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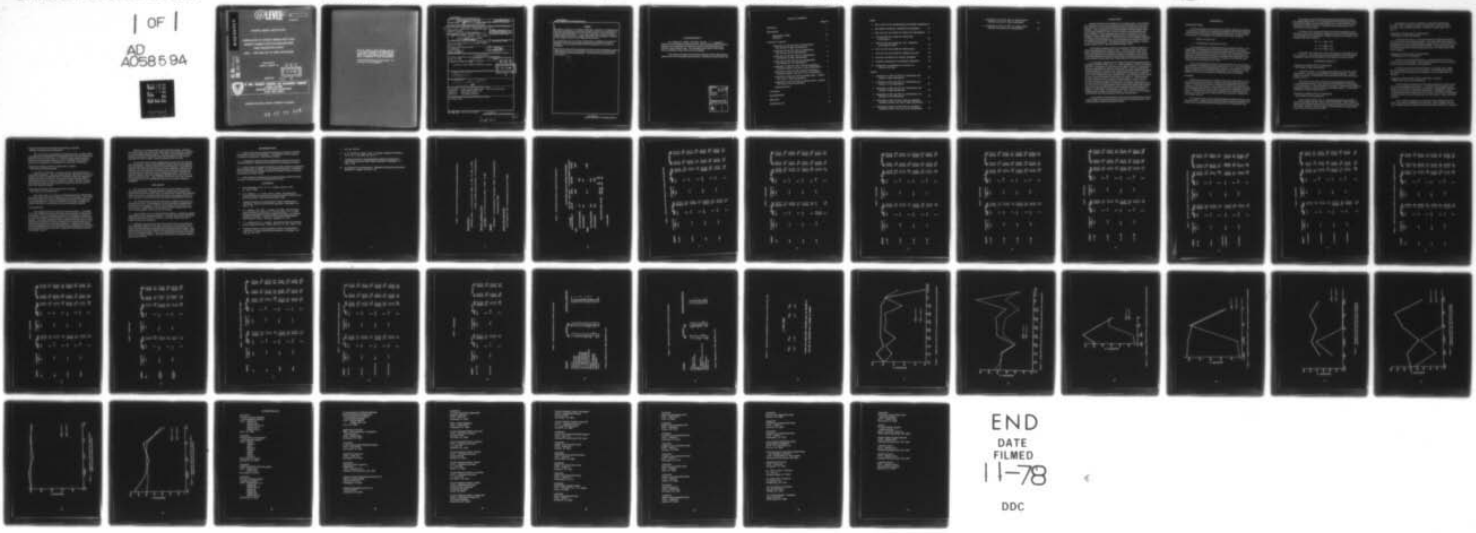

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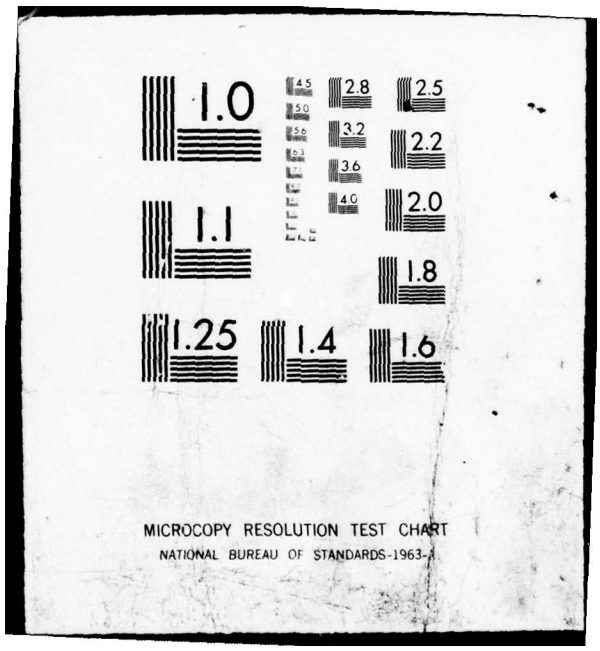
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TECHNICAL REPORT ARLCD-TR-77031

CORRELATION OF OXYGEN DEMAND AND TOTAL ORGANIC CARBON TESTS ON WASTEWATERS FROM AMMUNITION PLANTS

PART I. COD AND TOC OF PURE EXPLOSIVES

MILTON ROTH
JOSEPH M. MURPHY, JR.

JUNE 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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DOVER, NEW JERSEY

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ABSTRACT

New Federal regulations for Effluent Limitations, Guidelines, and Standards for Explosives Manufacturing, Point Source Category, has led to the evaluation of the specified oxygen demand tests in order to determine their applicability to munition unique wastewaters. In part one of this study, results of chemical oxygen demand (COD) and total organic carbon (TOC) tests performed on solutions of pure energetic materials are reported and discussed.

The experimental data was analyzed statistically to determine the correlation between the COD and TOC tests when measuring known solutions of energetic materials; the relationship between actual and theoretical values was also determined.

Experimental results show that response to the COD test varies significantly between compounds and is not an accurate indicator of organic loading of munition wastewaters despite its high level of precision. TOC is found to be more accurate and more sensitive.

ACKNOWLEDGMENTS

Mr. Nathaniel S. Gelber, Analytical Chemist, U. S. Armament Research and Development Command, Dover, New Jersey provided invaluable assistance by preparing all the standard solutions and performing all the chemical oxygen demand tests. His comments on the details of the testing and his evaluation of the results were most helpful.

This study was funded under the Environmental Quality R&D program administered by the DARCOM Lead Laboratory, Aberdeen Proving Ground, MD.

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INTRODUCTION

Effluent limitations and guidelines for existing sources, to be achieved by the application of the best practicable control technology currently available (BPCTCA), and the best available technology economically achievable (BATEA), were promulgated by the Environmental Protection Agency (EPA) in the Federal Register of 9 March 1976 for Explosive Manufacturing Point Source category. These regulations have led to an evaluation of the test methods for determining organic loading and the resulting oxygen demand of military-unique wastewaters. The interim final rule for effluent guidelines, for explosive manufacturing point source guidelines sets standards in terms of the following parameters: biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and total suspended solids (TSS).

The energetic materials found in wastewaters of different types of explosive manufacturing are listed in table 1. In the first part of this study, known concentrations were tested for COD and total organic carbon (TOC). The values obtained were statistically analyzed to determine which method is more appropriate for monitoring waste streams containing energetic materials and also to determine if any relationship exists between the methods.

The discharge standards set for explosive manufacturing point source category are listed in table 2 (ref. 1). These standards, in terms of kilograms (lb) BOD or kilograms (lb) COD allowed per 1000 kg (2200 lb) of product produced are established for BPCTCA and for BATEA. When the proposed discharge standards are projected over maximum production rates for nitroglycerin and trinitrotoluene and the water usage associated with their production, (ref. 2) the resulting discharge concentrations, in milligrams per liter (mg/ℓ), of COD in the waste streams are extremely low (table 2). These standards present a problem of how to measure these parameters at such low levels. The COD analysis has limited accuracy below 10 mg/ℓ of COD (ref.3). In order to evaluate the EPA environmental water quality standards for munition wastewaters, the applicability of the conventional oxygen demand parameters to low concentration levels of COD of military-unique compounds was studied. In this study, consideration was given to other tests capable of detecting these munition-unique pollutants. Thus, the TOC test is compared to the COD for the same compounds at the same concentration.

An evaluation of this type will not only show the precision and accuracy of each method, but also will indicate which is the most appropriate for monitoring explosive manufacturing point sources.

EXPERIMENTAL

Experimental Design

Since one objective of this study was to compare different test methods to evaluate their suitability for estimating compliance with the EPA standards, a factorial design was used with the intention of applying a variety of statistical analyses. In this design, the following factors were considered:

1. Method (COD and TOC)

2. Concentrations (high and low levels)

Four replications were conducted on each combination of factors. The replications were randomized to eliminate the effect of time on the results. Analyst effect was eliminated by having one analyst perform all the COD tests and a second analyst performed all the TOC tests. The test solutions were prepared as described in the procedure paragraph below and aliquots were taken from the same solution for all tests. In general, the COD tests were completed before beginning the TOC tests.

Prior to conducting the analysis of variance of the data, the variances were checked for homogeneity by the Bartlett test (ref. 5). The result showed that the variances were not homogeneous; therefore, the analysis of variance, which is based on the assumption of homogeneity, was not performed. The statistical tests that were performed are discussed later in this report.

Procedure

Standard solutions that are typically found in the wastewaters of army ammunition plants were prepared. Isomers of the compounds were also included in the experiment in order to examine the effect of the structure of a compound on the test response. Each standard solution was prepared by dissolving weighed amounts (to the nearest 0.1 mg) of the compounds in distilled water. The mixture was stirred with a magnetic stirrer until solution was complete. Several compounds required more than two days of constant stirring to effect solution.

The solutions were cooled to ambient temperature before diluting to the mark with water. Aliquots were transferred from the high concentration level solutions and diluted appropriately to prepare the low concentration level.

The chemical oxygen demand analyses were performed according to the standard method (ref. 6). The total organic carbon analyses were also performed according to the standard method (ref. 7) using a Beckman 915-A Total Organic Carbon Analyzer, a Hamilton spring-loaded syringe, and a sample size of 20 micro-liters.

Theoretical COD values were used as a basis for calculating the percentage of recovery for the different compounds. The theoretical COD values were calculated on the assumption of complete oxidation of all elements in the energetic materials as follows:

$$2H \longrightarrow H_2O$$

$$C \longrightarrow CO_2$$

$$2N \longrightarrow N_2O_5$$

Theoretical TOC values were used as the basis for calculating the percent of recovery. The percentage values were calculated on the assumption of complete combustion of the carbon in the compound to carbon dioxide.

DISCUSSION OF RESULTS

Comparison of COD and TOC for Nitrotoluenes and Toluene at High Concentrations

As shown in figure 1, at the high concentration level the TOC concentration shows a recovery of approximately one hundred percent. Toluene yielded low results, probably because of evaporation during the sample preparation (ref. 8).

The COD test at the high concentration level displayed results that varied with each compound. Low results were displayed by m-nitrotoluene; 2, 3 dinitrotoluene; 3, 4 dinitrotoluene; and toluene. Note that the nitrotoluenes yielding low results all had a nitro group in the meta position. All the other results were ± 5% from 100% recovery.

Comparison of COD and TOC for Nitrotoluenes and Toluene at Low Concentrations

At low concentrations (fig. 2), the mononitrotoluenes all yielded recoveries that range from 95% - 105% in both TOC and COD. These results indicate that the mononitrotoluenes can be analyzed with good recovery by either test method. However, the more highly nitrated toluenes were significantly lower by the COD test than by the TOC.

An analysis of a solution containing 6.41 ppm TNT (equivalent to 2.22 mg/L TOC) is likely to produce erratic results since the detection limit, under ordinary procedures, is limited to 1 mg/L (ppm) of TOC (ref. 9).

Comparison of COD and TOC for Nitrobenzenes and Benzene at High Concentration

At the high level (fig. 3), TOC and COD deviate significantly from full recovery for most of the compounds tested. The COD results of this group are consistently low, with the dinitrobenzenes registering very minimal COD values. Nitrobenzene and benzene also yielded low results. This could be the result of the refractoriness of aromatics which typically are not oxidized appreciably in COD analysis.

Comparison of COD and TOC for Nitrobenzenes and Benzene at Low Concentration

At the low level concentration (fig. 4), good recoveries for TOC are exhibited by the nitrobenzenes. Benzene again yielded a low result, probably due to losses from volatilization of the compound.

The COD results follow the same pattern as at the high level, except that the nitrobenzene recovery is now complete. This indicates that either the concentration of dichromate or the digestion time at the high level is inadequate.

Comparison of COD and TOC Tests for Nitramines, Guanidine Nitrate, and Urea at High Concentration

All the compounds tested by the TOC method yielded low results except for tetryl and guanidine nitrate (fig. 5). The COD test also displayed consistently low results for this group of compounds. Nitroguanidine, guanidine nitrate, and urea did not respond at all to the COD. Although it has been recognized that certain aromatics give low results in the COD test, this appears to be the first time it has been found that the urea structure resists dichromate oxidation.

Tetryl and RDX displayed low COD results which indicates that nitramines also respond incompletely to the COD test. Tetryl is higher than the rest, probably because it contains three nitro groups in addition to a nitramine.

Comparison of COD and TOC Tests for Nitramines, Guanidine Nitrate, and Urea at Low Concentration

TOC recoveries were satisfactory for HMX and RDX, but high results were obtained on nitroguanidine and guanidine nitrate, and low results were obtained on tetryl and urea (fig. 6). The COD results followed the same pattern found at the high concentration level, indicating that the effect of structure is independent of concentration for this group of compounds.

Comparison of COD and TOC for Nitrate Esters, Alcohols, and Acids at High Concentration

Both TOC and COD (fig. 7) appear to be very appropriate for monitoring these compounds. Glycerin, pentaerythritol, and acetic acid are more typical of the type of compounds found in industrial rather than explosives wastewaters and are at least part of the basis for assuming that COD is a representative measure of organic loading in a stream. However, the data from explosives and urea type compounds indicates that the COD test has still-to-be-defined limitations.

Comparison of COD and TOC for Nitrate Esters, Alcohols, and Acids at Low Concentration

TOC results (fig. 8) are erratic, probably because the measurements were made at the lower level of sensitivity of the TOC analyzer. COD results, with the exception of acetic acid, yielded good recoveries with these more conventional materials. Acetic acid yielded a low recovery, probably because of losses due to volatilization during the dichromate oxidation.

Experimental Data

The experimental data is reported in tables 3 through 7. The tables include the standard deviations and the percent recoveries of COD and TOC test results. In order to complete the study it was necessary to determine the correlation between the test methods to see if the methods could be interchanged. Correlation coefficients were calculated using the recovery values obtained from the COD and TOC test methods of the combined high and low levels of concentration for individual compounds. Significant correlations at the 95% confidence level were obtained by several compounds in each table, but no overall correlation was found. Results from the statistical analyses are in tables 8 and 9.

Generally, in both the aromatic and nonaromatic groups, variances were always higher on results from total organic carbon analyses as opposed to chemical oxygen demand analyses. The larger variances might be an indication of the greater sensitivity of the TOC test method and the need for replication in order to obtain a reliable estimate of the true value.

As a final test of the overall completeness of recovery of the COD and TOC test methods, t-tests were performed to compare the data from each test with the theoretical recovery value of one hundred percent. The statistical evaluation (see table 10) showed that there was a significant difference from 100% recovery at the 90% level of confidence with 23 degrees of freedom for the COD analyses at both high and low concentration levels. With the TOC analyses, however, there is no significant difference from 100% recovery at either concentration level. This indicates that the TOC test is more accurate and appears to be a more appropriate measure of the organic loading of a wastewater.

CONCLUSIONS

1. The results obtained by the COD test do not give complete recovery with many compounds. Although this fact is recognized for aromatic compounds and is confirmed in this study, the study also revealed that compounds with urea structure, nitramine groups and certain nitro groups yield low results. However, the precision of the COD method surpasses that of the TOC.

2. The results obtained by the TOC test do give complete recovery as indicated by the t-test. The principle of the TOC test makes it independent of the structure of a compound. However, the precision of the TOC test, particularly at low concentrations, would require numerous replications to obtain a reliable estimate of the true mean of a sample.

3. From the point of view of enforcement of standards, the COD test appears inappropriate for the explosives industry. The TOC test would be more meaningful from the point of view of accuracy, but further study of this test is needed to improve its precision.

4. Although it has been shown that TOC and COD tests are correlated for many industrial wastes (ref. 10), their correlation is not a general rule because of the widely different principles upon which the tests are based. The data presented in this study indicates that correlations occur by chance rather than by a unifying principle. Thus, the existing standard based on the COD test for the explosive industry, cannot be converted to an equivalent standard based on the TOC test.

RECOMMENDATIONS

1. Further study should be made of the COD test to determine the effect of molecular structure on oxidizability. The efficiency of other oxidants, as compared to dichromate, should also be studied.

2. Consideration should be given to replacing the COD test with TOC in the EPA Limitations, Guidelines and Standards for the Explosives Industry.

3. Further study of the general indicators of organic loading in wastewaters and receiving waters is needed. For the explosives industry, a combination of TOC and total organic nitrogen should be considered to obtain a more pertinent measure of water quality.

4. Actual samples of wastewaters from explosive plants should be tested to confirm results obtained from the theoretical studies.

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Table 1. Point sources from manufacturing and loading of explosives

TNT Production

Condensate Water: 2,3-dinitrotoluene (DNT), 2,4-DNT, 2,5-DNT, 2,6-DNT, 3,4-DNT, 3,5-DNT, mononitrotoluene, 1,3-dinitrobenzene

TNT Load, Assembly and Pack

Pink Water: 2,4,6-trinitrotoluene (TNT), 2,6-DNT, 4,6-DNT

RDX/HMX

Wastewaters: Cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX)

Nitrate Ester Wastewaters

Trinitroglycerol (NG), Triethyleneglycoldinitrate (TEGDN)

Table 2. EPA effluent limitations, guidelines and standards*

EFFLUENT CHARACTERISTIC	LIMITATIONS, kg/kkg OR LBS/1000 LBS PRODUCT FOR ANY 1 DAY, MAX BPCTCA	FOR ANY 1 DAY, MAX BATEA	AV OF 30 CONSEC DAYS, MAX BPCTCA	AV OF 30 CONSEC DAYS, MAX BATEA
COD	–	0.85[a]	–	0.55[b]
EXISTING SOURCES	7.77		2.59	
NEW SOURCES	3.6		2.3	
BOD_5	–	0.11	–	0.067
EXISTING SOURCES	0.72		0.24	
NEW SOURCES	0.35		0.23	

		[a]	[b]
COD @ MAX PROD. RATES:	NG, mg/l	26	17
	TNT, mg/l	5.4	3.5

* 9 MAR 1976

Table 3. COD and TOC test results for toluene and nitrotoluenes

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
Toluene	169.5	529.9	408.0	169.5	154.5	54.0	76.9	31.8
			385.0			33.8	72.6	19.9
			391.0			17.2	73.7	10.1
			362.0			33.8	68.3	20.0
		$\bar{X}$	387.0		$\bar{X}$	34.7	73.0	20.4
		s	19.0		s	15.06	3.60	8.88
Toluene	17.0	53.0	31.1	17.0	15.5	7.9	58.6	51.0
			33.0			7.0	62.3	45.2
			28.7			8.0	54.2	51.7
			29.4			7.9	55.5	51.0
		$\bar{X}$	30.6		$\bar{X}$	7.7	57.7	49.8
		s	1.9		s	0.47	3.6	3.03
o-NT	204.2	428.8	418.4	200.6	123.0	120.0	97.5	97.5
			418.4			122.0	97.5	99.2
			418.4			123.6	97.5	100.0
			419.4			118.0	97.8	95.9
		$\bar{X}$	418.7		$\bar{X}$	120.9	97.6	98.2
		s	0.5		s	2.43	0.15	1.83
o-NT	20.4	42.9	42.1	20.1	12.3	11.5	98.1	93.4
			39.7			13.5	92.5	109.7
			40.1			13.0	93.4	105.6
			41.7			14.8	97.2	120.3
		$\bar{X}$	40.9		$\bar{X}$	13.2	95.3	107.3
		s	1.2		s	1.36	2.76	11.1

Table 3. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
m-NT	192.9	405.1	336.9	193.8	118.8	134.0	83.2	112.7
			342.9			131.6	84.6	110.7
			347.0			136.0	85.7	114.4
			341.0			136.0	84.2	114.5
		$\bar{X}$	342.0		$\bar{X}$	134.4	84.4	113.1
		s	4.2		s	2.09	1.03	1.79
m-NT	19.3	40.5	37.4	19.4	11.9	11.0	92.3	92.5
			38.5			11.5	94.9	96.8
			39.6			11.0	97.7	92.5
			38.4			10.8	94.7	90.9
		$\bar{X}$	38.5		$\bar{X}$	11.1	95.0	93.2
		s	0.9		s	3.0	2.21	2.53
p-NT	31.6	66.4	62.7	31.6	19.3	19.0	94.4	98.7
			63.1			19.0	95.0	98.7
			63.3			19.5	95.3	101.3
			64.7			19.5	97.4	101.3
		$\bar{X}$	63.5		$\bar{X}$	19.3	95.6	100.0
		s	0.9		s	0.28	1.30	1.50
p-NT	6.10	12.8	12.6	6.34	3.89	4.1	98.4	105.3
		10.5				3.6	82.0	92.5
		12.1				3.7	94.5	95.1
		11.4				3.0	89.0	77.1
		$\bar{X}$	11.7		$\bar{X}$	3.6	91.0	92.5
		s	0.91		s	11.7	7.11	11.7

Table 3. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
2,3 DNT	50.5	79.8	62.8	50.5	23.4	24.5	78.7	103.8
			63.2			24.8	79.2	105.7
			62,7			24.8	78.6	105.7
			57.8			25.00	72.4	106.8
		$\bar{X}$	61.6		$\bar{X}$	24.8	77.2	105.8
		s	2.6		s	0.20	3.23	1.25
2,3 DNT	6.38	10.1	6.7	6.38	2.95	2.0	66.3	67.8
			5.4			1.7	53.5	57.6
			6.2			1.9	61.4	64.4
			7.0			1.7	69.3	57.6
		$\bar{X}$	6.3		$\bar{X}$	1.83	62.6	62.0
		s	0.7		s	0.15	6.90	5.1
2,4 DNT	99.9	157.9	153.0	99.9	46.3	49.0	96.8	105.8
			154.0			49.0	97.5	105.8
			156.0			48.8	98.7	105.3
			157.0			48.0	99.4	103.6
		$\bar{X}$	155.0		$\bar{X}$	48.7	98.1	105.2
		s	1.83		s	0.48	1.17	1.04
2,4 DNT	6.7	10.6	10.2	6.7	3.10	2.8	96.2	90.3
			10.1			3.0	95.3	96.8
			8.9			2.7	83.9	87.0
			8.7			2.7	82.0	87.0
		$\bar{X}$	9.5		$\bar{X}$	2.8	89.4	90.3
		s	0.8		s	0.14	7.44	4.62

Table 3. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
2,5 DNT	50.5	79.8	75.5	50.5	23.4	25.0	94.6	106.8
			77.6			24.5	97.2	104.7
			75.2			24.5	94.2	104.7
			76.4			24.5	95.7	104.7
		$\bar{X}$	76.2		$\bar{X}$	24.6	95.5	105.3
		s	1.1		s	0.25	1.34	1.05
2,5 DNT	6.45	10.2	8.8	6.45	2.98	2.5	86.2	83.8
			9.7			3.0	95.1	100.7
			9.4			4.0	92.2	134.2
			8.6			3.0	84.3	100.7
		$\bar{X}$	9.1		$\bar{X}$	3.13	89.0	105.0
		s	0.5		s	0.63	5.05	21.1
2,6 DNT	50.8	80.3	77.8	50.8	23.5	24.7	96.9	105.1
			79.2			23.8	98.6	101.2
			77.9			25.8	97.0	109.8
			79.3			24.7	97.8	105.3
		$\bar{X}$	78.6		$\bar{X}$	24.8	97.9	105.4
		s	0.8		s	0.82	0.98	3.52
2,6 DNT	6.48	10.2	6.1	6.48	3.0	3.0	59.8	100.0
			8.2			3.7	80.4	123.3
			9.9			3.2	97.0	106.7
			9.9			3.0	97.0	100.0
		$\bar{X}$	8.5		$\bar{X}$	3.23	83.0	107.5
		s	1.8		s	0.33	17.7	11.0

Table 3. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
3,4 DNT	53.8	85.1	56.6	53.9	25.0	26.8	66.5	107.4
			55.9			26.0	65.6	104.2
			54.9			25.5	64.5	102.2
			53.2			26.0	62.5	104.2
		$\bar{X}$	55.2		$\bar{X}$	26.1	64.8	104.5
		s	1.5		s	0.54	1.72	2.15
3,4 DNT	6.23	9.8	5.9	6.23	2.88	2.1	60.2	72.9
			4.3			2.0	43.8	69.4
			5.1			2.0	52.0	69.4
			5.9			3.5	60.2	121.5
		$\bar{X}$	5.3		$\bar{X}$	2.4	54.1	83.3
		s	0.77		s	0.74	7.85	25.5
2,4,6 TNT	100.4	127.3	124.1	100.4	37.2	37.0	97.5	99.5
			123.1			34.5	96.7	92.7
			124.1			35.0	97.5	94.1
			120.8			37.0	94.8	99.5
		$\bar{X}$	123.0		$\bar{X}$	35.9	96.6	96.5
		s	1.6		s	1.31	1.27	3.57
2,4,6 TNT	6.41	8.13	6.6	6.41	2.22	3.1	81.2	139.6
			6.3			4.5	77.5	202.0
			7.8			2.0	95.9	90.1
			7.5			4.0	92.2	180.1
		$\bar{X}$	7.1		$\bar{X}$	3.4	86.7	153.0
		s	0.71		s	1.10	8.75	49.2

Table 4. COD and TOC test results for benzene and nitrobenzenes

Compound	Concentration mg/l	COD, mg/l		Concentration mg/l	TOC, mg/l		Recovery, %	
		Added	Found		Added	Found	COD	TOC
Benzene	147.1	452.0	307.0	148.0	136.2	72.5	67.9	53.2
			288.0			68.0	63.7	49.9
			267.0			84.0	59.0	61.7
			270.0			75.0	59.7	55.1
		$\bar{X}$	283.0		$\bar{X}$	74.9	62.6	55.0
		s	18.5		s	6.74	4.11	4.97
Benzene	14.7	45.2	17.6	14.8	13.6	4.5	38.9	33.0
			17.0			4.5	37.6	33.0
			16.3			5.0	36.1	36.8
			10.6			2.1	23.5	15.4
		$\bar{X}$	15.4		$\bar{X}$	4.03	34.0	29.6
		s	3.2		s	1.30	7.11	9.6
Nitrobenzenes								
m-DN Benzene	150.2	214.5	18.0	150.2	64.4	72.0	8.39	111.8
			16.1			58.0	7.50	90.1
			12.2			58.0	5.69	90.1
			13.3			58.0	6.20	90.1
		$\bar{X}$	14.9		$\bar{X}$	61.5	6.95	95.5
		s	2.64		s	7.0	1.23	10.9
m-DN Benzene	15.02	21.45	1.9	15.02	6.44	7.0	8.86	108.7
			0.8			6.9	3.7	107.1
			1.6			7.0	7.4	108.7
			0.4			6.0	1.8	93.2
		$\bar{X}$	1.2		$\bar{X}$	6.73	5.44	104.4
		s	0.70		s	0.49	3.26	7.52

Table 4. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
p-DN Benzene	51.3	73.2	6.6	51.3	22.0	45.5	9.0	207.0
			7.5			21.6	10.2	98.3
			7.9			19.0	10.7	86.4
			6.3			24.5	8.6	111.5
		$\bar{X}$	7.1		$\bar{X}$	27.7	9.61	125.8
		s	0.8		s	12.1	1.02	55.1
p-DN Benzene	15.4	22.0	1.2	15.4	6.60	6.8	5.4	103.0
			2.0			6.0	9.09	90.9
			2.7			7.3	12.3	110.6
			2.4			6.9	10.9	104.5
		$\bar{X}$	2.1		$\bar{X}$	6.75	9.42	102.3
		s	0.7		s	0.55	2.99	8.25
Nitrobenzene	156.7	305.4	198.0	156.7	91.7	83.0	64.8	90.5
			180.0			80.0	58.9	87.2
			216.0			80.0	70.7	87.2
			201.0			99.0	65.8	107.9
		$\bar{X}$	199.0		$\bar{X}$	85.5	65.1	93.2
		s	14.8		s	9.11	4.84	9.92
Nitrobenzene	15.7	30.5	29.9	15.7	9.17	9.0	97.9	98.1
			31.8			8.4	104.1	91.6
			29.8			8.5	97.5	92.7
			30.5			8.8	99.9	96.0
		$\bar{X}$	30.5		$\bar{X}$	8.68	99.9	94.6
		s	0.9		s	0.28	3.02	2.99

Table 5. COD and TOC test results for urea, nitramines, and guanidine nitrate

Compound	Concentration mg/l	COD, mg/l		Concentration mg/l	TOC, mg/l		Recovery, %	
		Added	Found		Added	Found	COD	TOC
Urea	206.8	440.7	0.00	207.6	41.5	32.0	0	77.1
			-1.58			30.0	-0.36	72.2
			2.35			33.0	0.53	79.5
			0.79			30.0	0.18	72.2
		$\bar{X}$	0.39		$\bar{X}$	31.3	0.09	75.3
		s	1.62		s	1.5	0.37	3.6
Urea	20.7	44.1	-0.38	20.8	4.16	2.2	0.86	52.8
			-0.38			2.0	0.86	48.0
			-0.78			2.5	-1.76	60.1
			-1.58			3.5	-3.58	84.1
		$\bar{X}$	-0.78		$\bar{X}$	2.55	0.90	61.2
		s	0.57		s	0.67	2.16	16.0
NQ	502.6	927.3	1.17	502.2	57.7	45.0	0.13	78.0
			1.55			44.5	0.17	77.1
			1.96			48.5	0.21	84.0
			1.18			49.0	-0.13	84.8
		$\bar{X}$	0.88		$\bar{X}$	46.8	0.09	81.0
		s	1.41		s	2.33	0.04	4.0
NQ	6.02	11.1	-0.24	6.03	0.69	0.5	-2.16	72.5
			-0.40			0.4	-3.6	57.9
			-0.12			1.5	-1.08	217.3
			-0.82			1.0	7.38	144.9
		$\bar{X}$	0.02		$\bar{X}$	0.85	3.55	123.0
		s	0.55		s	0.51	2.75	73.4

Table 5. (Continued)

Compound	Concentration mg/l	COD, mg/l		Concentration mg/l	TOC, mg/l		Recovery, %	
		Added	Found		Added	Found	COD	TOC
RDX	30.4	39.4	13.2	31.0	5.05	3.6	33.5	71.3
			12.8			3.6	32.5	71.3
			11.8			3.6	29.9	71.3
			13.0			3.5	32.9	69.3
		$\bar{X}$	12.7		$\bar{X}$	3.6	32.2	70.8
		s	0.6		s	0.05	1.60	1.0
RDX	6.20	8.04	2.6	6.20	1.01	1.0	32.3	99.0
			1.9			1.0	23.6	99.0
			1.9			1.5	23.6	148.5
			1.2			1.0	32.3	99.0
		$\bar{X}$	1.9		$\bar{X}$	1.13	28.0	111.4
		s	0.6		s	.25	5.02	24.8
Tetryl	51.1	59.8	47.1	51.1	15.0	13.8	78.7	92.2
			49.0			14.0	81.9	93.5
			49.3			16.0	82.4	106.5
			48.5			14.0	81.1	93.5
		$\bar{X}$	48.5		$\bar{X}$	14.5	81.1	96.5
		s	1.0		s	1.03	1.64	6.74
Tetryl	6.14	7.18	4.1	6.14	1.80	1.0	57.1	55.5
			4.8			1.7	66.9	94.4
			4.6			1.0	64.1	55.5
			6.3			1.7	87.7	94.4
		$\bar{X}$	4.95		$\bar{X}$	1.35	68.9	75.0
		s	0.9		s	0.40	13.2	22.5

Table 5. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
HMX	5.8	7.58	7.0	5.8	0.94	0.5	92.3	53.2
			6.2			1.0	81.8	106.3
			6.8			1.0	89.7	106.3
			7.5			1.3	98.9	138.3
		$\bar{X}$	6.88		$\bar{X}$	0.95	90.7	101.2
		s	0.54		s	0.33	7.07	35.3
Guanidine Nitrate	300.9	473.0	0.8	301.0	29.6	28.8	0.17	97.3
			-0.8			30.5	-0.17	103.0
			-1.2			30.0	-0.25	101.3
			0.0			29.8	0	100.7
		$\bar{X}$	-0.3		$\bar{X}$	29.8	-0.06	100.6
		s	0.9		s	0.71	0.19	2.39
Guanidine Nitrate	30.12	47.4	0.4	30.1	3.47	5.2	0.84	149.8
			-0.4			5.0	-0.84	144.0
			0.4			5.1	0.84	146.9
			0			5.0	0	144.0
		$\bar{X}$	0.1		$\bar{X}$	5.08	0.21	146.18
		s	0.4		s	0.10	0.80	2.78

Table 6. COD and TOC test results for nitrate esters

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
NG	500.0	246.6	242.8	500.0	79.5	84.0	98.5	105.6
			242.9			80.0	98.5	100.6
			242.9			82.0	98.5	103.1
			244.6			71.0	99.2	89.1
		$\bar{X}$	243.3		$\bar{X}$	79.3	98.7	99.7
		s	0.9		s	5.73	0.35	7.29
NG	5.93	2.92	4.1	5.93	0.94	1.0	140.4	106.0
			2.2			1.2	75.3	127.3
			2.7			1.2	92.5	127.3
			3.1			1.5	106.2	159.0
		$\bar{X}$	3.0		$\bar{X}$	1.23	103.6	130.0
		s	0.8		s	0.206	27.6	21.8
TEGDN	479.2	478.9	481.3	479.0	143.2	135.0	100.5	94.3
			475.2			135.0	99.2	94.3
			473.0			141.0	98.8	98.5
			475.4			180.0	99.3	125.7
		$\bar{X}$	476.2		$\bar{X}$	148.0	99.4	103.3
		s	12.6		s	21.7	0.73	15.1
TEGDN	47.96	47.93	48.2	47.9	14.3	13.5	99.4	94.4
			45.3			13.5	94.5	94.4
			46.5			14.1	97.0	98.6
			45.7			18.0	95.3	125.8
		$\bar{X}$	46.4		$\bar{X}$	14.8	96.6	103.3
		s	1.3		s	2.17	2.17	15.1

Table 7. COD and TOC test results for alcohols and acids

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
Glycerine	395.9	481.4	477.1	398.0	156.7	145.3	99.1	92.7
			476.4			150.0	99.0	95.7
			478.5			145.0	99.4	92.5
			476.1			150.0	98.9	95.7
		$\bar{X}$	477.0		$\bar{X}$	147.5	99.1	94.2
		s	1.1		s	2.80	0.22	1.80
Glycerine	39.6	48.2	46.7	39.8	15.6	14.5	96.9	92.9
			48.5			14.5	100.6	92.9
			47.2			15.0	97.9	96.2
			46.4			15.0	95.9	96.2
		$\bar{X}$	47.2		$\bar{X}$	14.8	97.9	94.6
		s	0.9		s	0.08	2.02	1.91
Pentaerythritol	301.7	425.5	417.0	302.0	133.21	132.0	98.0	99.0
			417.0			134.2	98.0	100.7
			416.0			129.0	97.8	96.8
			418.0			134.0	98.2	100.6
		$\bar{X}$	417.0		$\bar{X}$	132.3	98.0	99.3
		s	0.82		s	0.67	0.18	1.82
Pentaerythritol	6.14	8.66	7.4	6.14	2.71	2.2	85.5	81.2
			10.2			2.5	117.7	92.3
			7.5			3.1	86.6	114.4
			8.5			3.7	98.2	136.5
		$\bar{X}$	8.4		$\bar{X}$	2.88	97.0	106.1
		s	1.3		s	0.67	15.0	24.5

Table 7. (Continued)

Compound	Concentration mg/l	COD, mg/l Added	COD, mg/l Found	Concentration mg/l	TOC, mg/l Added	TOC, mg/l Found	Recovery, % COD	Recovery, % TOC
Acetic Acid	313.2	333.9	328.0	313.2	125.3	120.0	98.2	95.8
			326.0			123.6	97.6	98.6
			325.0			120.0	97.3	95.7
			327.0			120.0	97.9	95.7
		$\bar{X}$	327.0		$\bar{X}$	120.9	97.8	96.5
		s	1.0		s	1.80	0.39	1.44
Acetic Acid	6.69	7.13	5.1	6.69	2.68	2.1	71.5	78.4
			4.3			1.6	60.3	59.7
			4.3			1.0	60.3	37.3
			3.9			1.0	54.6	37.3
		$\bar{X}$	4.4		$\bar{X}$	1.43	62.0	53.2
		s	0.5		s	0.53	7.08	19.9

Table 8. Statistical parameters for aromatic compounds

Compound	Variance		Correlation Coefficient
	COD	TOC	
Toluene	77.1	282.2	-0.85 *
o-Nitrotoluene	4.75	78.1	-0.44
m-Nitrotoluene	33.9	116.6	-0.94 *
p-Nitrotoluene	28.3	75.2	0.64
2,3 Dinitrotoluene	85.7	557.0	0.85 *
2,4 Dinitrotoluene	46.2	72.6	0.83 *
2,5 Dinitrotoluene	21.9	191.5	0.33
2,6 Dinitrotoluene	193.2	58.5	-0.071
3,4 Dinitrotoluene	60.5	409.7	0.73 *
2,4,6 Trinitrotoluene	61.6	1956.3	-0.80 *
Benzene	282.2	234.1	0.93 *
m-Dinitrobenzene	5.86	97.4	0.38
p-Dinitrobenzene	4.37	1490.0	-0.11
Nitrobenzene	359.9	46.6	0.11
Tetryl	116.9	367.1	0.82 *

* Values significant at 95% confidence level

Table 9. Statistical parameters for nonaromatic compounds

Compound	Variance		Correlation Coefficient
	COD	TOC	
Urea	2.34	171.6	-0.48
Nitroguanidine	10.4	2819.6	0.35
Guanidine Nitrate	0.31	599.8	0.30
RDX	17.2	734.4	-0.72 *
HMX	50.0	1246.1	0.24
Nitroglycerin	334.9	488.4	-0.145
Triethylene Glycol Dinitrate	4.67	196.0	0.21
Glycerin	2.25	2.99	-0.45
Pentaerythritol	96.0	272.3	0.055
Acetic Acid	392.0	707.6	0.95 *

* Values significant at 95% confidence level

Table 10. Comparison of completeness of recovery by COD and TOC tests

t - TEST VALUES

COD_{Hi}	COD_{Lo}	TOC_{Hi}	TOC_{Lo}
4.66*	5.76*	1.55	0.84

* VALUES ARE SIGNIFICANTLY DIFFERENT FROM 100% RECOVERY AT 90% LEVEL OF CONFIDENCE FOR 23 DEGREES OF FREEDOM.

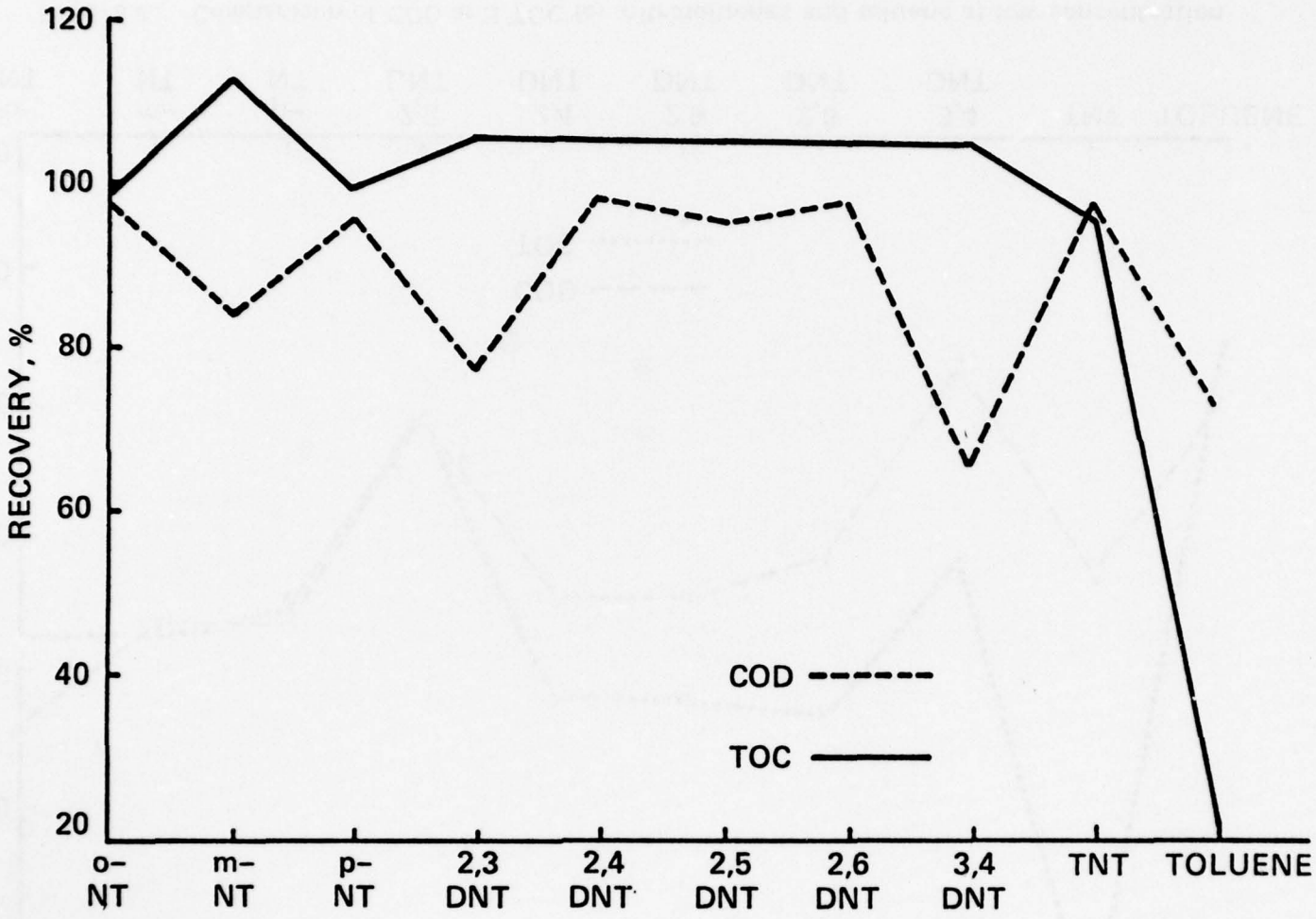

Figure 1. Comparison of COD and TOC for nitrotoluenes and toluene at high concentration

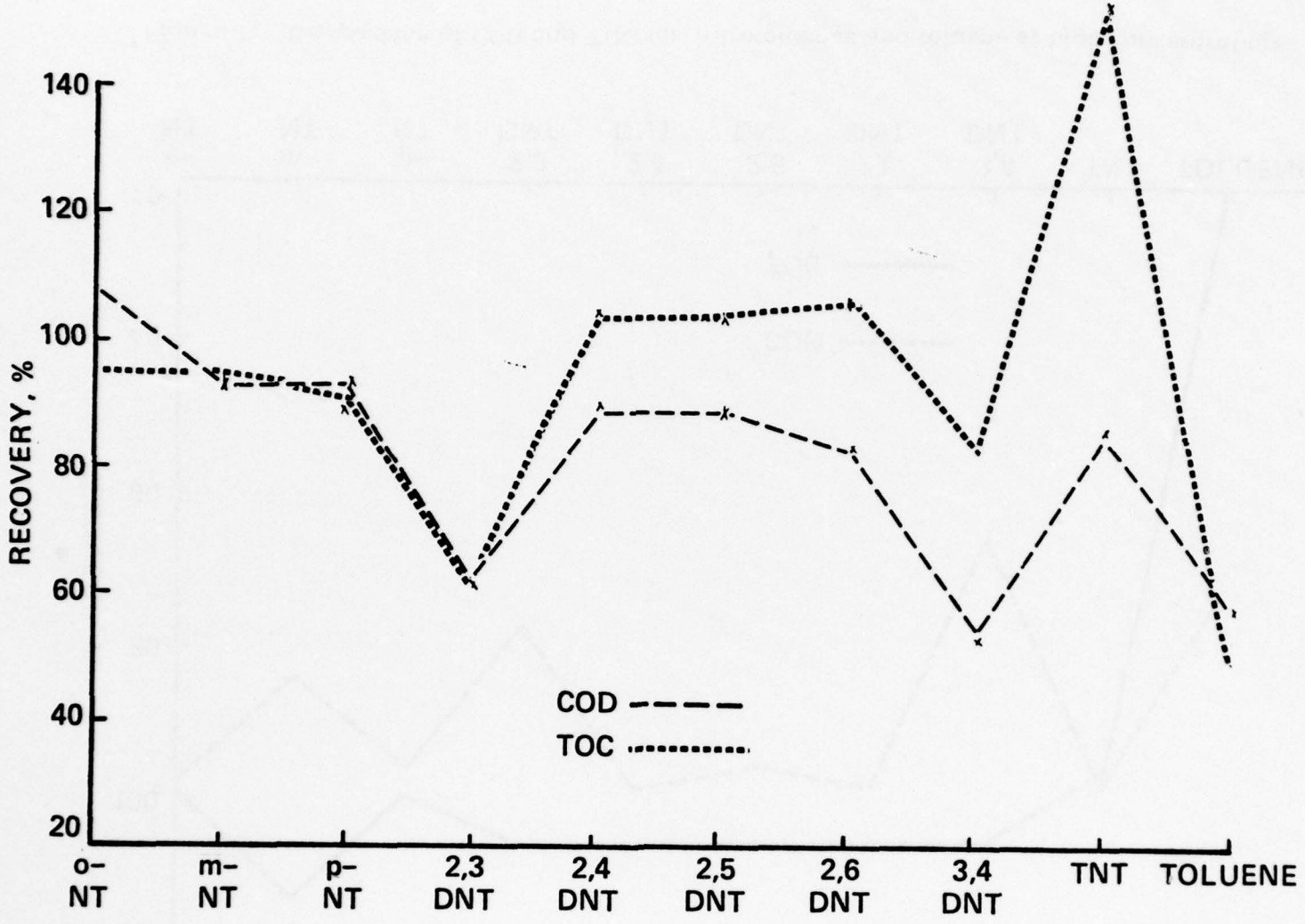

Figure 2. Comparison of COD and TOC for nitrotoluenes and toluene at low concentration

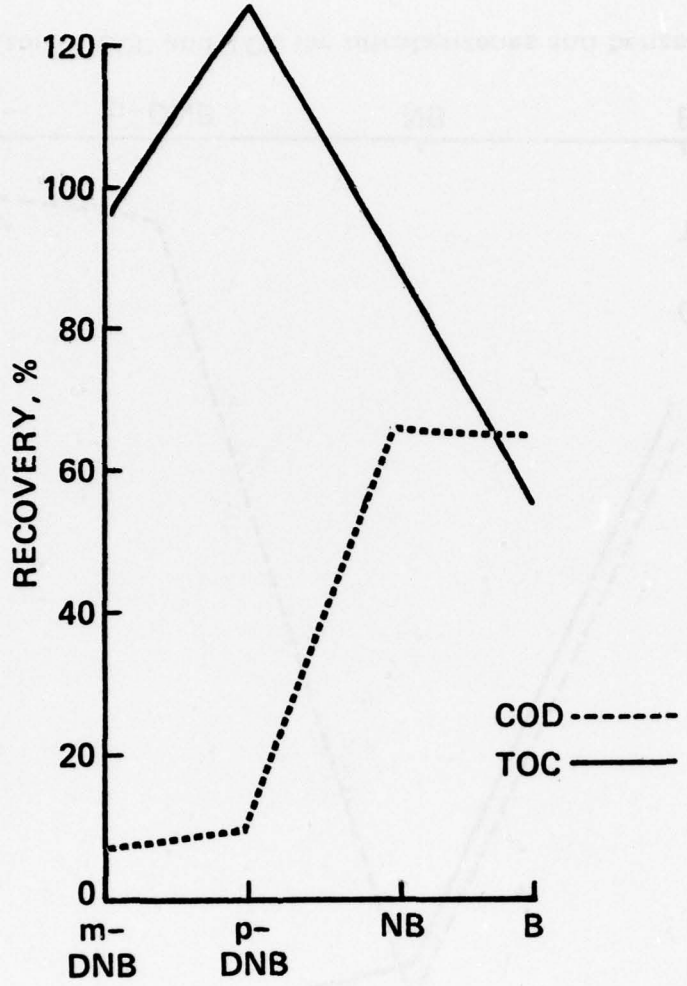

Figure 3. Comparison of COD and TOC for nitrobenzenes and benzene at high concentration

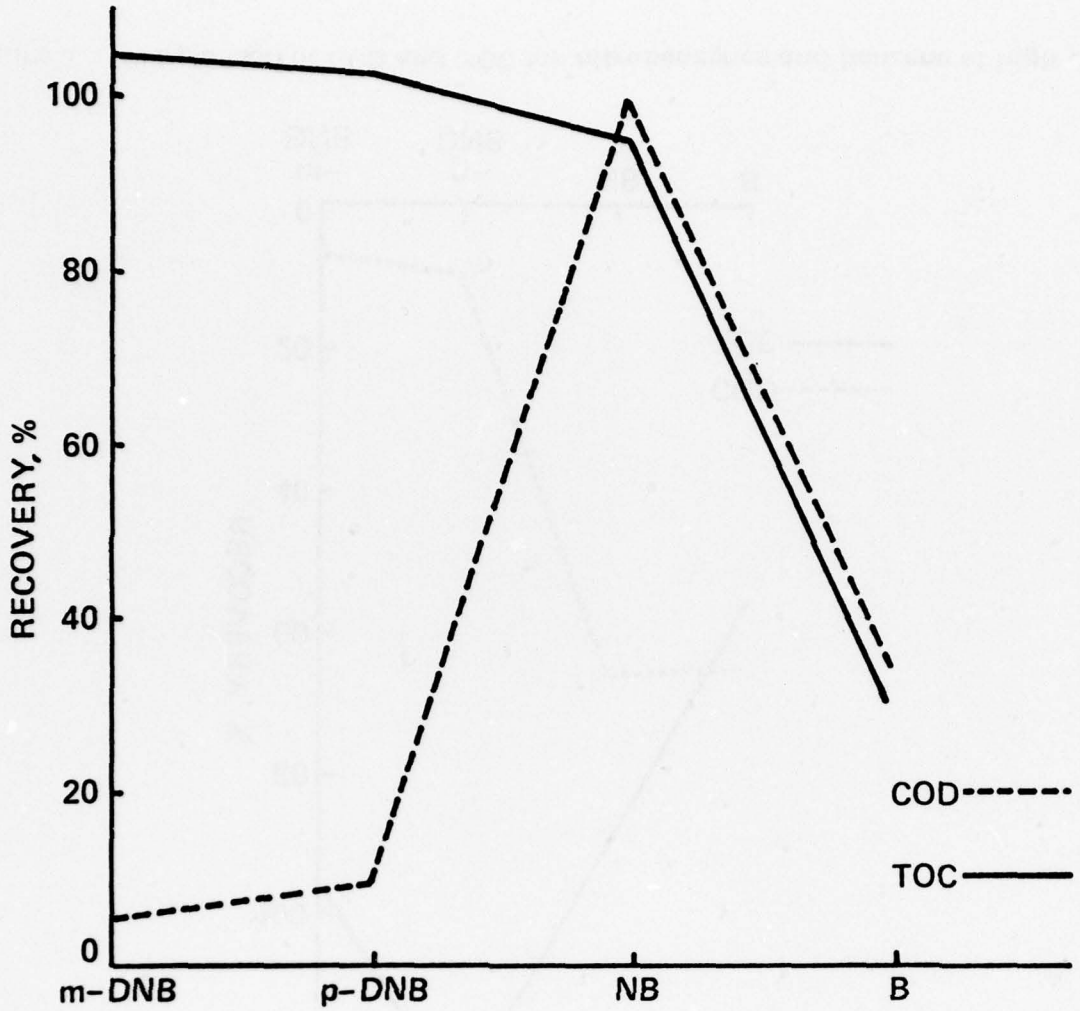

Figure 4. Comparison of COD and TOC for nitrobenzenes and benzene at low concentration

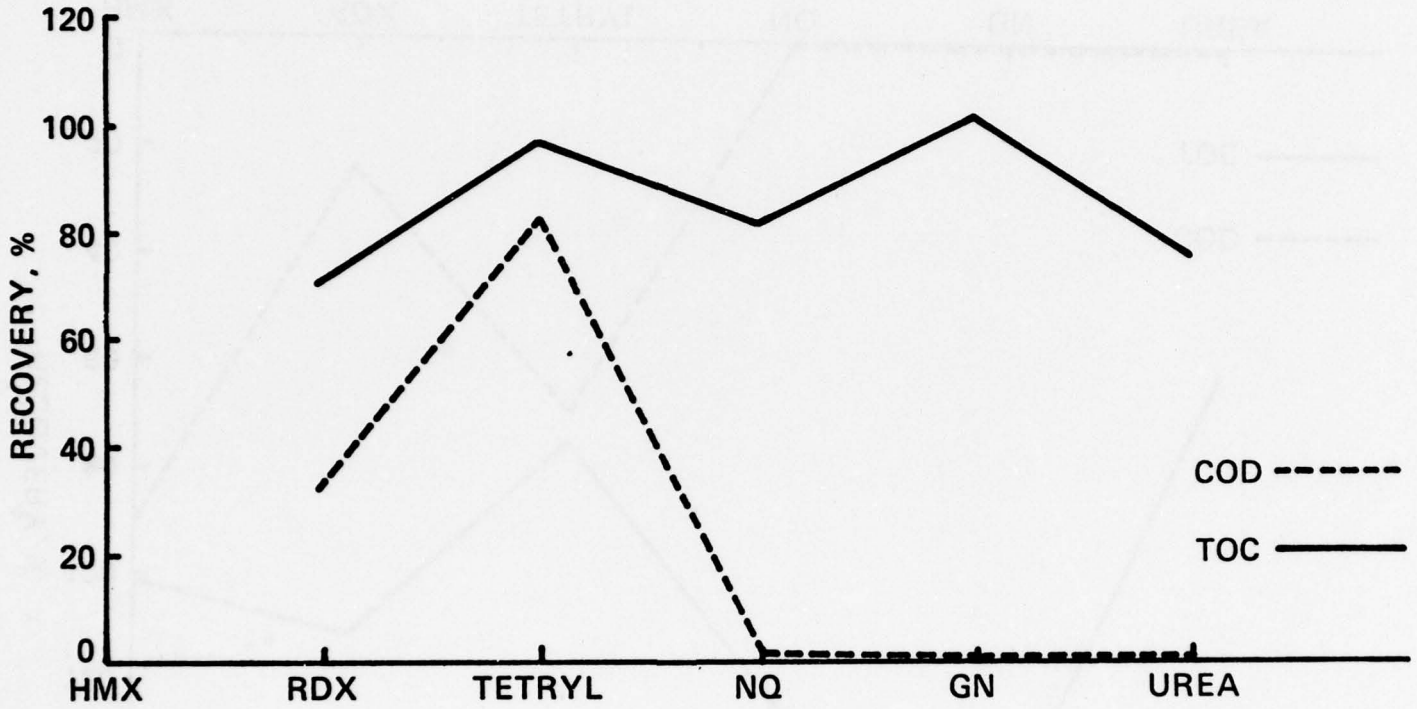

Figure 5. Comparison of COD and TOC tests for nitramines, guanidine nitrate, and urea at high concentration

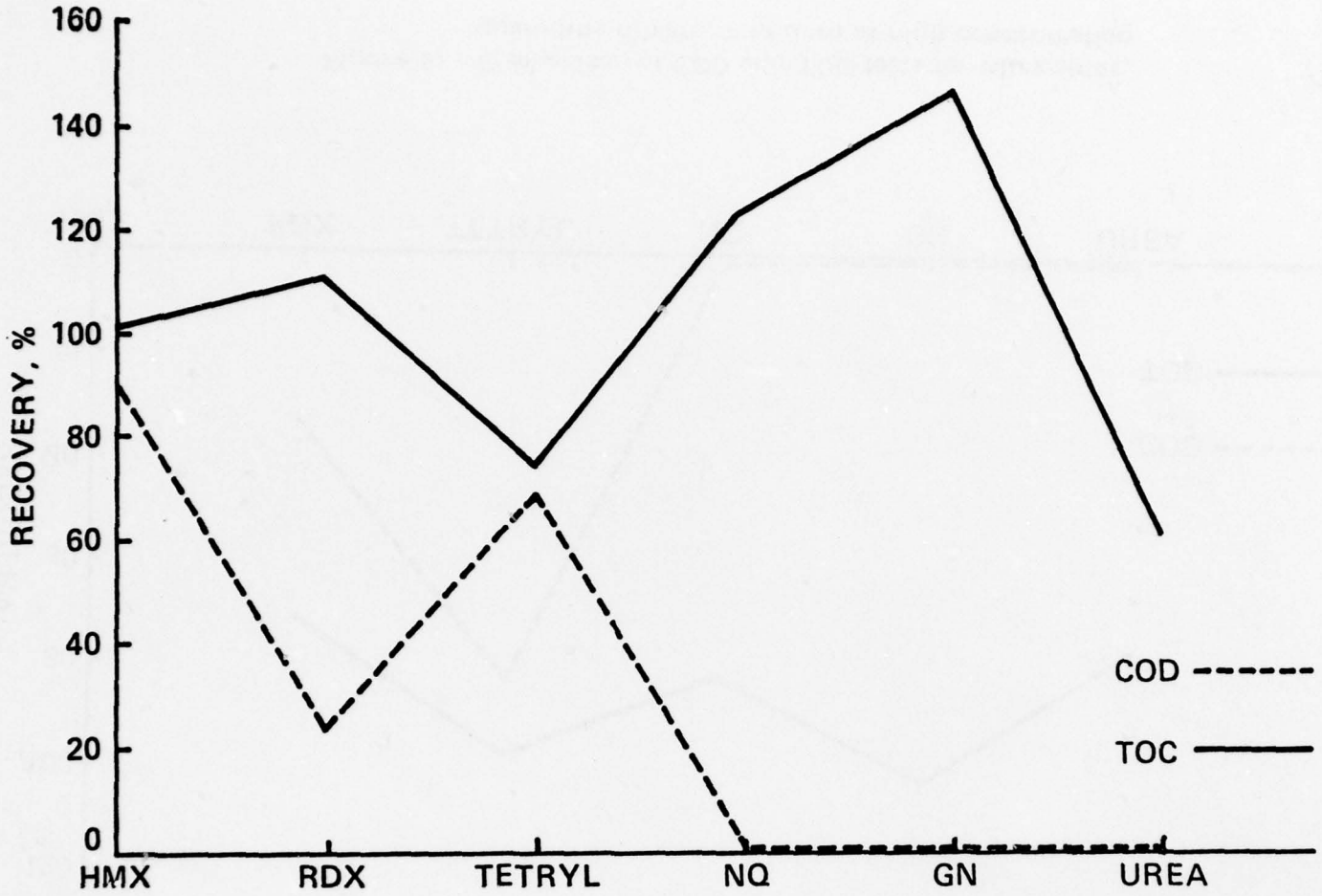

Figure 6. Comparison of COD and TOC tests for nitramines, guanidine nitrate, and urea at low concentration

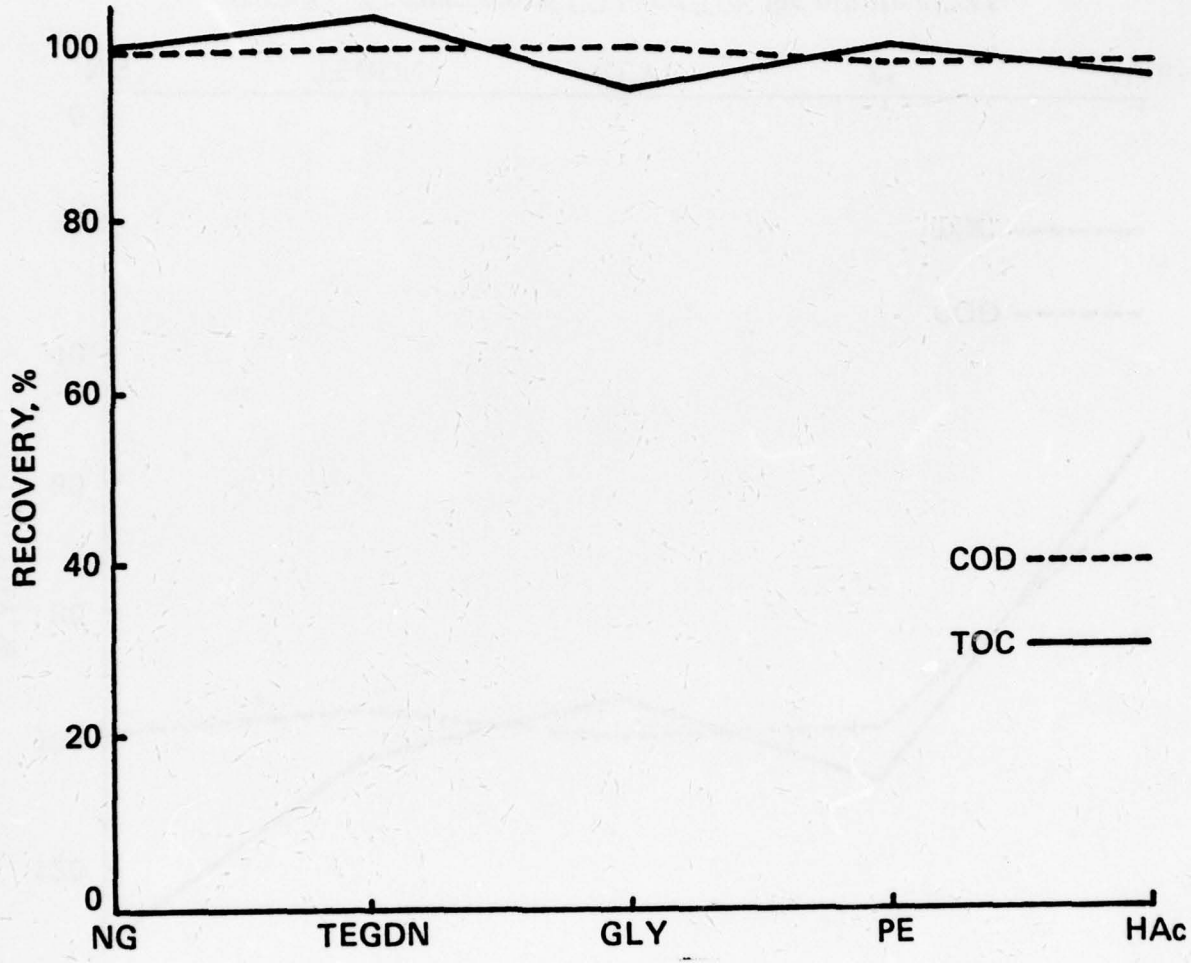

Figure 7. Comparison of COD and TOC for nitrate esters, alcohols and acids at high concentration

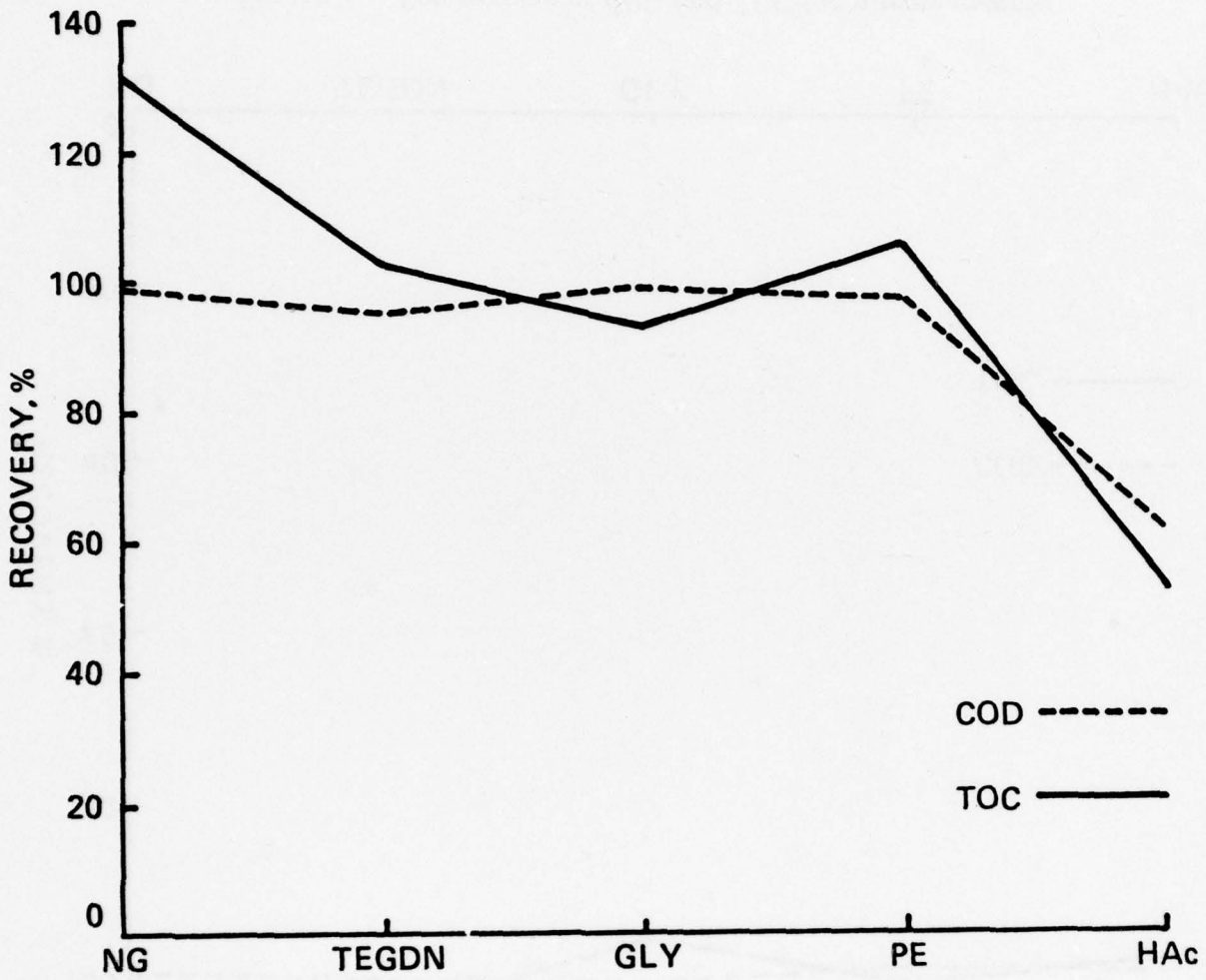

Figure 8. Comparison of COD and TOC for nitrate esters, alcohols and acids at low concentration

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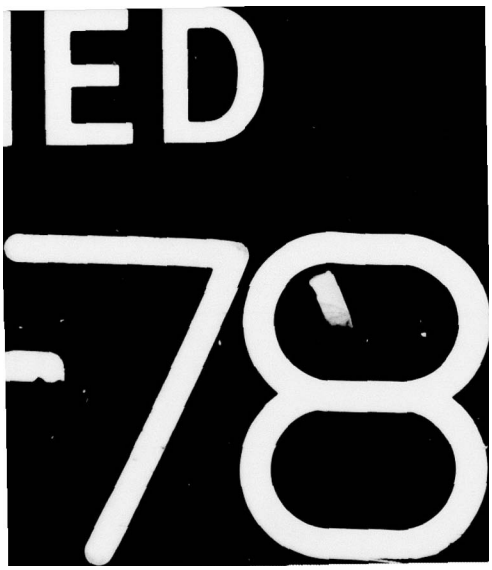
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