

# Simple Method for Estimating Oxygen Value of Wastes

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A SIMPLE and quick means for estimating the pollution load of dairy and other wastes of an organic nature is desirable. Such a method would be useful in the field and in the plant, especially if accessory heating equipment was not required.

This paper describes such a method. Very briefly, a known amount of concentrated sulfuric acid containing a small quantity of potassium dichromate is added to one-half its volume of an aqueous waste solution. The exothermic reaction is allowed to proceed for 15 minutes, after which the degree of oxidation is estimated visually.

A comparative study by Moore *et al*<sup>6</sup> of determining oxygen consumed chemically showed the effectiveness of dichromate as an oxidizing agent. The method now accepted as official for an oxygen consumed test has been described in detail by Moore *et al*<sup>5</sup>. A simpler non-reflux method<sup>8, 10</sup> has been used successfully by Hoover and Porges<sup>4, 9</sup> in their studies on dairy waste disposal.

These chemical methods have application in waste studies because of the relatively rapid availability of the results as compared with those obtainable by the official biochemical oxygen demand (B.O.D.) test, which requires a five-day incubation period.

Recently a modification of the Winnick<sup>13</sup> micro-diffusion method for the rapid determination of ethyl alcohol in biological fluids was presented by Sunshine and Nenad<sup>12</sup> as a means of detecting intoxication. Instead of determining iodometrically the excess dichromate after the diffused alcohol was oxidized, a photoelectric colorimeter was used for comparing the resulting color, and a value was obtained from a known calibration curve. Comparisons with prepared standards were also made.

The application of some of these ideas to dairy wastes seemed feasible, but many alterations were necessary. For example, the organic matter of a dairy waste cannot diffuse from one chamber in the Conway cell into the second chamber, which contains the oxidizing solution. On the other hand, adding the waste directly to the dichromate solution has a diluting effect on the resulting color owing to the water carrier of the waste. Further, a

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simple method should avoid added heating.

Moreover, laboratory trials soon showed that the oxidizing solution suggested by these authors was unsatisfactory with dairy waste. The use of a photometer was undesirable, as simplicity was then lost. It was found that prolonged periods of heating were unnecessary, although dairy waste is composed of various constituents that oxidize differently, such as lactose, which is readily oxidized, and casein, which is more refractive. The dichromate-acid oxidizing solution should contain only a minimum of water, the water being supplied in the waste or added if required.

## Oxidizing Agent

An oxidizing solution was prepared by dissolving 612.9 mg of  $K_2Cr_2O_7$  in about 50 ml of water and then adding a sufficient quantity of concentrated  $H_2SO_4$  to make 1 liter when cool. Hence, 10 ml of this 0.0125 normal solution is equivalent to 1.0 mg of oxygen. Therefore, if 10 ml of this acid-dichromate agent were required to oxidize all the organic matter in 1 ml of waste, the chemical oxygen demand (C.O.D.) of this waste would be 1,000 parts per million (ppm), but as shown later, complete oxidation did not occur. A 0.01 normal oxidizing solution was also used, but in that case, 10 ml was equivalent to 0.8 mg of oxygen.

## Acid-to-Water Ratio

In preliminary trials different amounts of lactose solution or skim milk solution were placed in test tubes. Varied amounts of the oxidizing agent were added to each series of tubes. Color changes were observed, but the intensity of color was variable and seemed related to the amount of re-

ductant and oxidant. A changing point was difficult to select.

Apparently the amounts of acid and water were important, and the desirable ratio was determined in the following manner. To each of a number of test tubes containing 0.5 ml of skim milk solution having 1,000 ppm C.O.D., water was added to give the volumes shown in Fig. 1. A constant amount, 6 ml of 0.01 normal oxidizing agent was added to each tube. The contents were thoroughly mixed by shaking. After standing for 15 minutes, the excess dichromate remaining in each tube was determined by iodometric titration. The quantities of dichromate oxidizing agent used were plotted against the water contents of the reacting mixtures. Fig. 1 shows the results.

Oxidation reached its peak in the presence of 6 ml of the acid-dichromate solution when 2.5 to 3 ml of water was present. These tests showed that the aqueous portion of the reacting mixture was important; it must be about one-third of the total volume. In other words, an acid to water ratio of 2 to 1 is necessary.

von Fellenburg<sup>1</sup> combined 3 to 6 mg of substance to be tested with 10 ml of 0.1 normal aqueous dichromate and then added 20 ml of concentrated  $H_2SO_4$ . If more than 10 ml of sample were present, an additional 2 ml of acid were required for each extra ml of sample. Varying the amount of acid by 20 per cent changed the final oxidation of the test material only 1 to 2.5 per cent.

## Use of Ferroin as an Indicator

Increments of solutions containing skim milk, casein and lactose were placed in test tubes. Water was added to give a volume of 2.5 ml in each tube. Five ml of oxidizing solution was added to each sample. After shaking and allowing the reaction to proceed for 15 minutes, the colors ranged from the intense yellow of the unreduced dichromate, through green, to the blue of the completely reduced chromate. Although colors were obvious, the selection of the proper color was often difficult, especially with incompletely oxidizable samples such as those containing casein or bacterial sludge.

A literature review showed that

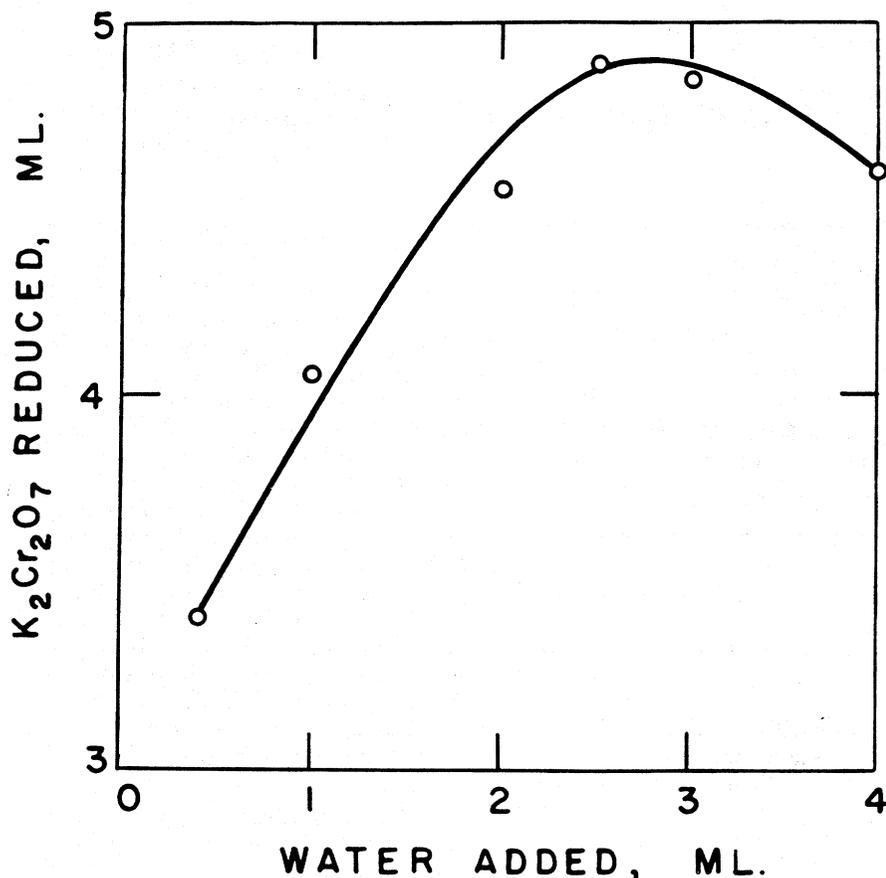


Fig. 1—EFFECT of water on the reduction of 0.01 normal  $K_2Cr_2O_7$  in concentrated  $H_2SO_4$  in presence of 0.5 mg of skim milk

ferroin (ferrous orthophenanthroline) gave a sharp color change near the stoichiometric point when used with dichromate titrations of iron<sup>11</sup>. This is the same indicator used by Moore and coworkers<sup>5,6</sup> in conjunction with standard ferrous ammonium sulfate in their studies with the oxygen consumed test.

Pierce and Haenisch<sup>7</sup> stated that the ferrous orthophenanthroline gave an accurate end point with dichromate titrations of iron only if the acidity of the solution was high. When the indicator was added to the treated waste solutions in the test tubes, the

color changes were fleeting and not sharp. Trials showed the necessity of diluting the acid prior to adding the dye. The strong acid destroyed the dye. This was overcome by adding 2 ml of water to each tube and cooling before adding the dye.

An additional improvement resulted when the indicator, which was purchased as a 0.025 M solution of 1,10 phenanthroline ferrous sulfate, was diluted with two parts of water. The resulting colors were sharp and lost their fugacity.

For the selection of the desired tube, it was necessary only to dilute

the contents of the three or four tubes that gave the green to blue transition. After the addition of 2 ml of water, the tubes were cooled and 1 drop of the diluted ferroin was added. The completely reduced solution gave a red color. Under the conditions of this test, the waste concentration in the red-colored tube and the less reduced adjacent tube was used to calculate the range of oxygen requirement.

#### General Procedure

Increments of waste to be estimated were placed in a series of test tubes of large diameter (25 to 32 mm). Increments used depend upon the expected concentration of the oxidizable matter in the waste. If possible, the greatest quantity of waste should not exceed 2.5 ml.

Sufficient water was added to each tube to give a volume of 2.5 ml, and then 5 ml of the dichromate oxidizing agent was added. The mixture was thoroughly shaken and allowed to stand for 15 minutes. (The reaction is violent and exothermic, and necessary precautions must be taken, such as the use of a holder for the tubes.)

The tube showing complete reduction of dichromate was selected easily. Two ml of water were added to each tube showing the transition color changes from green to blue. After mixing and cooling, one drop of the diluted indicator was added. The reduced solution was red; the others were colored from grey to blue.

#### Amount of Waste to Use

Often the approximate oxygen demand of a waste was completely unknown. In cases, fixed amounts of the waste (1 ml, or any desired quantity) were placed in a number of tubes. The chromate oxidizing agent was added in increments of 0.5 or 1 ml, then sufficient water or concentrated  $H_2SO_4$  was added to give the 2-to-1 acid-water ratio.

The quantity of waste that gave complete reduction was selected. To obtain greater precision this rough approximation was followed by the procedure using varying amounts of waste with fixed amounts of the oxidizing solution.

#### Calculation of Oxygen Value

The calculations are simple, as the volume of oxidizing solution, its normality, and the volume of waste are known. The oxygen value is between that of the tube containing the completely reduced chromate and the preceding tube. Hence,

$$\text{ppm oxygen value} = \frac{\text{ml chromate} \times \text{normality} \times 8 \times 1,000}{\text{ml waste solution in tube}}$$

TABLE 1

Oxygen Value Determined by Indicator Method Using 5 Ml of Oxidizing Agent

Material	C.O.D., ppm	$K_2Cr_2O_7$ Normality	Sample Required, ml	Oxygen Value, ppm
Skim milk	1,048	0.0125	0.7	710-833
		0.010	0.6	667-800
Lactose	1,036	0.0125	0.5	1000-1250
		0.010	0.4	1000-1333
Casein	992	0.0125	1.3	380-417
		0.010	1.0	400-444
Whey	889	0.0125	0.6	833-1000
		0.010	0.5	800-1000

An example follows. Increments of 0.1 ml of waste were placed in tubes. After water was added, each was treated with 5 ml of 0.0125 normal oxidizing agent. The chromate in the tube containing 0.4 ml was completely reduced. Therefore, the oxygen utilized by the waste by this test was:  $5 \times 0.0125 \times 8 \times 1,000 = 1,250$  ppm.

0.4

The preceding tube, containing 0.3 ml of waste, would give a value of 1,666 ppm. Hence, the oxygen value lies between these two extremes.

#### Experimental

Solutions of skim milk, lactose, casein and whey were prepared. The oxygen values were determined by this visual method and compared with the values obtained with high temperature<sup>10</sup>. The latter values are listed under C.O.D. in Table 1. Results obtained with both 0.0125 and 0.01 normal dichromate oxidizing solutions are included. The volume of sample that completely reduced 5 ml of oxidizing solution is shown. The last column lists the limits of oxygen values as calculated in the foregoing manner from the red-colored reduced sample in one tube and the preceding tube. The two normalities gave similar results.

The oxygen values for only lactose and whey as determined by this test approximated their total C.O.D. Skim milk values were somewhat low, and those for casein were much lower. It is apparent that the ease with which an ingredient is oxidized influences the result by this method.

In order to obtain closer values, other series containing varying amounts of these organic substances were prepared and treated. To obtain a closer approximation in these tests the actual amounts of organic matter oxidized in each tube showing the transition phase were determined by iodometric titration. Table 2 lists average percentages of that part of the total C.O.D. given by the oxygen value as determined by this method.

Again, the total oxygen requirements of the materials were not obtained, but only the oxygen required by that portion readily oxidized. Thus, the oxygen values for lactose and whey were high, approaching the C.O.D. On the other hand, only 40 to 41 per cent of the casein was easily oxidized; aerating sludge obtained by feeding skim milk showed 50 per cent oxidation.

The average oxygen value of the skim milk used in this test was only 64 per cent of the expected C.O.D.

**TABLE 2**  
Relation of Oxygen Value to the Total C.O.D.

Material	Part of C.O.D., %	Factor for Conversion to C.O.D.
Skim milk .....	64	1.56
Lactose .....	94	1.06
Casein .....	40	2.50
Whey .....	93	1.08
Aerating sludge <sup>2</sup> .....	50	2.00
Aerator waste <sup>3</sup> .....	39	2.56
Raw waste <sup>4</sup> .....	38	2.63
Aerator sludge <sup>4</sup> .....	34	2.76

<sup>1</sup> Average. <sup>2</sup> Skim milk. <sup>3</sup> Dairy. <sup>4</sup> Municipal.

The oxygen value for skim milk approximated the sum of the values of the casein and lactose fractions in the milk. These values, shown in Table 2, are practically the same as those obtainable from the lower oxygen values in Table 1.

Table 2 also includes results secured later for a well-aerated sludge obtained from a dairy waste disposal plant, and the raw waste and aerator sludge from a local municipal plant. Thus, if the type of waste is known, a fairly accurate estimation of the C.O.D. may be calculated from the oxygen values determined by this simple method.

Factors that may be used for such calculations are given in the last column of Table 2 for the few materials tested. These factors were obtained by dividing the total C.O.D. of each item by the value found by the visual method. Thus, the oxygen value obtained by this visual method multiplied by the appropriate factor gives a good indication of the C.O.D. of the waste. Factors for specific wastes should be determined by the operators.

#### Relation of Oxygen Value to B.O.D.

Practically all these studies on waste disposal used a simulated waste made from skim milk. It became apparent from the results in the preceding tables that by some coincidence the oxygen value visually estimated

approached the B.O.D. value.

This led to a comparison of results for C.O.D. and B.O.D. made at various times in the course of the studies during the past few years. Table 3 is a compilation of the average results.

Each substance had its own oxygen value by this visual method just as it has its C.O.D. or B.O.D. value. The B.O.D./C.O.D. value for the sludge was somewhat higher than that previously reported for an unfed sludge with a value of about 0.40<sup>2</sup>. The values for the raw waste indicated that the readily available high oxygen demanding material had been removed. This concurred with the idea expressed in the interpretation of the B.O.D. test<sup>3</sup> that the organic materials in sewage have in large part been assimilated by the organisms present.

The O.V. (oxygen value)/C.O.D. value is that portion of the total C.O.D. determined by the visual method. The B.O.D./C.O.D. ratios of four of the materials were within 10 per cent of the O.V./C.O.D. values. The extreme was 26 per cent deviation (the sample of casein). Thus, the oxygen value obtained by the visual method can be of aid in approximating the 5-day B.O.D. value.

This method may be useful in selecting the desirable dilutions to be used in the test bottles. Further the visual method should find application for rough estimation of the B.O.D. and C.O.D. in field tests. For example, the sample of raw waste from the Abington Township sewage treatment plant gave an oxygen value between 167 and 172 ppm by the visual method and a C.O.D. of 444 ppm. The 5-day B.O.D. later reported by the chief operator of the plant was 175 ppm.

#### Testing Solutions of Various Concentrations

Skim milk solutions and whey solutions of various concentrations were prepared, and the oxygen values were determined by the visual method. The results were multiplied by the appropriate factors selected from tables to obtain an estimated C.O.D. Table 4 presents the results.

**TABLE 3**  
Relationship Between O.V. (Oxygen Value), B.O.D. and C.O.D.

Material	O.V./C.O.D., %	B.O.D./C.O.D., %	O.V./B.O.D.
Skim milk .....	64	67	0.96
Lactose .....	94	83	1.13
Casein .....	40	54	0.74
Whey .....	93	86	1.08
Sludge (skim milk) .....	50	49	1.02
Raw waste (municipal) .....	38	39	0.97

**TABLE 4**  
**Oxygen Value and Estimated C.O.D. of Different Concentrations**  
**of Skim Milk and Whey**

Material	C.O.D., <sup>1</sup> ppm	O.V., ppm	Estimated	Estimated C.O.D.
			C.O.D., <sup>2</sup> ppm	Actual C.O.D. %
Skim milk	1,048	666	1,039	99
	524	333	519	99
Whey	888	800	864	97
	222	222	240	109

<sup>1</sup> C.O.D. determined by rapid method<sup>10</sup>.

<sup>2</sup> C.O.D. estimated by using factors from Table 2.

In this case, the O.V. was determined on the single tube that showed the red color of the indicator. This was possible because only small increments of solution were used. As noted, the results were within 10 per cent of the values obtained by the vigorous heating method of determining C.O.D. The B.O.D. may also be estimated by use of the ratios given in Table 3.

#### Chlorides

Chemical oxidation of NaCl by drastic oxidation has been shown to equal the theoretical value of 1 ppm C.O.D. = 7.3 ppm NaCl or 4.37 ppm chlorine<sup>5,8</sup>. An oxygen value was obtained for chlorine by the rapid visual test. A solution of NaCl gave an oxygen demand of 195 ppm upon strong oxidation.

Tests using 1 ml and 2.5 ml of this NaCl solution with 0.5 ml increments of the dilute dichromate solution showed that the 2.5 ml required 1 ml of the dichromate solution for oxidation. This gave an oxygen value of 40 ppm, or about 20 per cent of the value found by the heating method. Since

the chlorine content of most organic wastes is fairly low, correction for its oxygen value may be omitted with the visual method.

#### Summary

A simple method for estimating the oxygen demand of a waste is described. Concentrated H<sub>2</sub>SO<sub>4</sub> containing 0.0125 N dichromate is the oxidizing solution. Complete reduction of the dichromate is detected by means of the indicator, ferrous orthophenanthroline. The estimated oxygen values are lower than the C.O.D. values obtained by drastic oxidation. In many cases the oxygen value approaches the 5-day B.O.D.

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