxidation, most markedly noted in the cases of alanine, phenylalanine, tryptophan, casein, butyric acid and glycerol tributyrate. A decrease of only 4% in the acid ratio cut the oxidation of butyric acid by approximately

TABLE II

MAIN EFFECTS FOR DICHROMATE OXIDATION
(EXPRESSED AS Mg OXYGEN/G SUBSTRATE)

FACTOR:	VOLUME*		SUBSTRATE CONC.*		CATALYST*		
LEVEL :	1	2	1	2	1	2	3
SUBSTANCE							
GLUCOSE	1022.	1005.	1024.	1003.	1020.	993.	1027.
MALTOSE	1059.	1027.	1044.	1042.	1059.	1024.	1046.
STARCH	1053.	1022.	1033.	1042.	1061.	1010.	1042.
ALANINE	183.	18.	102.	100.	91.	124.	86.
PHENYLALANINE	812.	329.	492.	649.	304.	971.	436.
TRYPTOPHAN	1614.	1424.	1486.	1551.	1524.	1512.	1521.
CASEIN	716.	335.	518.	532.	513.	609.	454.
GLYCEROL	1168.	1125.	1142.	1151.	1145.	1151.	1144.
BUTYRIC ACID	626.	119.	379.	365.	272.	611.	233.
GLYCEROL TRIBUTYRATE	807.	411.	589.	629.	552.	755.	520.

*WHERE: TOTAL VOLUME: V1=30 ML V2=35 ML

SUBSTRATE CONCENTRATION: S1=.1% S2=.025%

CATALYST: C1=NO CATALYST C2=Ag CATALYST C3=Mn CATALYST

80% and the oxidation of glycerol tributyrate by 50%. These figures illustrate the importance of acid in the degradation of these compounds and the importance of adding precisely the same amount of acid to each sample being examined.

Phenylalanine, tryptophan, and glycerol tributyrate were found to be oxidized to a greater extent at the lower substrate concentration. No explanation can be given for this difference except in the case of tryptophan, where the dichromate was almost totally exhausted at the higher substrate concentration. Mainly, however, only small differences in the oxygen demand value were noted with concentration.

Silver catalyst proved to be most effective in increasing the oxidation of alanine, phenylalanine, casein, butyric acid and glycerol tributyrate. However, a decrease in oxidation was noted when silver was used to catalyze the oxidation of carbohydrate compounds. In the main, manganese inhibited oxidation with lower oxygen demand values being obtained than without the addition of catalyst. An increase in oxidation was found when manganese was used for the oxidation of phenylalanine.

Appendix IV features the analysis of variance tables for the dichromate oxidation of the ten organic compounds tested. Excluding glucose and tryptophan the "F" values for the main effects were ordered in terms of

total volume and then catalyst. Substrate concentration was found to be significant at the 1% level in all cases except for the compounds maltose, alanine, glycerol, and butyric acid. Catalyst was found to be non-significant in the oxidation of glycerol and tryptophan.

A statistical comparison of the oxidizing power of the ceric and dichromate ions for the 12 treatment combinations used in the modified dichromate method, can be found in Appendix V. Negative "paired t" values indicate the superiority of dichromate as an oxidant. At a 5% level of significance, dichromate was shown to be superior to ceric ion as an oxidant for 6 of the ten compounds tested. However, there was no statistical difference between the two reagents in the cases of alanine, tryptophan, casein, and butyric acid. Only with phenylalanine did the ceric ion surpass dichromate ion in oxidizing power.

Table III features a comparison of the means obtained from the ceric, modified dichromate, and Standard Methods(39) procedures. The means of the ceric and modified dichromate methods were obtained from samples which had a total volume of 30 ml, a substrate concentration of 0.25 g/l and which contained 0M perchloric acid. The Standard Methods procedure was carried out using a substrate concentration of 0.25 g/l. The modified dichromate procedure used silver as the

TABLE III

OXYGEN CONSUMED BY ORGANIC COMPOUNDS
USING POTASSIUM DICHROMATE AND
CERIC AMMONIUM SULPHATE (Mg OXYGEN/G SUBSTRATE)

COMPOUND	THEORETICAL OXYGEN CONSUMED VALUE	CERIUM(IV)				DICHROMATE	
		NO CAT.*	Ag*	Mn*	Ag+Mn*	MODIFIED METHOD	STANDARD METHOD
GLUCOSE	1066	466(43%)	703(65%)	520(48%)	681(63%)	1019(95%)	1020(95%)
MALTOSE	1122	471(41%)	793(70%)	576(51%)	807(71%)	1060(94%)	1047(93%)
STARCH	1185	495(41%)	748(63%)	568(47%)	740(62%)	1052(88%)	1062(89%)
ALANINE	1078	26(2%)	295(27%)	58(5%)	622(57%)	265(24%)	1046(97%)
PHENYLALANINE	1939	1556(80%)	1563(80%)	1503(77%)	1622(83%)	1033(53%)	1805(93%)
TRYPTOPHAN	1804	1419(78%)	1456(80%)	1402(77%)	1485(82%)	1625(90%)	1769(98%)
CASEIN	....	577(..%)	881(..%)	661(..%)	955(..%)	627(..%)	1381(..%)
GLYCEROL	1214	693(57%)	867(71%)	823(67%)	928(76%)	1186(97%)	1092(89%)
BUTYRIC ACID	1814	641(35%)	1285(70%)	577(31%)	1285(70%)	903(49%)	1772(97%)
G.T.B.***	1960	530(27%)	1039(53%)	567(28%)	1004(51%)	987(50%)	1947(99%)

*USING: TOTAL VOLUME=30 ML SUBSTRATE CONCENTRATION=.025% ACID TYPE=0M PERCHLORIC ACID

(--%)**= % OF THE THEORETICAL VALUE ***G.T.B.= GLYCEROL TRIBUTYRATE

catalyst. The results clearly indicated that the Standard Method was superior in all respects when compared with the results obtained from oxidation with either ceric ammonium sulphate solution. However, a comparison of the modified dichromate method and the ceric ammonium sulphate method(silver catalyst) revealed that superior oxidation was achieved by the latter procedure in the oxidation of glycerol tributyrate, butyric acid, casein, alanine, and phenylalanine. Thus at lower acid ratios, the ceric ammonium sulphate solution oxidized certain organic compounds to a greater extent than did the modified dichromate procedure.

It should be noted at this point that it would have been logical to have increased the acid ratios used in the cerium procedure to approximately 50%. However, with treatment combinations containing total volumes of between 45 and and 35 ml(acid ratios of 22-29%) and silver catalyst, a yellow precipitate began to form after combining acid and the ceric ammonium sulphate solution. The precipitate developed in all flasks, but upon heating it re-dissolved in the blank determinations. In flasks containing organic material the precipitate gradually settled to the bottom of the boiling flasks. In some cases, the precipitate developed as soon as the sulphuric acid-silver sulphate mixture was added, while in other identical samples the precipitate did not develop to the

same extent until the samples were heated. Tests indicated that the same type of precipitate developed no matter what form of cerium salt was used to prepare the initial oxidizing solutions. Silver ion was found to be present in all the precipitates. The precipitate increased in quantity as the acid ratios increased. The precipitate redissolved, however, after refluxing, when water was added. At higher acid ratios than 33%, greater amounts of precipitate developed. The large amount of precipitate that formed caused bumping in the flask, and work done on several compounds indicated that lower oxygen demand values were obtained, presumably because of the precipitation of the ceric ion from solution. El-Dib and Ramadan(14) have conducted experiments with cerium solutions using chromium and silver(silver at approximately the same concentration as in this study) sulphates as a combined catalyst. These workers reported no precipitation when acid ratios of 50% were used. Unfortunately, no mention was made of the specific compound used to prepare the cerium solutions.

4.2.3 Oxidation Rate Curves

Experiment 3 compared the oxidation rates of ceric ion with or without the inclusion of perchloric acid, versus those of dichromate, when a total volume of 30 ml and silver catalyst were employed.

Glucose(Fig. 1), maltose(Appendix VI),

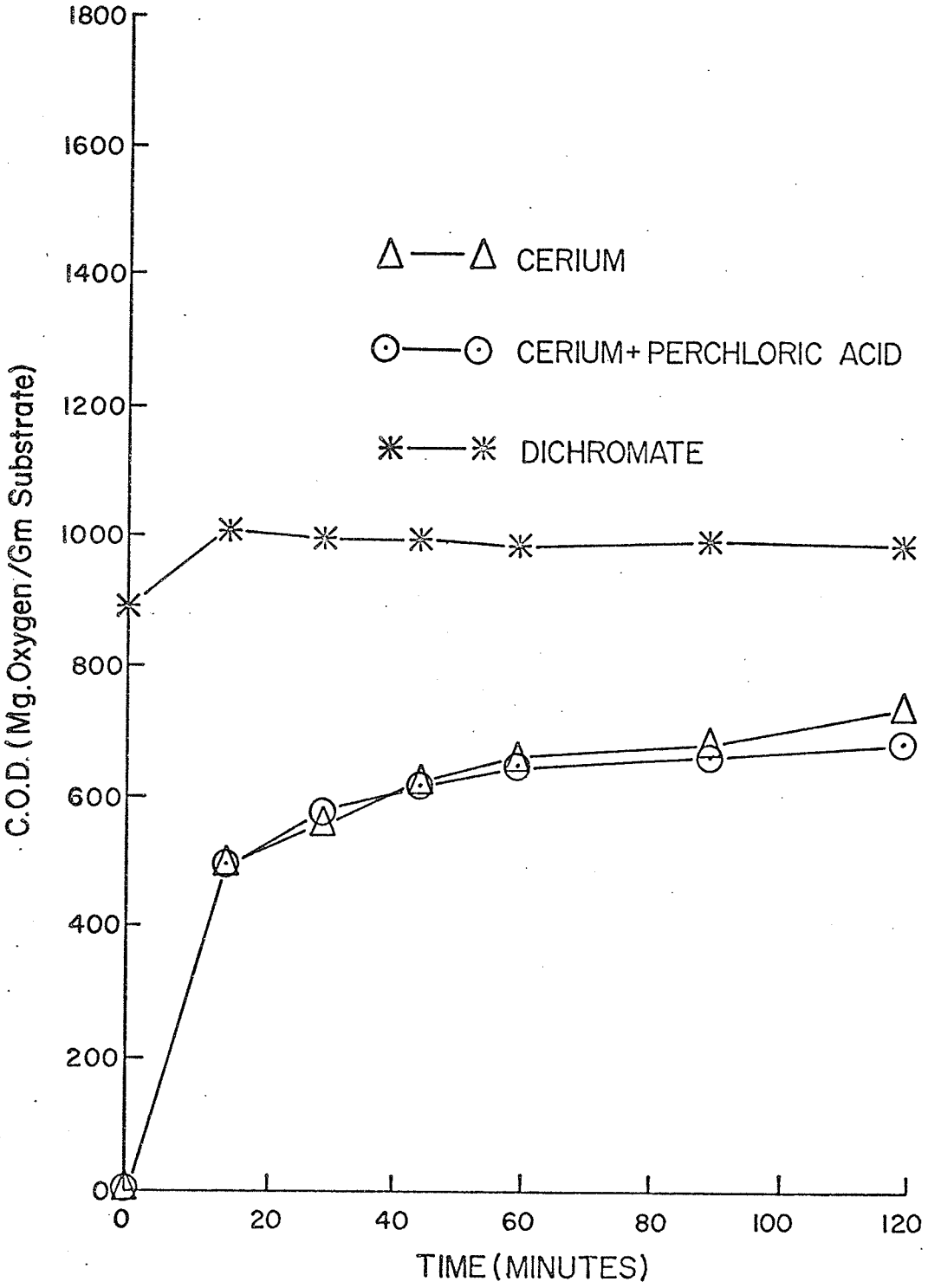


Fig. 1. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for glucose oxidation.

starch(Appendix VI), and glycerol(Appendix VI) appear to have the same oxidation pattern. With dichromate, these compounds were essentially 80-90% oxidized without refluxing, and oxidation was essentially complete after 15 minutes of refluxing. Both ceric ammonium sulphate solutions yielded no oxidation of substrate at 0 time, but oxidation increased slowly to a maximal limit after about 90 minutes of refluxing. Perchloric acid appeared to hinder the oxidation of starch, while it increased the rate of oxidation of glycerol. Perchloric acid appeared to have no effect on the oxidation of glucose or maltose.

Alanine(Appendix VI), was oxidized at a greater rate by both cerium solutions, although the solution that was 2M in perchloric acid gave the fastest rise in oxidation as well as the highest oxidation value. The latter solution had a rapid increase in oxidation after 15 minutes of refluxing, while any significant increase in oxidation with dichromate did not occur until 45 minutes had passed.

Phenylalanine(Fig. 2) was also oxidized to a greater extent by ceric ion and at a faster rate, even although at 0 time dichromate had a C.O.D. value twice that obtained through the use of either cerium solution. The maximum oxidation value was achieved after 45 minutes of refluxing, while dichromate oxidation steadily progressed over the 2 hour oxidation period.

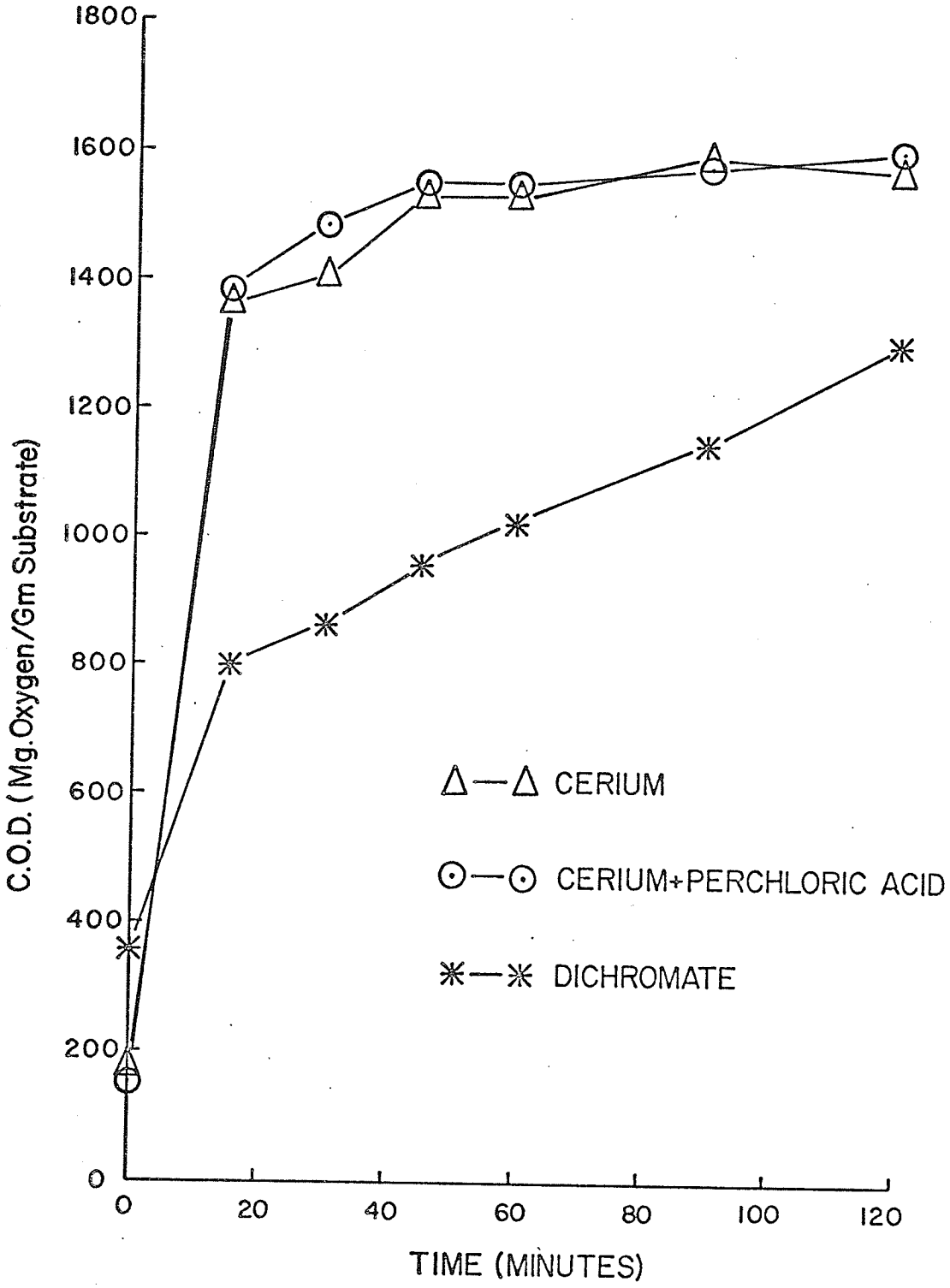


Fig. 2. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for phenylalanine oxidation.

Tryptophan(Appendix VI), was easily oxidized by all three oxidizing mixtures, with the plateau C.O.D. values obtained after 30 minutes of refluxing.

Casein(Appendix VI), was oxidized to a greater degree and at a faster rate by both ceric ammonium sulphate solutions, despite the fact that at 0 time the dichromate solution gave a C.O.D. figure three times that of either cerium solution.

The butyric acid rate curve(Fig. 3) was similar to that of phenylalanine. Ceric ion plus perchloric acid gave the fastest increase in oxidation, although at the end of the two hour reflux period the ceric solution without perchloric acid had surpassed the oxidation figure achieved by the former solution. Dichromate slowly oxidized butyric acid to a maximum value 50% below that obtained from the oxidation values obtained through the use of the ceric ammonium sulphate solutions.

Glycerol tributyrate(Appendix VI), gave the most eratic oxidation curves for all the compounds tested. In many cases, oxidation values decreased as the reflux time progressed. This can be explained by the fact that uniform sampling was difficult to achieve with this compound. All three oxidizing solutions gave approximately equal initial oxidation rates, although dichromate did not achieve a greater C.O.D. value throughout the test than the value obtained after 15

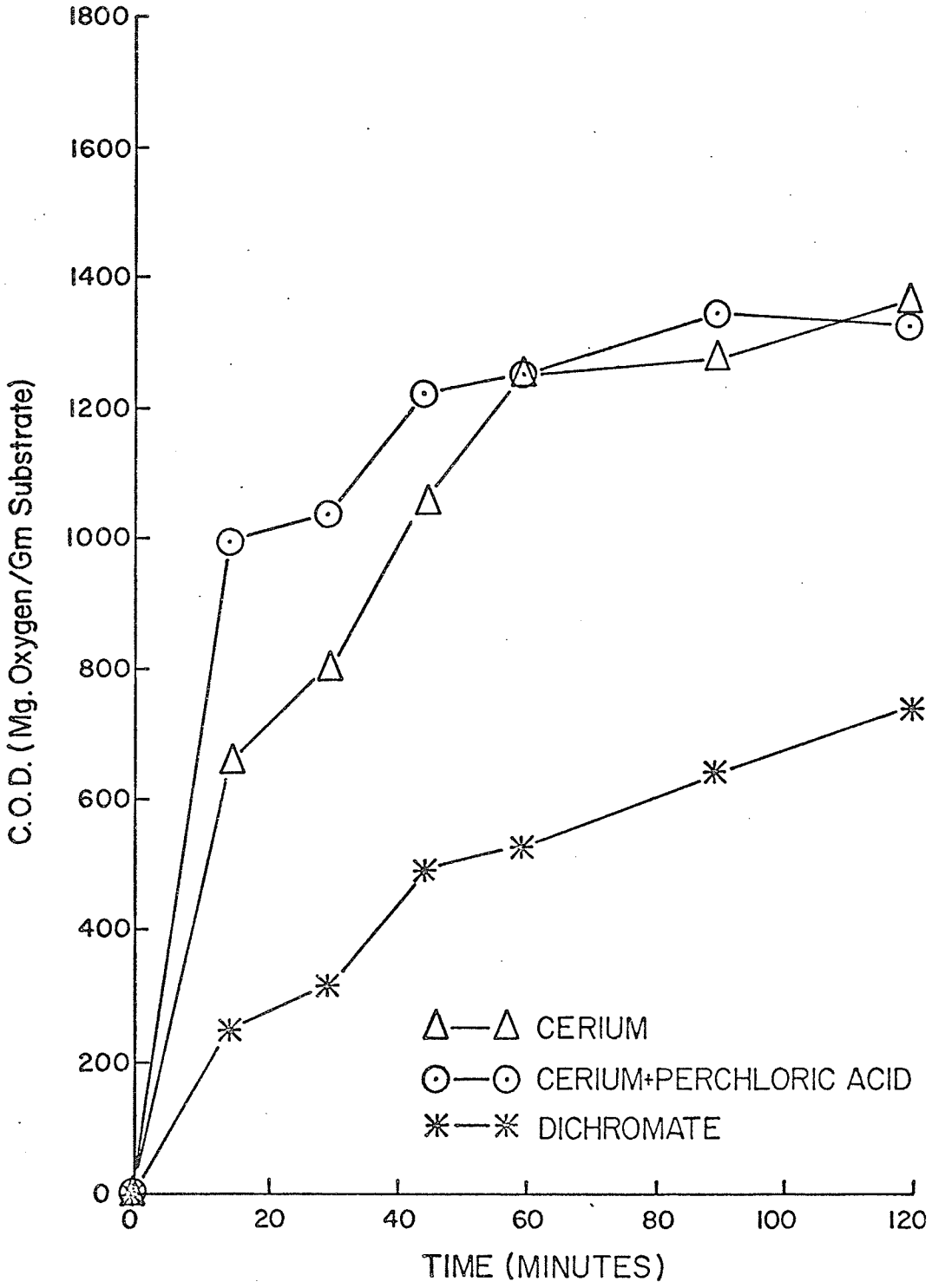


Fig. 3. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for butyric acid oxidation.

minutes of refluxing. The oxidation gains achieved by the cerium solutions were nil after the initial 15 minute reflux period, until the 60 minute mark, when both oxidizing solutions made substantial gains over dichromate.

4.2.4 Experiment 4 Chloride Interference

The results of this experiment tend to parallel those found in dichromate oxidations with regard to chloride interference. It was found that a 5 ml aliquot of a 1% sodium chloride solution completely reduced the ceric ammonium sulphate solution, while a 5 ml aliquot of a 0.05% sodium chloride solution resulted in an average C.O.D. increase of 37 ppm. Addition of mercuric sulphate in the procedure nullified the effect of chloride ion.

4.2.5 Experiment 5 Catalysis of Ceric Oxidation by Chromic Ion

The spectra recorded for this experiment are shown in Fig. 4. The wavelengths at which maximum absorption occurred are shown in Table IV.

TABLE IV

Solution	Absorbance at Band I	Wavelength of Band I	Band II
A	.88	320 nm	234 nm
B	---	---	---
C	.12	350 nm	255 nm
D	.14	350 nm	255 nm
E	.42	319 nm	235 nm

Fig. 4 and Table IV illustrate the effect of real(Solution D) and optical(solution E) mixtures of ceric ammonium sulphate and chromic sulphate solutions. Ceric ion, alone, was found to have a maximum absorbance of 0.88 at 320 nm. Chromic ion had no noticeable peaks in the region from 225 nm to 450 nm but remained at a constant absorbance of 0.04. The optical mixture(Solution E), had its absorbance almost halved at the Band I wavelength. This can be attributed to the increase in transmittance brought about by half of the solution being composed of chromic ion. However an actual combination of ceric and chromic ions resulted in a shift in the wavelength of maximum absorption and the absorbance value. The wavelength of maximum absorbance was 350 nm, the same wavelength found to give maximum absorption for the dichromate solution(solution C), alone. The absorbance value also decreased to a value of 0.14 at this wavelength, a value almost equivalent to that obtained from an equal millequivalent of dichromate solution(0.12).

The result of this experiment seems to indicate that in the experiments conducted by El-Dib and Ramadan(14) where a chromium catalyst was used to dramatically increase the oxidation values of organic materials, chromic ion is converted to dichromate ion by the ceric ion. The dichromate in turn would oxidize the

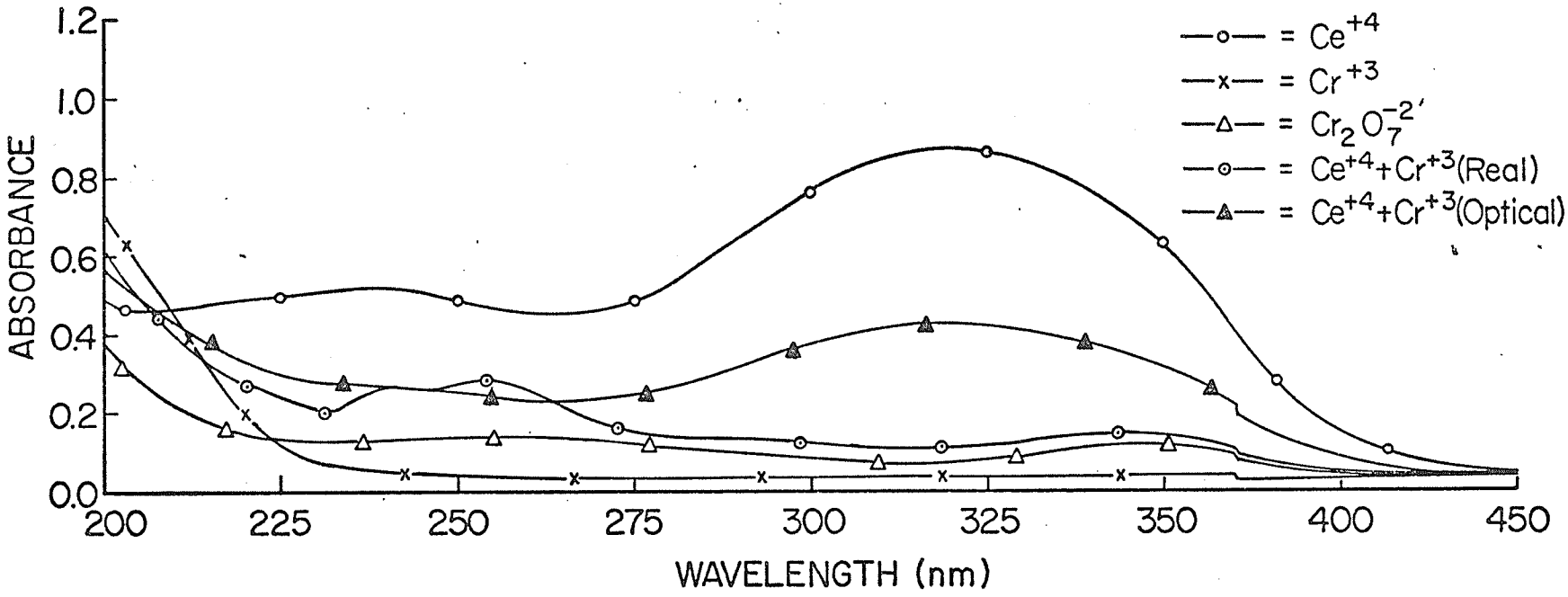
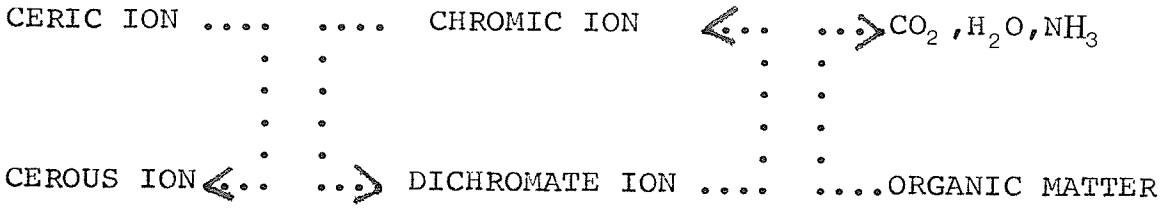


Fig. 4. Spectral Scans of Ionic Species Believed to be Involved in the Catalysis of Ceric Ion.

organic matter. Thus a coupled oxido-reduction chain was in fact present as shown below:



V. CONCLUSIONS

The results of this study have indicated that ceric ion, especially in the form ceric ammonium sulphate, is unsuitable as a replacement for potassium dichromate in the chemical oxygen demand test. Ceric ion itself did appear however, to have a greater oxidizing effect on certain organic compounds at at lower acid ratios. Ceric ion is especially unsuited for the oxidation of carbohydrate material which is easily oxidized by dichromate at lower than 50% acid ratios. Phenylalanine was one compound which was readily attacked by ceric ion, with or without the addition of silver catalyst.

The dichromate rate curves suggest that if a given type of waste, especially one high in soluble carbohydrate material, were under constant examination, it would be advisable to plot such rate curves to discover if oxidation were essentially complete in less than the two hour time period specified by Standard Methods(39).

Ceric ion did not oxidize organic material to the same extent as dichromate ion due, apparently, to experimental difficulties mentioned in the thesis. The latter necessitated the use of relatively low acid concentrations in the oxidation mixture. However, there are two reasons for continued interest in this reagent.

First of all, dichromate ion is highly toxic to man and other organisms(30) while cerium salts have a low toxicity. The release of high concentrations of dichromate ion from busy laboratories might well cause a serious pollution problem that could be avoided by the use of ceric salts. Secondly, oxidations with ceric ion may provide chemists with a more direct correlation between B.O.D. and C.O.D. in certain instances where a waste is high in a specific organic constituent. This has been shown by El-Dib and Ramadan(13) to be the case in the oxidation of starch, paperboard and gelatin wastes.

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APPENDIX I
RAW DATA FOR CERIC OXIDATIONS
(Expressed in mg Oxygen/g Substrate)

V1= Total Volume of 30 ml
V2= Total Volume of 35 ml
V3= Total Volume of 45 ml

S1= Substrate Concentration of 0.10%
S2= Substrate Concentration of 0.025%

A1= 0M Perchloric Acid
A2= 2M Perchloric Acid

C1= No Catalyst
C2= Ag Catalyst
C3= Mn Catalyst
C4= Ag + Mn Catalyst

CERIC OXIDATION OF GLUCOSE

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	581.	581.	583.	581.
1	1	1	2	682.	654.	658.	661.
1	1	1	3	580.	573.	567.	557.
1	1	1	4	656.	669.	662.	668.
1	2	1	1	454.	470.	454.	486.
1	2	1	2	700.	716.	697.	700.
1	2	1	3	508.	524.	508.	540.
1	2	1	4	675.	666.	697.	687.
2	1	1	1	570.	569.	562.	572.
2	1	1	2	627.	619.	611.	609.
2	1	1	3	559.	548.	548.	548.
2	1	1	4	587.	599.	606.	614.
2	2	1	1	394.	397.	394.	413.
2	2	1	2	640.	611.	630.	640.
2	2	1	3	566.	566.	592.	569.
2	2	1	4	670.	683.	711.	714.
3	1	1	1	524.	530.	546.	550.
3	1	1	2	579.	582.	579.	587.
3	1	1	3	509.	499.	507.	507.
3	1	1	4	555.	548.	548.	536.
3	2	1	1	377.	361.	352.	368.
3	2	1	2	646.	583.	580.	583.
3	2	1	3	428.	425.	421.	428.
3	2	1	4	561.	561.	567.	536.
1	1	2	1	587.	578.	584.	589.
1	1	2	2	713.	713.	713.	705.
1	1	2	3	564.	558.	563.	563.
1	1	2	4	678.	679.	679.	681.
1	2	2	1	508.	490.	511.	480.
1	2	2	2	737.	730.	698.	714.
1	2	2	3	540.	540.	534.	531.
1	2	2	4	717.	711.	711.	705.
2	1	2	1	567.	559.	558.	569.
2	1	2	2	633.	638.	644.	644.
2	1	2	3	548.	539.	542.	539.
2	1	2	4	644.	664.	654.	649.
2	2	2	1	397.	423.	420.	417.
2	2	2	2	689.	692.	676.	705.
2	2	2	3	508.	486.	492.	505.
2	2	2	4	691.	687.	675.	687.
3	1	2	1	550.	549.	553.	549.
3	1	2	2	573.	580.	575.	573.
3	1	2	3	523.	505.	519.	519.
3	1	2	4	562.	559.	563.	567.
3	2	2	1	318.	334.	318.	324.
3	2	2	2	567.	583.	561.	567.
3	2	2	3	444.	422.	390.	416.
3	2	2	4	595.	563.	563.	588.

CERIC OXIDATION OF MALTOSE

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	588.	591.	584.	586.
1	1	1	2	684.	675.	684.	689.
1	1	1	3	599.	591.	599.	593.
1	1	1	4	752.	737.	740.	744.
1	2	1	2	766.	769.	835.	804.
1	2	1	3	604.	575.	550.	575.
1	2	1	4	798.	836.	801.	798.
2	1	1	1	604.	597.	606.	605.
2	1	1	2	606.	603.	603.	605.
2	1	1	3	579.	581.	583.	575.
2	1	1	4	665.	659.	666.	673.
2	2	1	1	457.	450.	434.	450.
2	2	1	2	591.	588.	560.	623.
2	2	1	3	505.	492.	499.	499.
2	2	1	4	697.	694.	694.	694.
3	1	1	1	580.	578.	580.	581.
3	1	1	2	558.	557.	555.	558.
3	1	1	3	523.	524.	517.	524.
3	1	1	4	574.	579.	583.	575.
3	2	1	1	410.	388.	422.	486.
3	2	1	2	534.	543.	540.	540.
3	2	1	3	435.	422.	435.	428.
3	2	1	4	569.	598.	627.	598.
1	1	2	1	608.	608.	615.	616.
1	1	2	2	690.	682.	675.	681.
1	1	2	3	595.	583.	582.	588.
1	1	2	4	772.	749.	726.	763.
1	2	1	1	440.	468.	481.	497.
1	2	2	1	530.	504.	530.	495.
1	2	2	2	710.	742.	707.	710.
1	2	2	3	591.	601.	572.	569.
1	2	2	4	759.	743.	743.	743.
2	1	2	1	608.	606.	599.	591.
2	1	2	2	659.	656.	658.	650.
2	1	2	3	582.	575.	578.	582.
2	1	2	4	724.	724.	705.	717.
2	2	2	1	397.	391.	391.	391.
2	2	2	2	690.	706.	696.	683.
2	2	2	3	495.	521.	524.	527.
2	2	2	4	735.	767.	758.	753.
3	1	2	1	579.	579.	585.	571.
3	1	2	2	606.	604.	600.	603.
3	1	2	3	547.	541.	539.	547.
3	1	2	4	591.	600.	597.	585.
3	2	2	1	391.	404.	388.	388.
3	2	2	2	577.	580.	609.	596.
3	2	2	3	432.	432.	432.	425.
3	2	2	4	601.	614.	630.	607.

CERIC OXIDATION OF STARCH

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	607.	599.	600.	606.
1	1	1	2	700.	711.	704.	704.
1	1	1	3	610.	609.	612.	622.
1	1	1	4	701.	701.	709.	701.
1	2	1	1	492.	492.	520.	479.
1	2	1	2	737.	753.	753.	753.
1	2	1	3	541.	579.	579.	576.
1	2	1	4	780.	748.	713.	723.
2	1	1	1	584.	584.	588.	588.
2	1	1	2	660.	660.	660.	661.
2	1	1	3	586.	578.	582.	583.
2	1	1	4	636.	632.	639.	641.
2	2	1	1	445.	436.	439.	449.
2	2	1	2	609.	632.	641.	641.
2	2	1	3	479.	511.	479.	495.
2	2	1	4	687.	719.	684.	716.
3	1	1	1	573.	573.	573.	577.
3	1	1	2	596.	601.	603.	599.
3	1	1	3	541.	541.	548.	556.
3	1	1	4	589.	603.	619.	594.
3	2	1	1	413.	410.	397.	407.
3	2	1	2	543.	543.	559.	556.
3	2	1	3	438.	438.	416.	413.
3	2	1	4	562.	549.	559.	565.
1	1	2	1	621.	614.	613.	614.
1	1	2	2	696.	701.	707.	706.
1	1	2	3	629.	630.	629.	630.
1	1	2	4	715.	704.	713.	696.
1	2	2	1	541.	538.	541.	541.
1	2	2	2	731.	708.	731.	711.
1	2	2	3	570.	608.	582.	576.
1	2	2	4	687.	719.	694.	681.
2	1	2	1	605.	606.	603.	604.
2	1	2	2	666.	675.	661.	685.
2	1	2	3	619.	618.	621.	614.
2	1	2	4	703.	697.	694.	685.
2	2	2	1	442.	449.	442.	477.
2	2	2	2	661.	709.	709.	773.
2	2	2	3	499.	480.	486.	493.
2	2	2	4	667.	714.	714.	683.
3	1	2	1	585.	582.	582.	581.
3	1	2	2	617.	611.	617.	615.
3	1	2	3	544.	542.	550.	557.
3	1	2	4	627.	623.	621.	621.
3	2	2	1	407.	407.	398.	382.
3	2	2	2	597.	555.	539.	571.
3	2	2	3	446.	422.	446.	422.
3	2	2	4	572.	563.	559.	563.

CERIC OXIDATION OF ALANINE

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	10.	10.	17.	14.
1	1	1	2	179.	165.	245.	170.
1	1	1	3	22.	23.	24.	28.
1	1	1	4	181.	173.	187.	172.
1	2	1	1	30.	27.	24.	24.
1	2	1	2	291.	291.	284.	317.
1	2	1	3	48.	64.	54.	67.
1	2	1	4	558.	516.	597.	821.
2	1	1	1	10.	6.	11.	10.
2	1	1	2	74.	75.	67.	75.
2	1	1	3	14.	14.	16.	16.
2	1	1	4	86.	85.	78.	85.
2	2	1	1	0.	0.	0.	0.
2	2	1	2	137.	121.	134.	131.
2	2	1	3	29.	19.	32.	26.
2	2	1	4	136.	152.	117.	158.
3	1	1	1	4.	0.	3.	3.
3	1	1	2	25.	28.	35.	35.
3	1	1	3	8.	8.	10.	9.
3	1	1	4	45.	38.	39.	42.
3	2	1	1	0.	0.	0.	0.
3	2	1	2	49.	39.	61.	58.
3	2	1	3	16.	29.	22.	26.
3	2	1	4	59.	59.	56.	53.
1	1	2	1	20.	28.	32.	34.
1	1	2	2	186.	229.	246.	267.
1	1	2	3	42.	54.	62.	64.
1	1	2	4	222.	262.	258.	254.
1	2	2	1	0.	0.	0.	0.
1	2	2	2	427.	411.	378.	411.
1	2	2	3	61.	87.	61.	90.
1	2	2	4	563.	563.	460.	499.
2	1	2	1	6.	5.	10.	10.
2	1	2	2	126.	132.	132.	126.
2	1	2	3	21.	25.	25.	26.
2	1	2	4	135.	139.	136.	134.
2	2	2	1	0.	0.	10.	0.
2	2	2	2	148.	173.	173.	176.
2	2	2	3	45.	52.	45.	52.
2	2	2	4	204.	168.	229.	229.
3	1	2	1	2.	1.	1.	4.
3	1	2	2	54.	53.	50.	54.
3	1	2	3	14.	16.	16.	13.
3	1	2	4	62.	68.	63.	64.
3	2	2	1	0.	0.	2.	0.
3	2	2	2	48.	23.	23.	23.
3	2	2	3	45.	32.	23.	29.
3	2	2	4	75.	63.	75.	69.

CERIC OXIDATION OF PHENYLALANINE

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	1337.	1319.	1336.	1330.
1	1	1	2	1394.	1391.	1344.	1434.
1	1	1	3	1323.	1289.	1337.	1291.
1	1	1	4	1386.	1383.	1410.	1370.
2	1	1	1	1126.	1078.	1119.	1099.
2	1	1	2	1254.	1152.	1240.	1211.
2	1	1	3	1078.	1019.	1048.	1026.
2	1	1	4	1417.	1078.	1248.	1173.
3	1	1	1	951.	933.	933.	935.
3	1	1	2	968.	959.	966.	969.
3	1	1	3	909.	902.	927.	913.
3	1	1	4	912.	932.	956.	994.
1	2	1	1	1547.	1554.	1541.	1586.
1	2	1	2	1538.	1542.	1567.	1606.
1	2	1	3	1534.	1503.	1487.	1490.
1	2	1	4	1609.	1584.	1657.	1641.
2	2	1	1	1490.	1410.	1362.	1323.
2	2	1	2	1489.	1332.	1448.	1411.
2	2	1	3	1464.	1378.	1282.	1279.
2	2	1	4	1458.	1427.	1474.	1414.
3	2	1	1	1263.	1330.	1301.	1180.
3	2	1	2	1223.	1223.	1288.	1223.
3	2	1	3	1247.	1282.	1151.	1173.
3	2	1	4	1095.	1130.	1104.	1098.
1	1	2	1	1392.	1399.	1394.	1397.
1	1	2	2	1452.	1464.	1453.	1449.
1	1	2	3	1365.	1365.	1393.	1335.
1	1	2	4	1455.	1430.	1451.	1430.
2	1	2	1	1116.	1085.	1141.	1134.
2	1	2	2	1325.	1160.	1257.	1217.
2	1	2	3	1023.	1078.	1054.	1045.
2	1	2	4	1251.	1125.	1172.	1227.
3	1	2	1	950.	939.	936.	933.
3	1	2	2	1004.	990.	987.	990.
3	1	2	3	892.	916.	916.	909.
3	1	2	4	974.	981.	989.	1000.
1	2	2	1	1618.	1592.	1592.	1598.
1	2	2	2	1577.	1609.	1580.	1584.
1	2	2	3	1521.	1552.	1505.	1574.
1	2	2	4	1603.	1593.	1603.	1600.
2	2	2	1	1563.	1547.	1368.	1432.
2	2	2	2	1527.	1546.	1474.	1511.
2	2	2	3	1292.	1329.	1238.	1257.
2	2	2	4	1521.	1339.	1505.	1436.
3	2	2	1	1304.	1336.	1269.	1260.
3	2	2	2	1246.	1223.	1191.	1191.
3	2	2	3	1113.	1141.	1098.	1151.
3	2	2	4	1281.	1198.	1207.	1166.

CERIC OXIDATION OF TRYPTOPHAN

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	1409.	1407.	1407.	1407.
1	1	1	2	1425.	1427.	1429.	1426.
1	1	1	3	1417.	1420.	1413.	1419.
1	1	1	4	1418.	1409.	1414.	1413.
1	2	1	1	1417.	1426.	1401.	1433.
1	2	1	2	1473.	1442.	1435.	1476.
1	2	1	3	1385.	1401.	1423.	1401.
1	2	1	4	1505.	1489.	1464.	1486.
2	1	1	1	1375.	1375.	1373.	1377.
2	1	1	2	1387.	1395.	1382.	1393.
2	1	1	3	1384.	1393.	1385.	1386.
2	1	1	4	1385.	1388.	1392.	1391.
2	2	1	1	1366.	1376.	1369.	1385.
2	2	1	2	1400.	1391.	1369.	1385.
2	2	1	3	1366.	1366.	1366.	1366.
2	2	1	4	1362.	1337.	1362.	1385.
3	1	1	1	1334.	1334.	1337.	1339.
3	1	1	2	1350.	1350.	1349.	1355.
3	1	1	3	1356.	1359.	1356.	1360.
3	1	1	4	1333.	1330.	1335.	1331.
3	2	1	1	1369.	1331.	1337.	1331.
3	2	1	2	1312.	1321.	1308.	1305.
3	2	1	3	1337.	1337.	1337.	1337.
3	2	1	4	1293.	1302.	1327.	1315.
1	1	2	1	1395.	1398.	1399.	1398.
1	1	2	2	1437.	1433.	1436.	1449.
1	1	2	3	1390.	1386.	1388.	1383.
1	1	2	4	1425.	1419.	1422.	1419.
1	2	2	1	1411.	1411.	1404.	1388.
1	2	2	2	1466.	1470.	1473.	1470.
1	2	2	3	1472.	1453.	1545.	1545.
1	2	2	4	1481.	1493.	1471.	1455.
2	1	2	1	1372.	1366.	1369.	1366.
2	1	2	2	1394.	1401.	1416.	1414.
2	1	2	3	1365.	1350.	1362.	1365.
2	1	2	4	1392.	1394.	1397.	1394.
2	2	2	1	1347.	1391.	1350.	1350.
2	2	2	2	1441.	1409.	1415.	1447.
2	2	2	3	1536.	1527.	1489.	1393.
2	2	2	4	1473.	1461.	1437.	1473.
3	1	2	1	1325.	1318.	1326.	1320.
3	1	2	2	1358.	1353.	1350.	1356.
3	1	2	3	1326.	1317.	1312.	1326.
3	1	2	4	1350.	1359.	1350.	1353.
3	2	2	1	1290.	1309.	1309.	1309.
3	2	2	2	1329.	1329.	1313.	1345.
3	2	2	3	1368.	1355.	1323.	1298.
3	2	2	4	1362.	1362.	1286.	1312.

CERIC OXIDATION OF CASEIN

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	513.	528.	555.	554.
1	1	1	2	814.	842.	822.	821.
1	1	1	3	842.	829.	826.	869.
1	1	1	4	658.	687.	683.	684.
1	2	1	1	563.	605.	519.	624.
1	2	1	2	859.	862.	919.	884.
1	2	1	3	632.	654.	696.	664.
1	2	1	4	960.	963.	954.	944.
2	1	1	1	443.	461.	450.	442.
2	1	1	2	719.	698.	694.	692.
2	1	1	3	705.	698.	708.	687.
2	1	1	4	601.	611.	614.	604.
2	2	1	1	477.	493.	528.	528.
2	2	1	2	758.	771.	765.	765.
2	2	1	3	609.	597.	606.	622.
2	2	1	4	777.	765.	771.	771.
3	1	1	1	375.	380.	389.	372.
3	1	1	2	617.	609.	617.	601.
3	1	1	3	609.	608.	609.	607.
3	1	1	4	560.	578.	556.	554.
3	2	1	1	439.	429.	423.	430.
3	2	1	2	660.	664.	660.	654.
3	2	1	3	606.	591.	571.	575.
3	2	1	4	676.	736.	676.	676.
1	1	2	1	617.	524.	584.	563.
1	1	2	2	844.	874.	885.	889.
1	1	2	3	693.	730.	730.	732.
1	1	2	4	885.	875.	877.	886.
1	2	2	1	617.	740.	647.	663.
1	2	2	2	955.	1041.	992.	961.
1	2	2	3	797.	766.	769.	760.
1	2	2	4	975.	993.	969.	996.
2	1	2	1	458.	456.	474.	453.
2	1	2	2	740.	739.	735.	734.
2	1	2	3	643.	640.	641.	642.
2	1	2	4	769.	760.	761.	767.
2	2	2	1	506.	524.	512.	494.
2	2	2	2	869.	829.	853.	866.
2	2	2	3	680.	683.	664.	661.
2	2	2	4	806.	837.	821.	837.
3	1	2	1	384.	391.	383.	384.
3	1	2	2	619.	639.	629.	631.
3	1	2	3	567.	571.	570.	566.
3	1	2	4	644.	645.	656.	636.
3	2	2	1	401.	435.	417.	392.
3	2	2	2	737.	730.	730.	712.
3	2	2	3	597.	624.	615.	621.
3	2	2	4	717.	689.	661.	686.

CERIC OXIDATION OF GLYCEROL

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	683.	683.	677.	681.
1	1	1	2	799.	791.	795.	796.
1	1	1	3	707.	709.	706.	715.
1	1	1	4	817.	805.	805.	811.
1	2	1	1	693.	693.	687.	702.
1	2	1	2	860.	860.	869.	881.
1	2	1	3	815.	815.	833.	830.
1	2	1	4	902.	902.	955.	955.
2	1	1	1	660.	656.	667.	667.
2	1	1	2	730.	732.	732.	732.
2	1	1	3	694.	690.	687.	696.
2	1	1	4	709.	724.	724.	720.
2	2	1	1	651.	630.	672.	633.
2	2	1	2	766.	762.	769.	775.
2	2	1	3	753.	764.	753.	753.
2	2	1	4	886.	877.	902.	874.
3	1	1	1	652.	652.	658.	652.
3	1	1	2	686.	677.	677.	676.
3	1	1	3	678.	678.	676.	681.
3	1	1	4	654.	663.	659.	665.
3	2	1	1	627.	681.	654.	651.
3	2	1	2	678.	655.	665.	672.
3	2	1	3	714.	717.	714.	699.
3	2	1	4	751.	751.	745.	751.
1	1	2	1	778.	768.	780.	769.
1	1	2	2	781.	782.	783.	797.
1	1	2	3	725.	724.	722.	721.
1	1	2	4	810.	826.	810.	804.
1	2	2	1	692.	669.	707.	677.
1	2	2	2	852.	855.	852.	874.
1	2	2	3	800.	761.	776.	747.
1	2	2	4	921.	918.	921.	913.
2	1	2	1	744.	743.	740.	739.
2	1	2	2	741.	759.	744.	742.
2	1	2	3	697.	700.	699.	695.
2	1	2	4	776.	774.	774.	765.
2	2	2	1	669.	627.	625.	633.
2	2	2	2	845.	842.	814.	839.
2	2	2	3	747.	744.	747.	761.
2	2	2	4	885.	863.	874.	860.
3	1	2	1	665.	661.	656.	664.
3	1	2	2	665.	675.	688.	669.
3	1	2	3	670.	684.	675.	672.
3	1	2	4	683.	682.	685.	686.
3	2	2	1	589.	604.	627.	604.
3	2	2	2	695.	730.	689.	689.
3	2	2	3	732.	696.	702.	702.
3	2	2	4	740.	746.	751.	751.

CERIC OXIDATION OF BUTYRIC ACID

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	268.	279.	330.	296.
1	1	1	2	722.	765.	681.	745.
1	1	1	3	313.	282.	295.	310.
1	1	1	4	643.	601.	638.	591.
1	2	1	1	690.	622.	589.	666.
1	2	1	2	1306.	1247.	1333.	1257.
1	2	1	3	633.	600.	527.	550.
1	2	1	4	1322.	1224.	1255.	1342.
2	1	1	1	239.	237.	225.	245.
2	1	1	2	472.	497.	360.	368.
2	1	1	3	211.	226.	212.	223.
2	1	1	4	436.	445.	452.	382.
2	2	1	1	427.	431.	404.	441.
2	2	1	2	1042.	1181.	719.	709.
2	2	1	3	399.	419.	399.	406.
2	2	1	4	1090.	1124.	811.	747.
3	1	1	1	128.	132.	99.	92.
3	1	1	2	387.	379.	425.	327.
3	1	1	3	117.	109.	102.	110.
3	1	1	4	380.	359.	401.	399.
3	2	1	1	192.	202.	188.	225.
3	2	1	2	927.	844.	788.	686.
3	2	1	3	156.	146.	163.	143.
3	2	1	4	777.	592.	639.	530.
1	1	2	1	509.	541.	526.	570.
1	1	2	2	980.	990.	997.	998.
1	1	2	3	444.	454.	454.	536.
1	1	2	4	1010.	1024.	1094.	970.
1	2	2	1	791.	824.	854.	758.
1	2	2	2	1365.	1394.	1437.	1397.
1	2	2	3	682.	1236.	817.	798.
1	2	2	4	1356.	1376.	1267.	1360.
2	1	2	1	354.	323.	354.	353.
2	1	2	2	583.	691.	562.	493.
2	1	2	3	360.	361.	383.	352.
2	1	2	4	765.	715.	593.	545.
2	2	2	1	593.	583.	590.	557.
2	2	2	2	900.	1276.	775.	1190.
2	2	2	3	527.	547.	524.	550.
2	2	2	4	1033.	1007.	845.	806.
3	1	2	1	149.	136.	155.	141.
3	1	2	2	460.	454.	404.	437.
3	1	2	3	148.	139.	157.	150.
3	1	2	4	422.	437.	355.	429.
3	2	2	1	204.	234.	231.	201.
3	2	2	2	850.	847.	946.	580.
3	2	2	3	221.	254.	237.	221.
3	2	2	4	895.	849.	875.	648.

CERIC OXIDATION OF GLYCEROL TRIBUTYRATE

TREATMENT COMBINATION				REPLICATIONS			
V	S	A	C				
1	1	1	1	406.	361.	400.	389.
1	1	1	2	779.	790.	797.	836.
1	1	1	3	410.	460.	441.	420.
1	1	1	4	849.	849.	825.	799.
1	2	1	1	515.	578.	515.	512.
1	2	1	2	1059.	1085.	974.	1039.
1	2	1	3	542.	574.	577.	577.
1	2	1	4	946.	978.	1054.	1039.
2	1	1	1	300.	316.	302.	299.
2	1	1	2	484.	514.	500.	515.
2	1	1	3	340.	334.	316.	332.
2	1	1	4	522.	492.	493.	471.
2	2	1	1	384.	387.	419.	422.
2	2	1	2	672.	720.	676.	634.
2	2	1	3	447.	476.	438.	431.
2	2	1	4	774.	870.	753.	607.
3	1	1	1	216.	206.	212.	208.
3	1	1	2	452.	413.	400.	387.
3	1	1	3	245.	258.	248.	265.
3	1	1	4	441.	470.	374.	353.
3	2	1	1	265.	265.	284.	265.
3	2	1	2	704.	764.	758.	473.
3	2	1	3	273.	289.	304.	257.
3	2	1	4	689.	683.	654.	537.
1	1	2	1	530.	520.	528.	527.
1	1	2	2	971.	975.	985.	1012.
1	2	2	3	534.	519.	532.	529.
1	1	2	4	948.	965.	972.	936.
1	2	2	1	703.	694.	755.	716.
1	2	2	2	1163.	1071.	1169.	1151.
1	2	2	3	765.	774.	777.	774.
1	2	2	4	1150.	1121.	1097.	1106.
2	1	2	1	357.	382.	369.	368.
2	1	2	2	737.	821.	613.	565.
2	1	2	3	381.	394.	406.	381.
2	1	2	4	689.	735.	660.	626.
2	2	2	1	467.	483.	498.	498.
2	2	2	2	642.	811.	703.	648.
2	2	2	3	565.	544.	559.	562.
2	2	2	4	712.	975.	799.	799.
3	1	2	1	233.	227.	228.	227.
3	1	2	2	481.	540.	448.	444.
3	1	2	3	246.	327.	312.	304.
3	1	2	4	456.	493.	488.	431.
3	2	2	1	222.	234.	238.	225.
3	2	2	2	477.	780.	780.	780.
3	2	2	3	320.	311.	299.	317.
3	2	2	4	682.	712.	566.	566.

APPENDIX II
RAW DATA FOR DICHROMATE OXIDATIONS
(Expressed in mg Oxygen/g Substrate)

V1= Total Volume of 30 ml
V2= Total Volume of 35 ml

S1= Substrate Concentration of 0.10%
S2= Substrate Concentration of 0.025%

C1= No catalyst
C2= Ag catalyst
C3= Mn catalyst

DICHROMATE OXIDATION OF GLUCOSE

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	1048.	1065.	1077.	1064.
1	1	2	1008.	1020.	1007.	1011.
1	1	3	1049.	1040.	1043.	1042.
2	1	1	1024.	1026.	1025.	1050.
2	1	2	972.	973.	976.	989.
2	1	3	1032.	1003.	1009.	1019.
1	2	1	977.	1010.	1013.	1000.
1	2	2	1018.	1012.	1021.	1024.
1	2	3	988.	988.	1007.	988.
2	2	1	988.	985.	994.	975.
2	2	2	978.	953.	962.	962.
2	2	3	1056.	1056.	1052.	1065.

DICHROMATE OXIDATION OF MALTOSE

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	1070.	1068.	1068.	1068.
1	1	2	1052.	1042.	1036.	1039.
1	1	3	1058.	1058.	1059.	1058.
2	1	1	1043.	1046.	1052.	1044.
2	1	2	1016.	1011.	1002.	1005.
2	1	3	1050.	1036.	1042.	1044.
1	2	1	1114.	1065.	1046.	1052.
1	2	2	1084.	1039.	1058.	1058.
1	2	3	1065.	1058.	1052.	1049.
2	2	1	1055.	1065.	1046.	1046.
2	2	2	972.	985.	985.	1004.
2	2	3	1023.	1020.	1046.	1020.

DICHROMATE OXIDATION OF STARCH

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	1069.	1070.	1069.	1069.
1	1	2	1014.	1020.	996.	1011.
1	1	3	1059.	1054.	1052.	1048.
2	1	1	1049.	1044.	1043.	1046.
2	1	2	988.	982.	982.	985.
2	1	3	1039.	1038.	1036.	1036.
1	2	1	1072.	1082.	1078.	1069.
1	2	2	1046.	1072.	1037.	1053.
1	2	3	1060.	1057.	1058.	1061.
2	2	1	1043.	1075.	1053.	1046.
2	2	2	1008.	983.	1008.	970.
2	2	3	1015.	1024.	1018.	1021.

DICHROMATE OXIDATION OF ALANINE

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	179.	201.	188.	187.
1	1	3	177.	169.	170.	177.
1	1	2	202.	180.	177.	196.
2	1	1	21.	19.	25.	20.
2	1	2	25.	19.	19.	19.
2	1	3	19.	19.	19.	19.
1	2	1	159.	120.	149.	152.
1	2	2	213.	281.	265.	303.
1	2	3	130.	127.	143.	149.
2	2	1	18.	0.	24.	0.
2	2	2	24.	24.	14.	27.
2	2	3	0.	24.	24.	18.

DICHROMATE OXIDATION OF PHENYLALANINE

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	484.	428.	443.	466.
1	1	2	1048.	1031.	1043.	1011.
1	1	3	530.	499.	539.	548.
1	2	1	534.	438.	559.	502.
1	2	2	1556.	1365.	1305.	1394.
1	2	3	980.	1043.	884.	856.
2	1	1	143.	138.	135.	133.
2	1	2	664.	673.	651.	658.
2	1	3	141.	160.	120.	124.
2	2	1	100.	110.	125.	132.
2	2	2	793.	803.	771.	778.
2	2	3	148.	138.	141.	125.

DICHROMATE OXIDATION OF TRYPTOPHAN

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	1553.	1544.	1552.	1550.
1	1	2	1587.	1575.	1586.	1590.
1	1	3	1550.	1541.	1536.	1550.
2	1	1	1365.	1349.	1359.	1359.
2	1	2	1410.	1398.	1397.	1415.
2	1	3	1476.	1470.	1474.	1478.
1	2	1	1684.	1694.	1691.	1694.
1	2	2	1594.	1619.	1676.	1613.
1	2	3	1684.	1684.	1694.	1684.
2	2	1	1493.	1493.	1500.	1497.
2	2	2	1435.	1444.	1435.	1412.
2	2	3	1380.	1380.	1365.	1380.

DICHROMATE OXIDATION OF CASEIN

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	685.	691.	689.	677.
1	1	2	758.	757.	758.	758.
1	1	3	624.	621.	629.	639.
2	1	1	335.	329.	331.	335.
2	1	2	461.	440.	452.	444.
2	1	3	259.	263.	259.	249.
1	2	1	719.	742.	749.	726.
1	2	2	813.	781.	836.	781.
1	2	3	716.	680.	684.	661.
2	2	1	318.	288.	288.	305.
2	2	2	418.	441.	418.	424.
2	2	3	256.	256.	237.	233.

DICHROMATE OXIDATION OF GLYCEROL

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	1156.	1148.	1155.	1148.
1	1	2	1158.	1156.	1154.	1156.
1	1	3	1170.	1162.	1156.	1155.
2	1	1	1126.	1131.	1132.	1131.
2	1	2	1157.	1118.	1118.	1125.
2	1	3	1126.	1125.	1125.	1126.
1	2	1	1201.	1170.	1173.	1173.
1	2	2	1198.	1173.	1180.	1195.
1	2	3	1143.	1177.	1198.	1170.
2	2	1	1118.	1109.	1134.	1112.
2	2	2	1134.	1127.	1127.	1137.
2	2	3	1112.	1115.	1121.	1121.

DICHROMATE OXIDATION OF BUTYRIC ACID

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	440.	560.	434.	489.
1	1	2	934.	987.	921.	944.
1	1	3	451.	421.	446.	412.
2	1	1	40.	30.	19.	51.
2	1	2	409.	381.	405.	289.
2	1	3	6.	6.	7.	11.
1	2	1	496.	533.	435.	604.
1	2	2	993.	875.	939.	807.
1	2	3	475.	455.	519.	441.
2	2	1	69.	32.	62.	59.
2	2	2	238.	259.	201.	191.
2	2	3	38.	0.	21.	21.

DICHROMATE OXIDATION OF GLYCEROL TRIBUTYRATE

TREATMENT COMBINATION			REPLICATION			
V	S	C				
1	1	1	646.	657.	658.	660.
1	1	2	961.	1011.	1016.	968.
1	1	3	687.	551.	650.	574.
2	1	1	364.	398.	390.	380.
2	1	2	573.	580.	590.	503.
2	1	3	344.	324.	332.	323.
1	2	1	664.	765.	881.	891.
1	2	2	918.	1056.	949.	1028.
1	2	3	765.	793.	805.	811.
2	2	1	364.	337.	383.	389.
2	2	2	493.	514.	459.	459.
2	2	3	331.	352.	346.	340.

APPENDIX III
ANALYSIS OF VARIANCE FOR CERIC OXIDATIONS

ANALYSIS OF VARIANCE CERIC OXIDATION OF GLUCOSE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	596.	199.	1.62	3.88
TOTAL VOLUME(V)	2	351433.	175716.	1435.87*	4.71
SUBSTRATE CONCENTRATION(S)	1	63389.	63389.	517.98*	6.76
V X S	2	24158.	12079.	98.70*	4.71
ACID TYPE(A)	1	2712.	2712.	22.16*	6.76
V X A	2	3848.	1924.	15.72*	4.71
S X A	1	1327.	1327.	10.84*	6.76
V X S X A	2	2229.	1114.	9.11*	4.71
CATALYST(C)	3	900278.	300093.	2452.22*	3.88
V X C	6	23597.	3933.	32.14*	2.90
S X C	3	261782.	87261.	713.05*	3.88
V X S X C	6	15504.	2584.	21.12*	2.90
A X C	3	8409.	2803.	22.91*	3.88
V X A X C	6	11676.	1946.	15.90*	2.90
S X A X C	3	635.	212.	1.73	3.88
V X S X A X C	6	11990.	1998.	16.33*	2.90
ERROR	141	17255.	122.		
TOTAL	191	1700818.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF MALTOSE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	105.	35.	0.20	3.88
TOTAL VOLUME(V)	2	441959.	220979.	1241.61*	4.71
SUBSTRATE CONCENTRATION(S)	1	80844.	80844.	454.24*	6.76
V X S	2	35106.	17553.	98.62*	4.71
ACID TYPE(A)	1	6490.	6490.	36.46*	6.76
V X A	2	10551.	5276.	29.64*	4.71
S X A	1	1541.	1541.	8.66*	6.76
V X S X A	2	2287.	1143.	6.42*	4.71
CATALYST(C)	3	982352.	327451.	1839.83*	3.88
V X C	6	73088.	12181.	68.44*	2.90
S X C	3	260835.	86945.	488.51*	3.88
V X S X C	6	12072.	2012.	11.30*	2.90
A X C	3	7176.	2392.	13.44*	3.88
V X A X C	6	41035.	6839.	38.43*	2.90
S X A X C	3	1496.	499.	2.80	3.88
V X S X A X C	6	13400.	2233.	12.55*	2.90
ERROR	141	25095.	178.		
TOTAL	191	1995435.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF STARCH

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	223.	74.	0.43	3.88
TOTAL VOLUME(V)	2	400868.	200434.	1167.49*	4.71
SUBSTRATE CONCENTRATION(S)	1	165640.	165640.	959.86*	6.76
V X S	2	45370.	22685.	131.46*	4.71
ACID TYPE(A)	1	7136.	7136.	41.35*	6.76
V X A	2	4845.	2423.	14.04*	4.71
S X A	1	999.	999.	5.79	6.76
V X S X A	2	43.	21.	0.12	4.71
CATALYST(C)	3	744217.	248372.	1437.54*	3.88
V X C	6	27640.	4607.	26.70*	2.90
S X C	3	162225.	54075.	313.36*	3.88
V X S X C	6	10324.	1721.	9.97*	2.90
A X C	3	626.	209.	1.21	3.88
V X A X C	6	9408.	1568.	9.09*	2.90
S X A X C	3	5738.	1913.	11.08*	3.88
V X S X A X C	6	8659.	1443.	8.36*	2.90
ERROR	141	24332.	173.		
TOTAL	191	1618293.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF ALANINE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	2767.	922.	1.65	3.88
TOTAL VOLUME(V)	2	824302.	412151.	739.50*	4.71
SUBSTRATE CONCENTRATION(S)	1	147521.	147521.	264.85*	6.76
V X S	2	136816.	68408.	122.74*	4.71
ACID TYPE(A)	1	17226.	17226.	30.91*	6.76
V X A	2	4743.	2371.	4.26	4.71
S X A	1	3262.	3262.	5.85	6.76
V X S X A	2	3799.	1900.	3.41	4.71
CATALYST(C)	3	1190522.	396841.	712.03*	3.88
V X C	6	631851.	105308.	188.95*	2.90
S X C	3	155585.	51862.	93.05*	3.88
V X S X C	6	185253.	30876.	55.40*	2.90
A X C	3	11034.	3678.	6.60*	3.88
V X A X C	6	19289.	3215.	5.77*	2.90
S X A X C	3	6447.	2149.	3.86	3.88
V X S X A X C	6	25734.	4289.	7.70*	2.90
ERROR	141	78584.	557.		
TOTAL	191	3444738.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF PHENYLALANINE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	25709.	8570.	4.79*	3.88
TOTAL VOLUME(V)	2	5094200.	2547100.	1425.47*	4.71
SUBSTRATE CONCENTRATION(S)	1	2722443.	2722443.	1523.60*	6.76
V X S	2	62802.	31401.	17.57*	4.71
ACID TYPE(A)	1	22260.	22260.	12.46*	6.76
V X A	2	7970.	3985.	2.23	4.71
S X A	1	933.	933.	0.52	6.76
V X S X A	2	8431.	4215.	2.36	4.71
CATALYST(C)	3	280504.	93501.	52.33*	3.88
V X C	6	105829.	17638.	9.87*	2.90
S X C	3	55428.	18476.	10.34*	3.88
V X S X C	6	18653.	3109.	1.74	2.90
A X C	3	18304.	6101.	3.42	3.88
V X A X C	6	37704.	6284.	3.52*	2.90
S X A X C	3	12268.	4089.	2.29	3.88
V X S X A X C	6	19194.	3199.	1.79	2.90
ERROR	141	251945.	1787.		
TOTAL	191	8744577.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF TRYPTOPHAN

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	655.	218.	0.76	3.88
TOTAL VOLUME(V)	2	324070.	162035.	566.80*	4.71
SUBSTRATE CONCENTRATION(S)	1	9170.	9170.	32.08*	6.76
V X S	2	24212.	12106.	42.35*	4.71
ACID TYPE(A)	1	6242.	6242.	21.84*	6.76
V X A	2	8999.	4500.	15.74*	4.71
S X A	1	12792.	12792.	44.75*	6.76
V X S X A	2	6950.	3475.	12.16*	4.71
CATALYST(C)	3	24290.	8097.	28.32*	3.88
V X C	6	8464.	1411.	4.93*	2.90
S X C	3	9225.	3075.	10.76*	3.88
V X S X C	6	7028.	1171.	4.10*	2.90
A X C	3	12660.	4220.	14.76*	3.88
V X A X C	6	8394.	1399.	4.89*	2.90
S X A X C	3	23019.	7673.	26.84*	3.88
V X S X A X C	6	8010.	1335.	4.67*	2.90
ERROR	141	40309.	286.		
TOTAL	191	534490.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF CASEIN

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	1707.	569.	1.65	3.88
TOTAL VOLUME(V)	2	1303288.	651644.	1892.44*	4.71
SUBSTRATE CONCENTRATION(S)	1	169615.	169615.	492.58*	6.76
V X S	2	2578.	1289.	3.74	4.71
ACID TYPE(A)	1	82877.	82877.	240.69*	6.76
V X A	2	16091.	8045.	23.36*	4.71
S X A	1	4710.	4710.	13.68*	6.76
V X S X A	2	3439.	1720.	4.99*	4.71
CATALYST(C)	3	2377992.	792664.	2301.98*	3.88
V X C	6	33745.	5624.	16.33*	2.90
S X C	3	156434.	52145.	151.43*	3.88
V X S X C	6	34520.	5753.	16.71*	2.90
A X C	3	57721.	19240.	55.88*	3.88
V X A X C	6	10142.	1690.	4.91*	2.90
S X A X C	3	107083.	35694.	103.66*	3.88
V X S X A X C	6	18418.	3070.	8.92*	2.90
ERROR	141	48552.	344.		
TOTAL	191	4428916.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF GLYCEROL

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	163.	54.	.44	3.88
TOTAL VOLUME(V)	2	376573.	188286.	1541.72*	4.71
SUBSTRATE CONCENTRATION(S)	1	86289.	86289.	706.54*	6.76
V X S	2	10546.	5273.	43.18*	4.71
ACID TYPE(A)	1	3951.	3951.	32.35*	6.76
V X A	2	5398.	2699.	22.10*	4.71
S X A	1	9345.	9345.	76.52*	6.76
V X S X A	2	2314.	1157.	9.47*	4.71
CATALYST(C)	3	386160.	128720.	1053.98*	3.88
V X C	6	66642.	11107.	90.95*	2.90
S X C	3	137620.	45873.	375.62*	3.88
V X S X C	6	12458.	2076.	17.00*	2.90
A X C	3	5114.	1705.	1396.00*	3.88
V X A X C	6	10894.	1816.	14.87*	2.90
S X A X C	3	18528.	6176.	50.57*	3.88
V X S X A X C	6	4256.	709.	5.81*	2.90
ERROR	141	17220.	122.		
TOTAL	191	1153470.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF BUTYRIC ACID

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	103408.	34469.	5.46*	3.88
TOTAL VOLUME(V)	2	6499984.	3249992.	514.54*	4.71
SUBSTRATE CONCENTRATION(S)	1	4696528.	4696528.	743.55*	6.76
V X S	2	285008.	142504.	22.56*	4.71
ACID TYPE(A)	1	843600.	843600.	133.56*	6.76
V X A	2	208336.	104168.	16.49*	4.71
S X A	1	27392.	27392.	4.34	6.76
V X S X A	2	41664.	20832.	3.30	4.71
CATALYST(C)	3	8881952.	2960650.	468.73*	3.88
V X C	6	245744.	40957.	6.48*	2.90
S X C	3	640816.	213605.	33.82*	3.88
V X S X C	6	50048.	8341.	1.32	2.90
A X C	3	7584.	2528.	0.40	3.88
V X A X C	6	19296.	3216.	0.51	2.90
S X A X C	3	68064.	22688.	3.59	3.88
V X S X A X C	6	128032.	21339.	3.38*	2.90
ERROR	141	890608.	6316.		
TOTAL	191	23638064.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE CERIC OXIDATION OF GLYCEROL TRIBUTYRATE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	43214.	14405.	5.15*	3.88
TOTAL VOLUME(V)	2	4368144.	2184072.	945.57*	4.71
SUBSTRATE CONCENTRATION(S)	1	1029573.	1029573.	445.74*	6.76
V X S	2	28264.	14132.	6.12*	4.71
ACID TYPE(A)	1	375181.	375181.	162.43*	6.76
V X A	2	115645.	57823.	25.03*	4.71
S X A	1	8136.	8136.	3.52	6.76
V X S X A	2	10337.	5168.	2.24	4.71
CATALYST(C)	3	5065372.	1688457.	730.99*	3.88
V X C	6	291576.	48596.	21.04*	2.90
S X C	3	67880.	22627.	9.80*	3.88
V X S X C	6	118255.	19709.	8.53*	2.90
A X C	3	3261.	1087.	0.47	3.88
V X A X C	6	14712.	2452.	1.06	2.90
S X A X C	3	36869.	12290.	5.32*	3.88
V X S X A X C	6	15667.	2611.	1.13	2.90
ERROR	141	394592.	2799.		
TOTAL	191	11917772.			

* SIGNIFICANT AT 1% LEVEL

APPENDIX IV
ANALYSIS OF VARIANCE FOR DICHROMATE OXIDATIONS

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF GLUCOSE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	144.	48.	0.51	4.42
TOTAL VOLUME(V)	1	3264.	3264.	34.52*	7.44
SUBSTRATE CONCENTRATION(S)	1	5120.	5120.	54.15*	7.44
V X S	1	2624.	2624.	27.75*	7.44
CATALYST(C)	2	10496.	5248.	55.51*	5.29
V X C	2	8240.	4120.	43.58*	5.29
S X C	2	6864.	3432.	36.30*	5.29
V X S X C	2	6592.	3296.	34.86*	5.29
ERROR	33	3120.	95.		
TOTAL	47	46464.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF MALTOSE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	672.	224.	1.51	4.42
TOTAL VOLUME(V)	1	11968.	11968.	80.93*	7.44
SUBSTRATE CONCENTRATION(S)	1	48.	48.	0.33	7.44
V X S	1	752.	752.	5.09	7.44
CATALYST(C)	2	9920.	4960.	33.54*	5.29
V X C	2	2912.	1456.	9.85*	5.29
S X C	2	352.	176.	1.19	5.29
V X S X C	2	976.	488.	3.30	5.29
ERROR	33	4880.	148.		
TOTAL	47	32480.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF STARCH

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	272.	91.	1.14	4.42
TOTAL VOLUME(V)	1	11536.	11536.	145.08*	7.44
SUBSTRATE CONCENTRATION(S)	1	912.	912.	11.47*	7.44
V X S	1	1024.	1024.	12.88*	7.44
CATALYST(C)	2	21552.	10776.	135.52*	5.29
V X C	2	896.	448.	5.63*	5.29
S X C	2	1920.	960.	12.07*	5.29
V X S X C	2	672.	336.	4.23	5.29
ERROR	33	2624.	80.		
TOTAL	47	41408.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF ALANINE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	503.	168.	0.81	4.42
TOTAL VOLUME(V)	1	325980.	325980.	1576.88*	7.44
SUBSTRATE CONCENTRATION(S)	1	68.	68.	0.33	7.44
V X S	1	20.	20.	0.10	7.44
CATALYST(C)	2	13548.	6774.	32.77*	5.29
V X C	2	10460.	5230.	25.30*	5.29
S X C	2	10567.	5284.	25.56*	5.29
V X S X C	2	7710.	3855.	18.65*	5.29
ERROR	33	6822.	207.		
TOTAL	47	375678.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF PHENYLALANINE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	8901.	2967.	1.55	4.42
TOTAL VOLUME(V)	1	2794752.	2794752.	1459.77*	7.44
SUBSTRATE CONCENTRATION(S)	1	296062.	296062.	154.64*	7.44
V X S	1	177346.	177346.	92.63*	7.44
CATALYST(C)	2	3993968.	1996984.	1043.08*	5.29
V X C	2	119232.	59616.	31.14*	5.29
S X C	2	122706.	61353.	32.05*	5.29
V X S X C	2	56590.	28295.	14.78*	5.29
ERROR	33	63179.	1915.		
TOTAL	47	7632736.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF TRYPTOPHAN

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	229.	76.	0.49	4.42
TOTAL VOLUME(V)	1	433704.	433704.	2761.00*	7.44
SUBSTRATE CONCENTRATION(S)	1	50692.	50692.	322.73*	7.44
V X S	1	22174.	22174.	141.17*	7.44
CATALYST(C)	2	1206.	603.	3.84	5.29
V X C	2	92.	46.	0.29	5.29
S X C	2	33437.	16718.	106.44*	5.29
V X S X C	2	35834.	17917.	114.07*	5.29
ERROR	33	5183.	157.		
TOTAL	47	582771.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF CASEIN

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	779.	260.	1.54	4.42
TOTAL VOLUME(V)	1	1738355.	1738355.	10276.91*	7.44
SUBSTRATE CONCENTRATION(S)	1	2241.	2241.	13.25*	7.44
V X S	1	16077.	16077.	95.05*	7.44
CATALYST(C)	2	195037.	97519.	576.52*	5.29
V X C	2	8826.	4413.	26.09*	5.29
S X C	2	494.	247.	1.46	5.29
V X S X C	2	74.	37.	0.22	5.29
ERROR	33	5582.	169.		
TOTAL	47	1967465.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF GLYCEROL

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	224.	75.	0.62	4.42
TOTAL VOLUME(V)	1	21584.	21584.	179.50*	7.44
SUBSTRATE CONCENTRATION(S)	1	880.	880.	7.32	7.44
V X S	1	2560.	2560.	21.29*	7.44
CATALYST(C)	2	416.	208.	1.73	5.29
V X C	2	32.	16.	0.13	5.29
S X C	2	416.	208.	1.73	5.29
V X S X C	2	176.	88.	0.73	5.29
ERROR	33	3968.	120.		
TOTAL	47	30256.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF BUTYRIC ACID

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	3763.	1254.	0.66	4.42
TOTAL VOLUME(V)	1	3082984.	3082984.	1627.82*	7.44
SUBSTRATE CONCENTRATION(S)	1	2281.	2281.	1.20	7.44
V X S	1	7484.	7484.	3.95	7.44
CATALYST(C)	2	1380665.	690333.	364.50*	5.29
V X C	2	89171.	44586.	23.54*	5.29
S X C	2	40448.	20224.	10.68*	5.29
V X S X C	2	4832.	2416.	1.28	5.29
ERROR	33	62500.	1894.		
TOTAL	47	4674128.			

* SIGNIFICANT AT 1% LEVEL

ANALYSIS OF VARIANCE DICHROMATE OXIDATION OF GLYCEROL TRIBUTYRATE

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	CALCULATED F	TABULATED F(.01)
REPLICATIONS	3	5299.	1766.	0.86	4.42
TOTAL VOLUME(V)	1	1880950.	1880950.	916.49*	7.44
SUBSTRATE CONCENTRATION(S)	1	18808.	18808.	9.16*	7.44
V X S	1	54635.	54635.	26.62*	7.44
CATALYST(C)	2	518524.	259262.	126.32*	5.29
V X C	2	30882.	15441.	7.52*	5.29
S X C	2	40480.	20240.	9.86*	5.29
V X S X C	2	4732.	2366.	1.15	5.29
ERROR	33	67727.	2052.		
TOTAL	47	2622037.			

* SIGNIFICANT AT 1% LEVEL

APPENDIX V
PAIRED "T" VALUES FOR CERIC AND DICHROMATE (MODIFIED) OXIDATIONS

PAIRED "T" VALUES FOR CERIC AND DICHROMATE(MODIFIED) OXIDATIONS

SUBSTANCE	CALCULATED "T"	TABULATED "T"(.05)
GLUCOSE	-5.24*	2.20
MALTOSE	-4.78*	2.20
STARCH	-4.30*	2.20
ALANINE	-0.34	2.20
PHENYLALANINE	2.30*	2.20
TRYPTOPHAN	-1.22	2.20
CASEIN	0.76	2.20
GLYCEROL	-6.99*	2.20
BUTYRIC ACID	0.62	2.20
GLYCEROL TRIBUTYRATE	-0.48	2.20

* SIGNIFICANT AT THE 5% LEVEL

APPENDIX VI
FIGURES FOR THE COMPARISON OF THE OXIDATION RATES OF CERIC ION, CERIC ION + PERCHLORIC ACID AND DICHROMATE ION

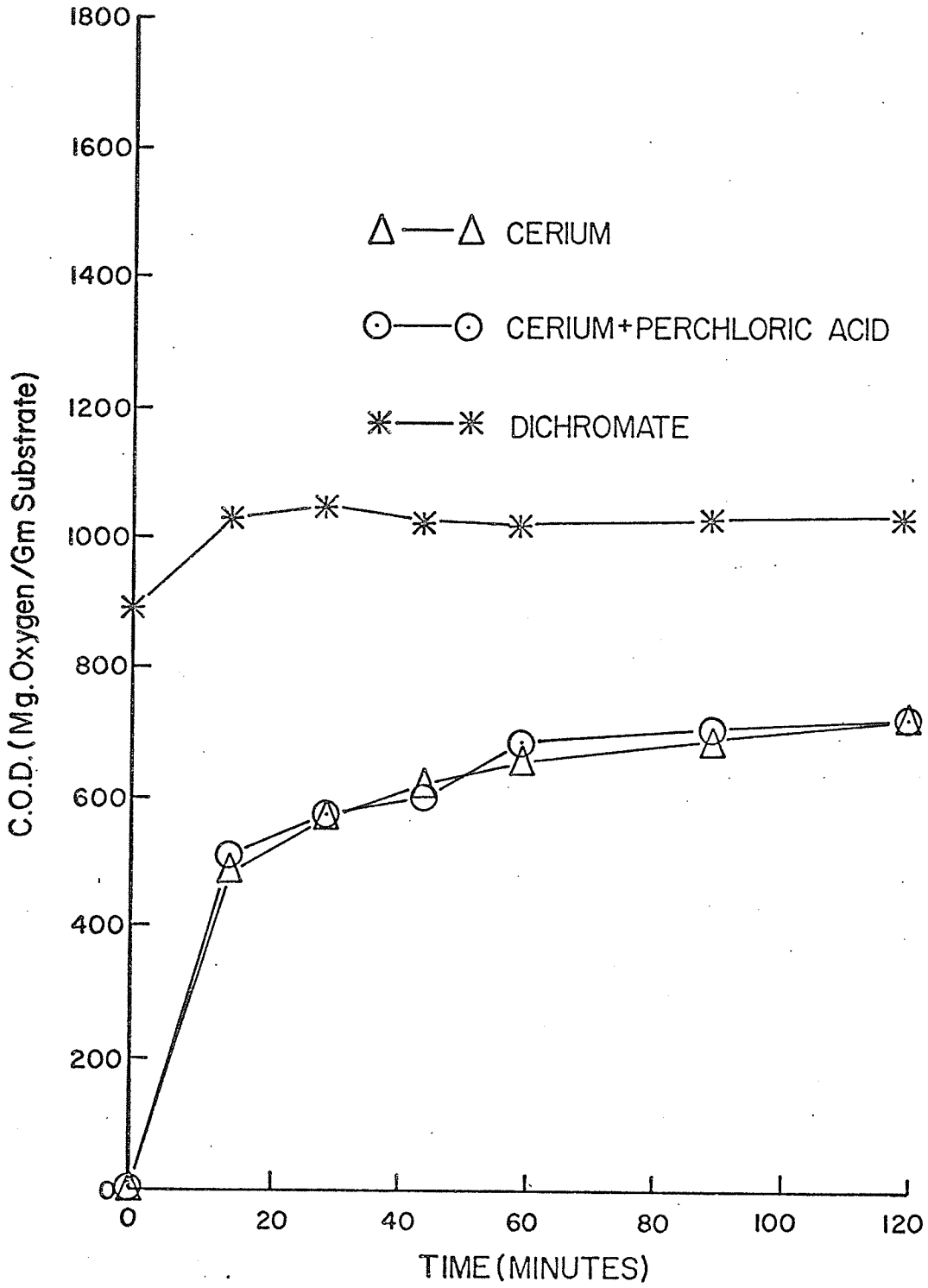

Fig. 1. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for maltose oxidation.

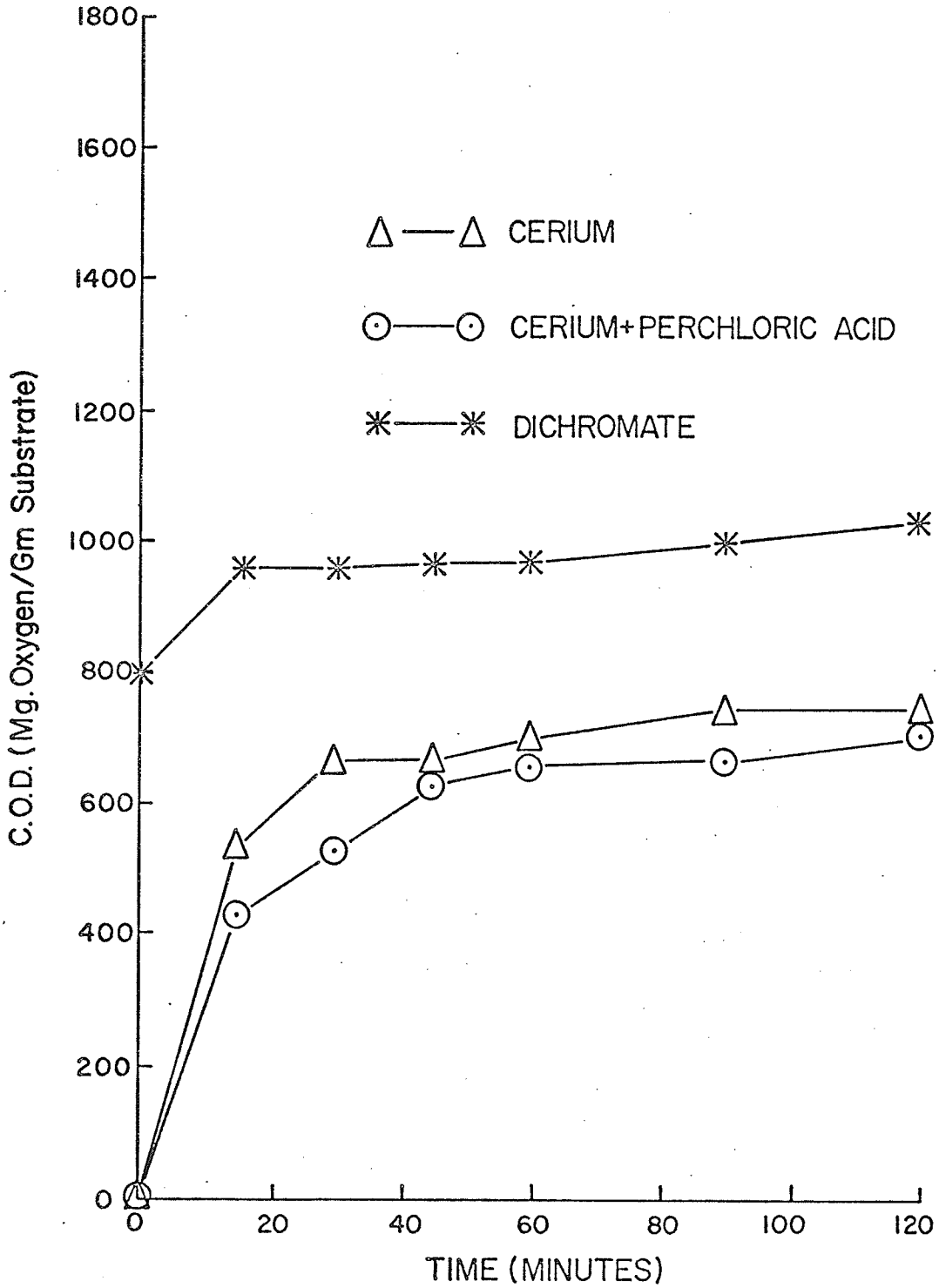

Fig. 2. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for starch oxidation.

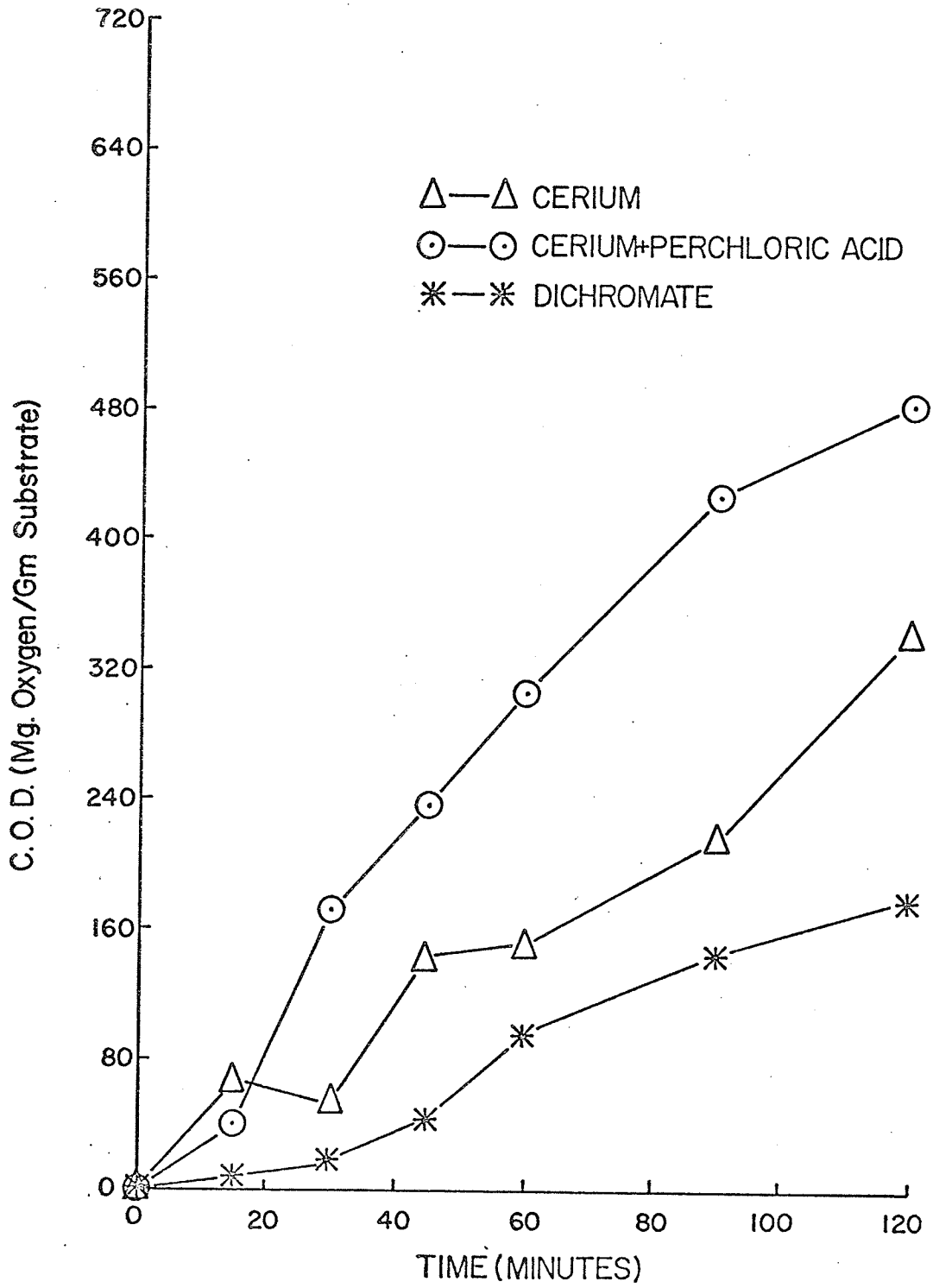

Fig. 3. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for alanine oxidation.

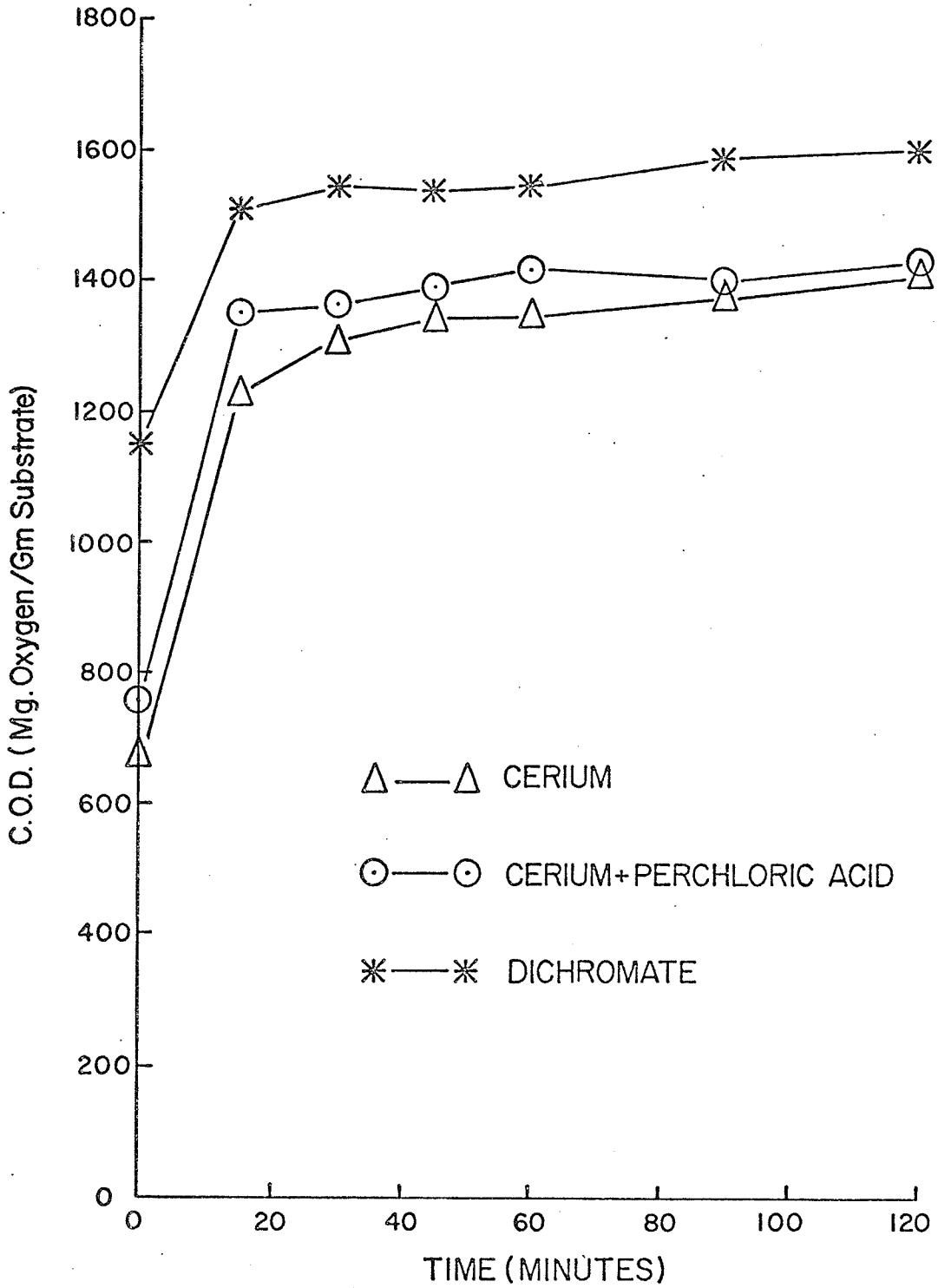

Fig. 4. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for tryptophan oxidation.

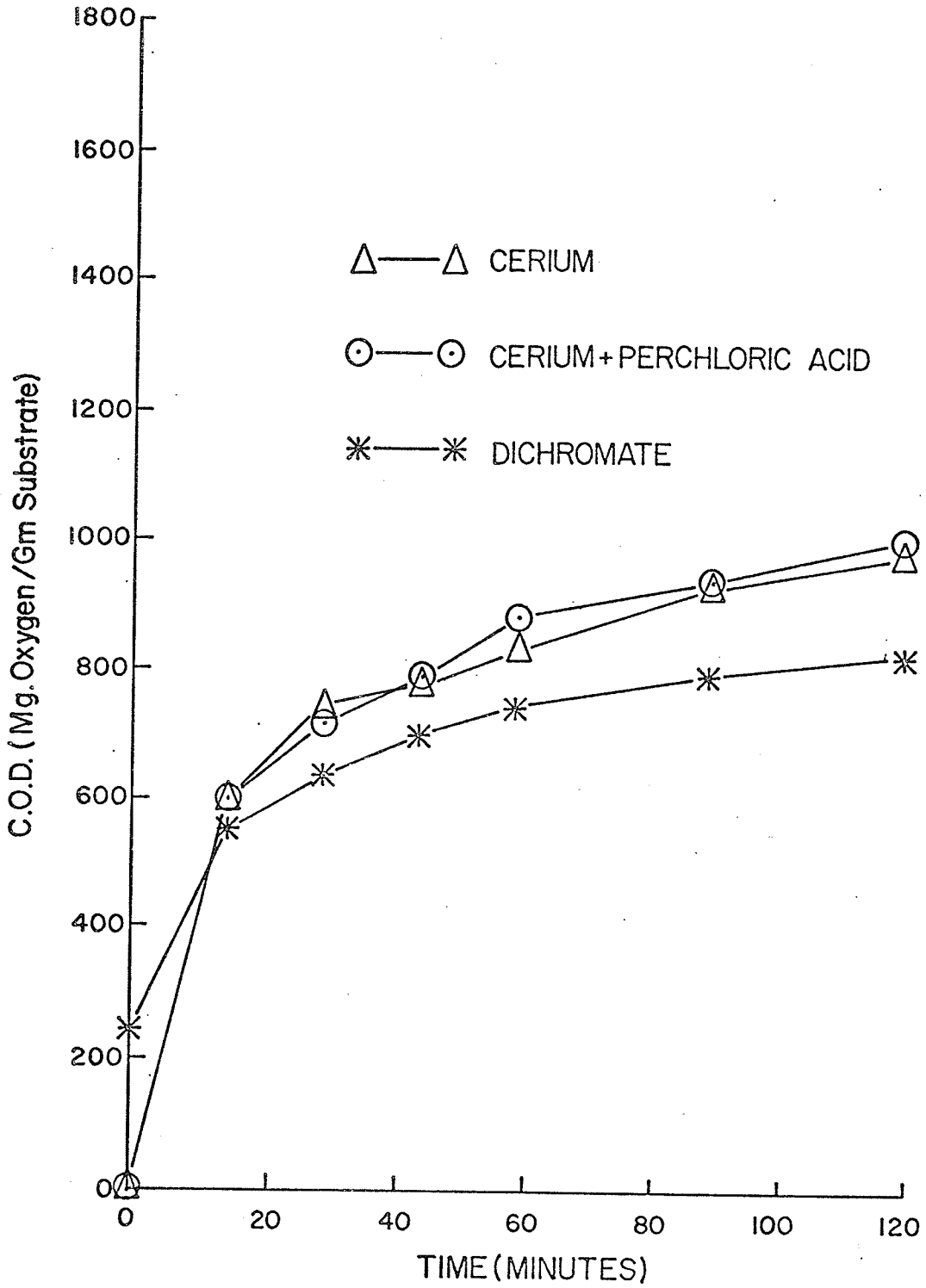

Fig. 5. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for casein oxidation.

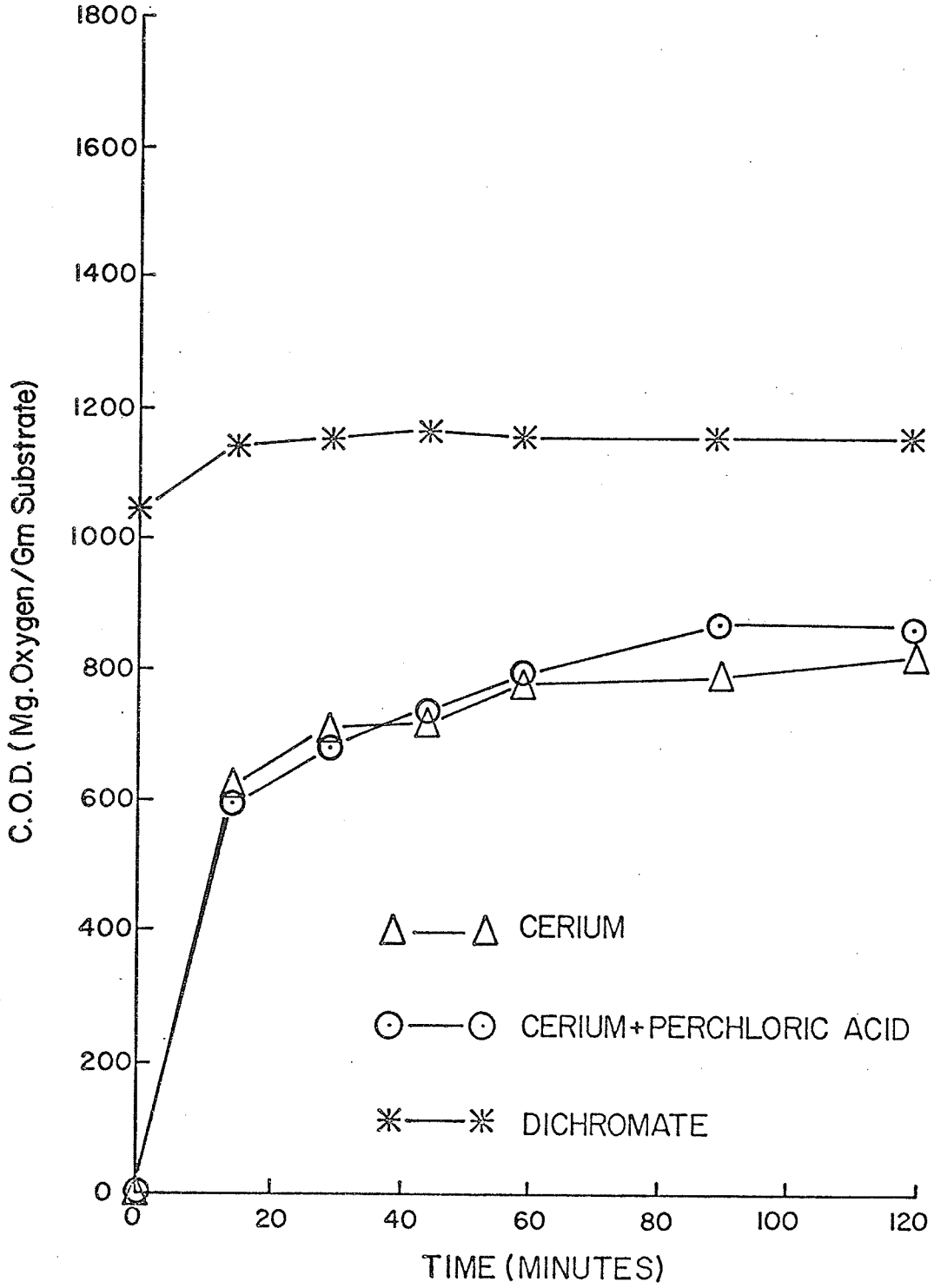

Fig. 6. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for glycerol oxidation.

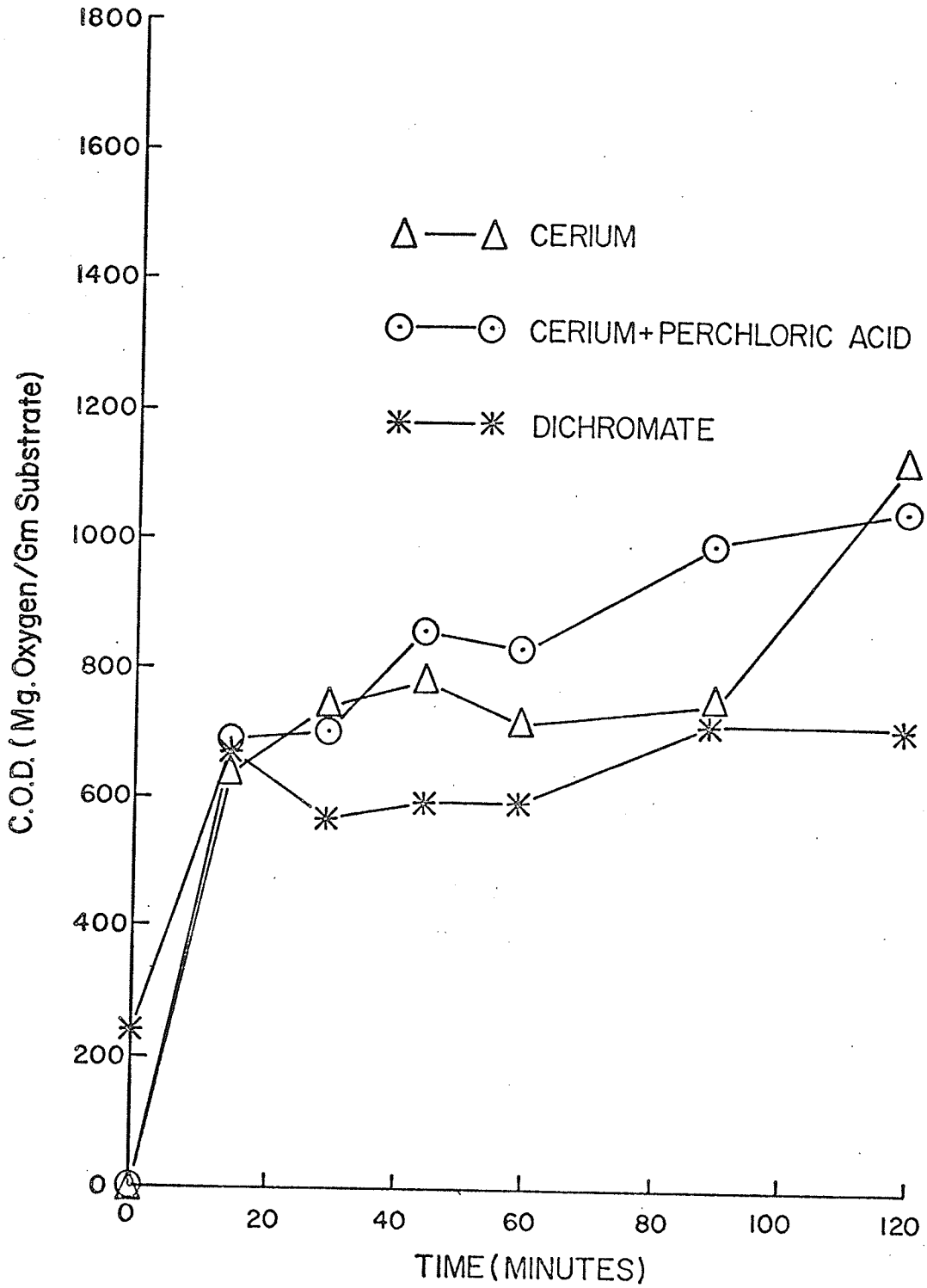

Fig. 7. Comparison of the oxidation rates for ceric ion, ceric ion + perchloric acid, and dichromate ion for glycerol tributyrate oxidation.