

## USE OF TOC AS AN ALTERNATIVE TO COD FOR MONITORING THE BIOOXIDATION OF TANNERY UNHAIRING WASTE\*

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### Abstract

A test for chemical oxygen demand (COD), requiring approximately 4 hr, is commonly used to monitor the biooxidation of wastes. A test for total organic carbon (TOC), which requires only 3 to 5 min, was compared with the more time-consuming method to determine if it could be used to estimate the COD test and to monitor the biooxidation. Both TOC and COD were determined for various proteins and amino acids, and the results of the two methods correlated well. The biooxidation of tannery unhairing wastes, complex industrial wastes characterized by high solids content, was monitored by both TOC and COD tests. The results obtained indicate that the TOC test is an acceptable alternative to the COD test when the composition of the waste does not vary significantly with time.

### Introduction

The control of bioreactors such as activated sludge plants and trickling filters by various chemical and bioassay methods has proven to be time consuming and unreliable (1, 2). Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are commonly used for measuring the amounts of oxidizable materials in waste waters. However, the tests require 5 days for BOD and 4 hr for COD. Also, there is no direct relationship between the two because the mechanism by which microorganisms utilize oxygen for nitrogen conversion,

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and carbohydrates and fat for energy, is entirely different from that by which the organic moieties are oxidized by acid chromate.

The COD test depends on the oxidation of these various waste materials by acid chromate, and many organic compounds are only partially oxidized by this method (3). The total oxygen demand of industrial wastes containing acetic acid and toluene cannot be determined by the acid-chromate method. Only 24 percent of toluene can be oxidized by the standard acid chromate procedure (4), although benzoic acid, one of the byproducts of this reaction, is almost completely oxidized (99 percent). Other products not detectable by acid-chromate oxidation are benzaldehyde, o-, m-, and p-tolylketones and the neutral products phenyl o-, m-, and p-tolylketones, phenyl o-, -m-, and -p-tolylmethanes (5). The kinetics of acid-chromate oxidation of alcohols, triethylmethane, and other hydrocarbons (6-9) have been reported.

A number of amino acids are only partially oxidized, and certain ring structures, benzene and pyridine, are affected only slightly by the COD procedure. However, organisms are able to metabolize these types of compounds when acclimated, thus producing a considerable BOD which is not measurable by the acid-chromate method (1,10).

The TOC test analyzes all of the carbon in a material that is detectable as carbon dioxide following combustion and requires only 3 to 5 min. It does not, however, measure other oxidizable material. This report concerns the potential of the TOC method for estimating the COD of various organic compounds and wastes: keratin, casein, gelatin, amino acids, and tannery unhairing liquors.

## Experimental

*Apparatus.* A Beckman Total Carbon Analyzer\*, Model 915, was used for all combustion analyses. Pyrex stills, heated by Glas-col heaters, were used for acid-chromate oxidation of all samples.

*Bioreactors.* A two-stage Horizon Ecology bench-scale biooxidation apparatus (Figure 1) described in a previous publication (11) was monitored by the various testing procedures under discussion. Probes were added to the unit for continuous pH monitoring. The feed to unit B was changed to the mixing zone rather than the settling inner cone area.

*Reagents.* All reagents were ACS grade. Potassium hydrogen phthalate was certified ACS grade acidimetric standard, Fisher Scientific Co.

*Test compounds.* The amino acids were obtained from the Sigma Chemical Co., Kit No. LAA21. DL-Asparagine and keratin were purchased from Pfaltz and Bauer, Inc. Zein, casein hydrolysate, collagen, and keratin were purchased from Sigma Chemical Co. Gelatin was purchased from J. T. Baker Chemical Co.

\* Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

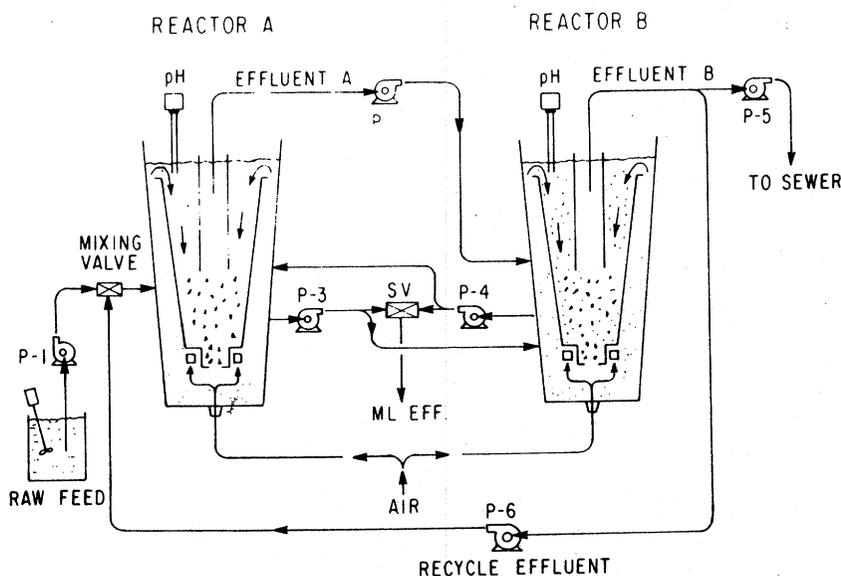


FIGURE 1. — Schematic of biooxidation units; P-1 raw feed pump, P-2 effluent from A and feed to B pump, P-3, P-4 mixed liquor transfer pumps, P-5 final effluent pump, P-6 recycle pump. SV solenoid three-way valve. ML EFF mixed liquor effluent. Working volume of each vessel is 5 liters.

*Test solutions.* The various test compounds were dissolved in CO<sub>2</sub>-free water (prepared according to ASTM-D-2579-69) in the concentrations shown in Tables I and II.

*TOC and COD Analyses.* For the analysis of total organic carbon, 20 μl of each test solution was injected into the Beckman analyzer, set at 950°C. The chemical oxygen demand analyses were carried out according to Standard Methods for the Examination of Water and Wastewater (12).

*Tannery unhairing wastes.* Concentrated lime-sulfide unhairing effluents were obtained from a side-leather tanner who used the high-sulfide, hair pulping process. The waste was passed through a progressive cavity grinder pump before being treated in the pilot plant (13, 14).

## Results and Discussion

The COD and TOC methods were compared with the theoretical oxygen demand of organic nitrogen compounds, using 25 organic compounds and 5 proteins. The results are tabulated in Tables I and II. Potassium biphthalate was used to check the precision of the procedure and had a deviation of 0.02 percent from the theoretical carbon content, with ten replicate samples.

The COD/TOC ratios of the amino acids in Table I average 2.452. Those for

TABLE I

COMPARISON OF TOTAL ORGANIC CARBON WITH CHEMICAL OXYGEN DEMAND

Sample	Concentration	COD	TOC	Theoretical TOC	COD	TOC - Theor. TOC
					TOC	Theor. TOC
	mg/l	mg/l	mg/l	mg/l		%
Potassium Biphthalate	2125	2545	1000	1000	2.545	0
L-Proline	1000	1022	570	522	1.793	+9
Alanine	1000	585	430	404	1.360	+6
OH-Proline	500	569	227	229	2.506	-1
Arginine • HCl	500	393	165	171	2.382	-4
Histidine	500	371	155	232	2.344	-33
Glutamic Acid	500	479	200	204	2.395	-2
Glutamine	500	484	200	205	2.420	-2
Asparagine	500	303	150	182	2.020	-18
Isoleucine	500	831	280	275	2.968	+2
Leucine	500	856	280	275	3.057	+2
Lysine	500	497	205	247	2.424	-7
Lysine	500	360	180	180	2.000	0
Aspartic Acid	500	323	150	160	2.153	-6
Glycine	500	585	210	201	2.786	-4
Methionine	500	585	210	201	2.786	-4
Serine	500	376	170	171	2.212	-1
Threonine	500	420	210	202	2.000	+4
Phenylalanine	500	968	365	327	2.652	+12
Tryptophan	500	870	345	324	2.522	+6
Valine	500	778	265	256	2.936	+4
Tyrosine	500	824	335	298	2.460	+12
Cystine	1000	941	335	300	2.809	+12
Cysteine	500	556	140	149	3.971	-6
Lanthionine	1000	783	359	346	2.803	+4

TABLE II

TOC, COD DATA ON SELECTED PROTEINS

Sample	Conc.	TOC	COD	COD
				TOC
	mg/l	mg/l	mg/l	
Gelatin	1000	385	411	1.07
Keratin	1000	280	670	2.39
Collagen	1000	245	750	3.06
Zein (Corn Starch)	1000	390	761	1.95
Casein	1000	545	1210	2.22

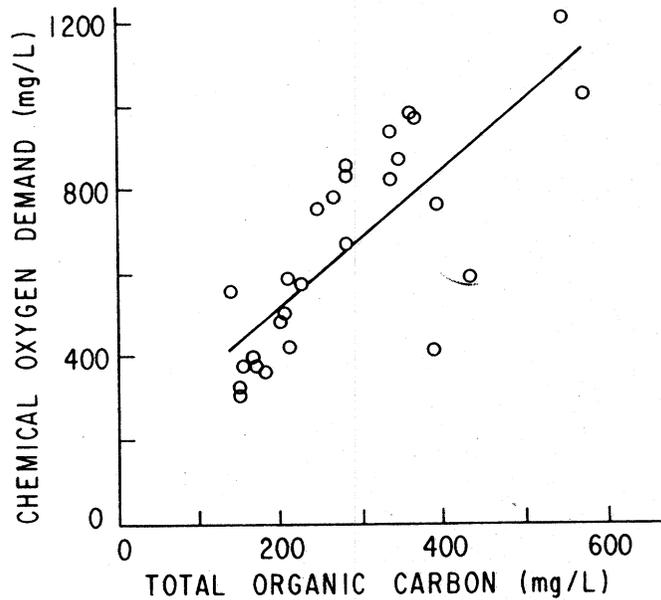


FIGURE 2. — Linear regression analysis of TOC and COD methods—pure compounds.

the proteins in Table II average 2.138. The curve in Figure 2 was developed from these data and fitted to an equation of the form  $y = mx + b$  to give:

$$\text{COD} = 1.69 (\text{TOC}) + 180$$

While the simple ratios could be used to estimate COD from TOC measurements, a closer estimate may be calculated with this equation. According to this equation, at zero TOC there is still oxidizable material, as would be expected.

The next phase of the experiment was to control an activated sludge pilot plant by TOC and COD measurements. Since tannery unhairing wastes and the mixed liquor samples contain a considerable quantity of suspended and settleable solids, it is not possible to compare directly the COD and TOC results of these samples. We therefore filtered all samples from the bench-scale pilot plant to remove the solids with Whatman No. 1 filter paper and operated the bio-unit on the basis of soluble TOC and COD.

The daily operating conditions of the biooxidation unit (Figure 1), based on TOC's and COD's, are shown in Figures 3 and 4. The raw feed to Reactor A was highly variable in composition as shown in Figure 3. Peak loadings, 1,280 to 1,300 mg/l COD (400 to 500 mg/l TOC) on Reactor A caused a corresponding response in the effluent COD 500 mg/l. (TOC 200 mg/l) on January 14. The high loading impact on the system was reduced by increasing the air rate to the

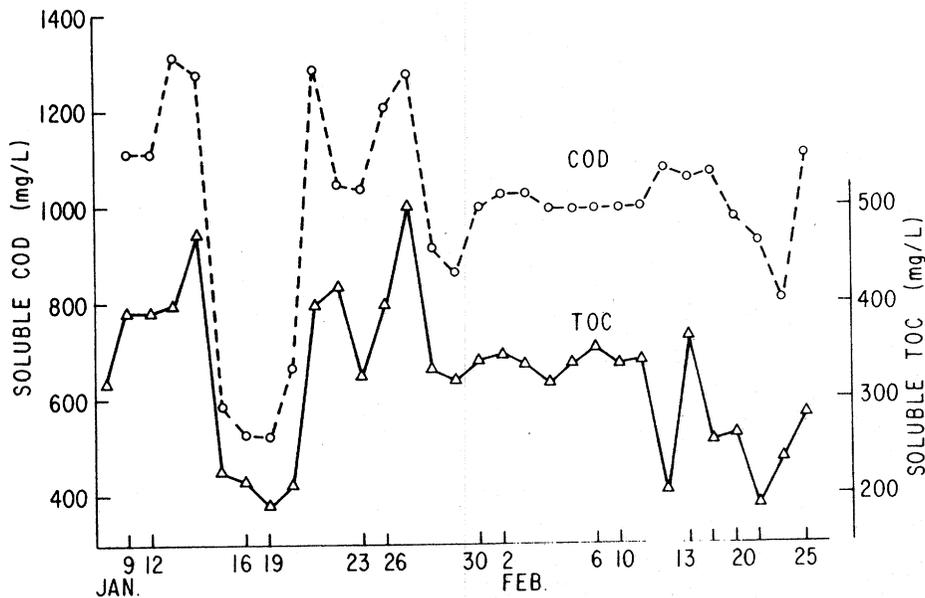


FIGURE 3. — Comparison of TOC and COD methods on the influents to bioreactor.

bioreactors and increasing the return sludge rate (15). The response of the bioreactors to these adjustments is shown in Figure 4, January 13-15. The time

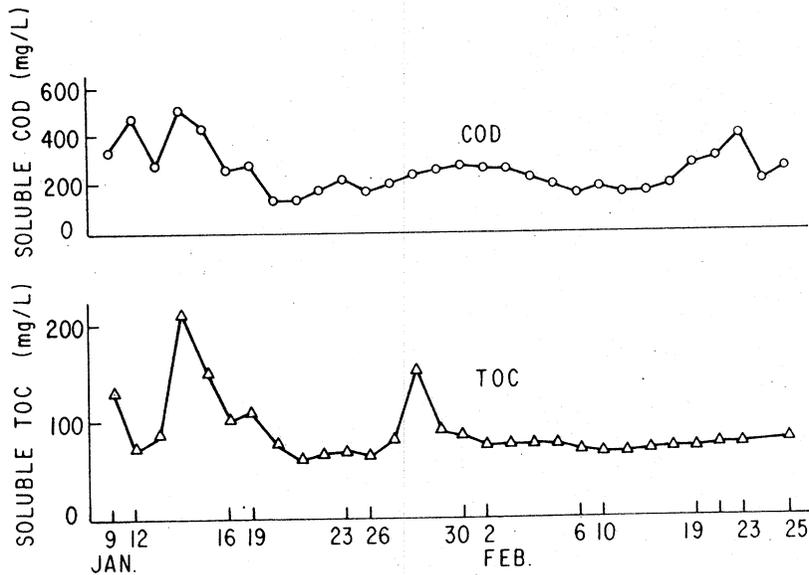


FIGURE 4. — Comparison of TOC and COD methods on the effluents from bioreactor.

lapse for the corrective effects to appear after overloading was approximately 24 hr, as seen in the return to steady state conditions. The data points from February 2 to 25 are about the same  $75 \pm 10$  mg/l TOC for the effluent.

The data points from Figures 3 (influent) and 4 (effluent) were plotted in the same fashion as the data from Table 1. The influent data gave the result shown in Figure 5 and the following equation:

$$\text{COD} = 1.92 (\text{TOC}) + 390$$

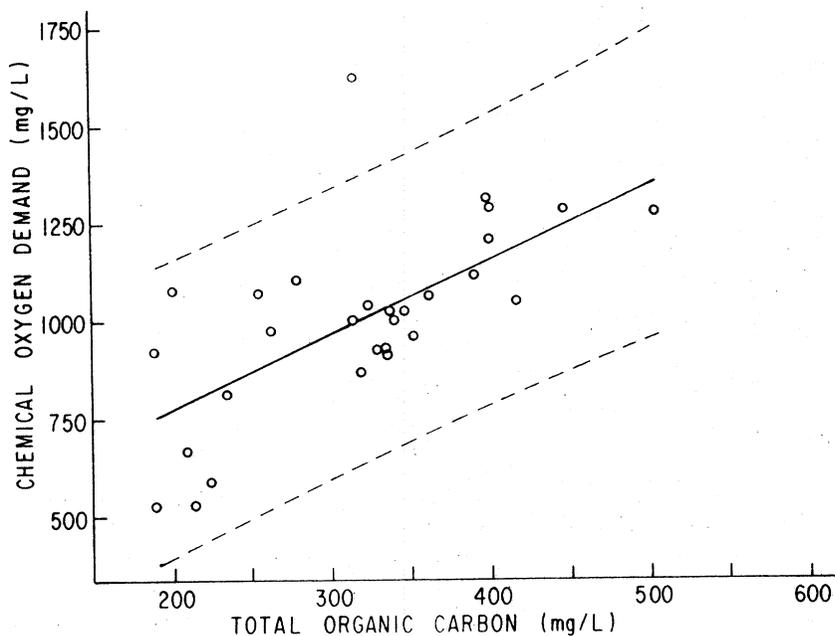


FIGURE 5.—Linear regression analysis of COD and TOC—bioreactor influents (Figure 3).

The slope (1.92) is somewhat greater and the intercept (390) is greater by a factor of 2.17 than the values found with the pure compounds. The greater intercept (an indication of the amount of noncarbonaceous oxidizable material) probably reflects the sulfide ion common to these wastes.

The effluent data gave the result shown in Figure 6 and the equation:

$$\text{COD} = 1.68 (\text{TOC}) + 127$$

This material thus resembles more closely the pure compounds as far as this relationship of COD and TOC is concerned.

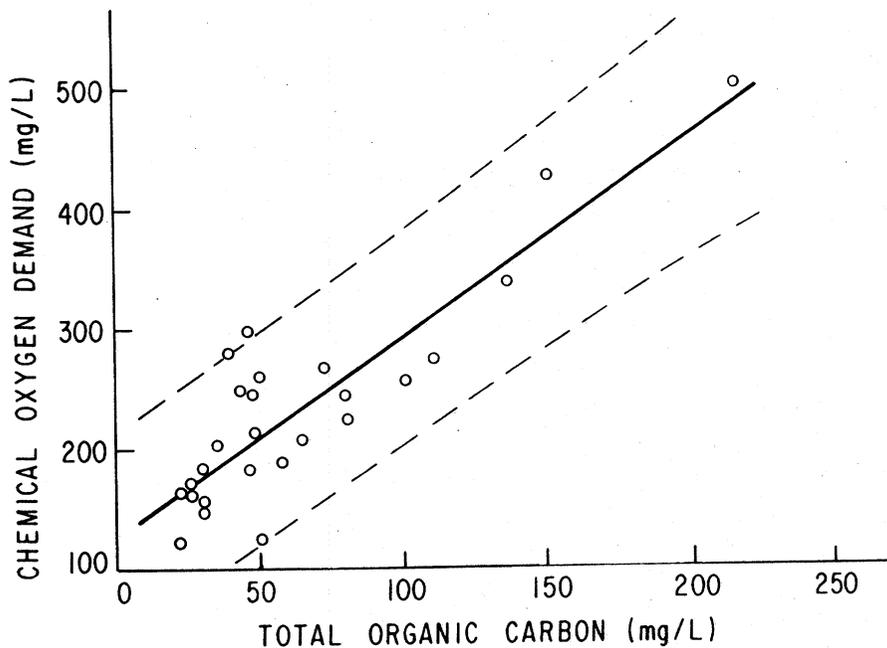


FIGURE 6. — Linear regression analysis of COD and TOC—bioreactor effluents (Figure 4).

### Conclusion

The determination of the total organic carbon concentrations of tannery unhairing liquors for organic loadings (1,000 to 2,500 mg/l and higher) requires 2 to 3 min of the operator's time and thus enables him to make quick adjustments in air rates and recycle sludge and effluent return to offset immediately the overloading issues of the aeration system. The COD technique requires a period of time equivalent to the hydraulic detention time of most primary clarifiers, 2 hr, which is entirely too long a time to prevent drastic results in the next stage, the aeration system.

The loading on primary, aeration, and final clarifiers may be estimated in a few minutes by measuring the TOC and converting to soluble COD by empirically determined relationships as described above.

### Acknowledgments

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