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Environmental Monitoring Series

A STUDY OF NEW CATALYTIC AGENTS TO DETERMINE CHEMICAL OXYGEN DEMAND



Environmental Monitoring and Support Laboratory
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A STUDY OF NEW CATALYTIC AGENTS TO DETERMINE
CHEMICAL OXYGEN DEMAND

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- o Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- o Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- o Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

There is an ever-increasing interest in improving methods to analyze water and waste samples, whether the resulting data are to be used for research, surveillance, compliance monitoring, or enforcement purposes. Accordingly, the Environmental Monitoring and Support Laboratory has an on-going methods research effort in the development, evaluation, and modification of standard procedures. This particular report pertains to procedural modification for chemical oxygen demand measurement. The method has potential routine application for the analysis of chemical oxygen demand in surface waters and domestic and industrial wastes.

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ABSTRACT

Of the several methods proposed for chemical oxygen demand (COD) determinations, the dichromate reflux method has generally been adopted as the standard procedure using silver sulfate as the catalyst. Inasmuch as silver sulfate is extremely expensive, the purpose of this study was to ascertain which of the nontoxic elements, iron, copper, zinc, aluminum, etc. could be employed for a substitute catalyst for silver sulfate in the procedure. The results obtained in this study show that among the catalysts investigated, silver sulfate is generally the best for carrying out COD determinations. However, substantially the same results could be obtained from samples in the high-level range of approximately 500 milligrams by using a reduced amount of silver sulfate in combination with magnesium sulfate.

A procedure is described for determining the COD values of solutions having sample concentrations in the range 5 to 50 milligrams. The method is a modification of the standard Moore procedure, in that a combination of silver sulfate, aluminum sulfate, and magnesium sulfate is used to replace the silver sulfate catalyst. This revised procedure is generally comparable in completeness of oxidation and is less expensive than the Moore procedure. Data are reported for pure synthetic organic samples and for certain bayou samples.

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SECTION I

INTRODUCTION

Previously several methods have been proposed for determination of chemical oxygen demand (COD) values in certain waters and wastes. The dichromate reflux method (1) using silver sulfate as a catalyst is generally accepted as the standard procedure (2) for COD determinations. This method suffers from the fact that the availability of silver sulfate is low and the cost of this catalyst is extremely high, presently approximately \$400 per pound. In addition to the dichromate procedure, several other less well accepted methods have been proposed, e.g., the iodic method of Dzyadzio (3), later modified by Johnson, Halvorson, and Tsuchiya (4), the permanganate method (5), the perchloratoceric acid procedure (6), and the elimination of chloride interference in the dichromate reflux COD test by Dobbs (7) and Williams and Baumann (8) by the addition of mercuric sulfate to form unionized mercuric chloride.

In attempting to control our environment, we frequently need to know the amount and extent of oxidation of organic matter in our water and waste systems. Thus, there is a need for an economical, sensitive, and rapid determination of oxygen required to oxidize the organic matter in waste samples. The low availability and high cost of silver sulfate catalyst employed in the standard COD procedure give rise to a need for finding a low-cost substitute catalyst. This study was undertaken, first, to ascertain which of the nontoxic elements (iron, nickel, copper, zinc, aluminum, etc.), may be used for a substitute or partial substitute catalyst for silver sulfate in the standard COD procedure and secondly, to evaluate the best replacement catalytic agent for COD determination, standardize the procedure, and test its validity.

This project was divided into two phases. Phase (I) was concerned with high level COD determinations and involved: (a) an evaluation of the effect of sulfuric acid on the completeness of oxidation, (b) effect of different proposed substitute catalysts, (c) effect of different combination catalysts, (d) effect of time of heating, and (e) a comparison of COD values using the Friedrich's condenser versus a dry ice condenser. In Phase (II), low level COD studies in the concentration range 5 to 50 milligrams per sample were carried out involving considerations similar to those for high level COD determinations.

SECTION II

CONCLUSIONS

This work has demonstrated

1. that among the catalysts studied, silver sulfate is generally the best catalyst for carry out COD determinations.
2. that in the high-level, revised COD procedure substantially the same COD values could be obtained using 15 ml of silver sulfate solution in combination with 1 magnesium sulfate instead of the 70 ml of silver sulfate solution required in the standard COD procedure.
3. that in the low-level, proposed procedure comparable results could be obtained by using 20 ml of silver sulfate solution in combination with 1 g aluminum sulfate and 1 g magnesium sulfate instead of the 70 ml of silver sulfate solution required in the standard procedure.
4. that the data obtained using the standard method vs. the revised method for measuring COD values of real water samples showed that the revised method is comparable to the standard method.

Preliminary work indicated that the COD values for certain extremely volatile organic compounds could be materially increased by using a dry ice condenser filled with crushed ice instead of a Friedrich's condenser. These studies suggest that further studies using a dry ice or modified dry ice condenser are desirable.

SECTION III

RECOMMENDATIONS

1. In this study the Friedrich's reflux condenser was generally employed; however, a limited number of determinations were carried out using a dry ice condenser. The COD values for certain volatile compounds was substantially higher when a dry ice condenser filled with crushed ice was used. Thus more studies should be carried out using a dry ice condenser.
2. Further studies should be carried out using a dry ice condenser filled with different freezing point mixtures.
3. It is recommended that further studies be carried out on the variables such as time of heating and temperature of refluxing medium using a dry ice or modified dry ice condenser.
4. It is recommended that the silver sulfate-magnesium sulfate-aluminum sulfate catalyst replace the silver sulfate catalyst in the Standard Chemical Oxygen Demand Method.

SECTION IV

EXPERIMENTAL PROCEDURES

APPARATUS

Each reflux apparatus used consisted of a pyrex 500 ml round bottom or Erlenmeyer flask fitted with a 24/40 taper-joint neck connected with a Friedrich's reflux condenser or a dry ice condenser, in designated cases, in which crushed ice was used. Standard hot plates were employed to heat the reflux solutions. All samples, unless otherwise indicated, were run in triplicate, simultaneously with a blank containing 50 ml of deionized water.

A total organic carbon analyzer, model DC-50, obtained from the Dohrmann Division, Division of Envirotech Corporation, Mountain View, California, was used to verify the carbon content in the COD samples used in this study. This instrument was standardized before each series of determinations against reagent grade potassium hydrogen phthalate dissolved in deionized water.

REAGENTS AND SOLUTIONS

All solutions were prepared from reagent grade chemicals. For high-level range COD determinations (approximate range of 500 mg of sample per liter), standard potassium dichromate, 0.250 N, was prepared by dissolving 12.2588 g of dried $K_2Cr_2O_7$ in a 1 liter flask and diluting the solution to volume. Sulfuric acid² containing 23.5 g of silver sulfate per 9 lb bottle was employed after allowing two days for complete dissolution. Phenanthroline ferrous sulfate (ferrion) indicator solution was prepared by dissolving 98 g of 1-10 (ortho) phenanthroline monohydrate and 0.70 g of $FeSO_4 \cdot 7H_2O$. Standard ferrous ammonium sulfate, approximately 0.250 N was prepared² by dissolving 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in deionized water, then adding 20 ml of concentrated sulfuric acid, cooling, and diluting the solution to a volume of 1 l. The standard ferrous ammonium sulfate was standardized daily as its concentration decreases on standing.

Standard reagents solutions for low level COD determinations were prepared as described above for the high level procedure, except the solutions were made one-tenth the concentrations used in the high-level procedure. For bayou samples which contained chlorides, mercuric sulfate was added to the digestion flask to complex the chlorides, thus eliminating the chloride interference, except for samples which contained a very high chloride and required a chloride correction (2).

CALCULATIONS

1. Theoretical COD: A typical theoretically calculated COD, Mg/l, for acetic acid is presented using the following balanced equation



The theoretical COD in this case for a 500 mg sample of acetic acid is:

$$\text{COD, mg/l} = 500 \frac{\text{mg of HC}_2\text{H}_3\text{O}_2}{60 \text{ mg of HC}_2\text{H}_3\text{O}_2 \text{ mmoles}} \times \frac{64 \text{ mg of O}_2 / 2 \text{ mmoles}}{1} = 533 \frac{\text{mg of O}_2}{1}$$

2. Experimental COD value: The experimental COD values reported in this study are expressed in mg/l using the following equation.

$$\text{mg/l COD} = \frac{(A - B)C \times 8,000}{\text{ml sample}}$$

where: COD = Chemical Oxygen Demand, mg/l of sample

A = ml of ferrous ammonium sulfate used for blank

B = ml of ferrous ammonium sulfate used for sample

C = the normality of ferrous ammonium sulfate.

RECOMMENDED REVISED MOORE HIGH LEVEL COD PROCEDURE

Several boiling stones are placed in a reflux flask which has been placed in an ice bath. To this flask is added 25 ml of potassium dichromate solution, 15 ml of silver sulfate solution (23.5 g of silver sulfate per 9-16 bottle of conc. sulfuric acid) plus one gram magnesium sulfate. While swirling the resulting solution, 55 ml of concentrated sulfuric acid and 50 ml of a test COD sample which contained an accurately known amount of compound ranging from approximately 250 to 500 mg of sample per liter are added to the mixture in the reflux flask. After this solution is refluxed for two hours, the flask is allowed to cool, and the inside of the condenser is washed with 25 ml of deionized water. Ten drops of ferrion indicator are added to the solution at room temperature and the excess potassium dichromate is titrated with 0.25 N ferrous ammonium sulfate to the ferrion end point, where the solution changes from blue green to reddish brown. The COD values of the aromatic hydrocarbons are increased markedly by substituting a dry ice cooled condenser, filled with crushed ice (frozen water), in place of a Friedrich's condenser.

RECOMMENDED REVISED MOORE LOW LEVEL COD PROCEDURE

Several boiling stones are placed in a reflux flask which has been placed in an ice bath. To this flask is added 25 ml of potassium dichromate, 20 ml of silver sulfate solution (23.5 g of silver sulfate per 9-lb bottle of conc. sulfuric acid) plus one gram magnesium sulfate and one gram aluminum sulfate. While swirling the resulting solution, 50 ml of concentrated sulfuric acid and 50 ml of a test COD sample which contained an accurately known amount of compound ranging from approximately 5 to 50 mg of sample per liter are added to the mixture in the reflux flask. After this solution is refluxed for two hours, the flask is allowed to cool, and the inside of the condenser is washed with 25 ml of deionized water. Ten drops of ferrion indicator are added to the solution at room temperature and the excess potassium dichromate is titrated with 0.025 N ferrous ammonium sulfate the ferrion end point.

SECTION V

RESULTS AND DISCUSSION

PHASE I

The first part of this study consisted of evaluating the COD values of ten selected organic compounds by using various amounts of silver sulfate solution (23.5 g Ag_2SO_4 per 9 oz bottle) as a catalyst. The concentration effect of silver sulfate as a catalyst was ascertained by determining the COD values for each of ten selected compounds in the presence of 5, 10, 15, 20, 35, 50, 70 ml of the silver sulfate solution. The organic compounds selected represent different classes of organic substances that may be found in wastewater. A solution of each of the ten organic compounds was prepared by dissolving approximately 500 mg of each in 100 ml of de-ionized water and diluting to 1000 ml. The results of the oxidation of these compounds are shown in Table 1. According to these tabular data acetic acid and ethyl alcohol gave essentially the same results in the presence of 15 ml of silver sulfate solution as the 70 ml recommended in the standard procedure. These results suggest that using 15 ml of silver sulfate solution gives substantially the same catalytic effect as 70 ml. Such reduction in the required amount of silver sulfate catalyst gives rise to approximately a 4-fold reduction in the cost of running a COD determination because of the materially high cost of silver sulfate.

The effect of sulfuric acid concentration on typical COD values obtained using the standard Moore COD procedure is shown in Table 2. These results show that high-percentage results are generally obtained with high sulfuric acid concentrations. For the compounds studied, that are almost completely oxidized by 15 ml of silver sulfate solution plus 55 ml of sulfuric acid, significantly lower COD values were obtained at very low sulfuric acid concentrations.

In the third part of this study 16 suggested substitute catalysts were employed to obtain chemical oxygen demand values for the same organic compounds which were used in the first step. It should be emphasized that, although used for this study, none of these individual catalysts could be used as a replacement for silver sulfate giving the same completeness of oxidation of the compounds studied as are shown in Table 3. These data, however, do indicate that several of the catalysts do give high COD values for certain of the high molecular weight organic compounds.

The various combination of different catalysts such as

- 1" 1 g $\text{Fe}_2(\text{SO}_4)_3$ + 1 g $\text{Al}_2(\text{SO}_4)_3$
- 2" 1 g $\text{Al}_2(\text{SO}_4)_3$ + 1 g MgSO_4
- 3" 1 g $\text{Fe}_2(\text{SO}_4)_3$ + 1 g MgSO_4
- 4" 1 g MgSO_4 + 15 ml Ag_2SO_4 solution
- 5" 1 g $\text{Al}_2(\text{SO}_4)_3$ + 15 ml Ag_2SO_4 solution
- 6" 1 g $\text{Fe}_2(\text{SO}_4)_3$ + 15 ml Ag_2SO_4 solution
- 7" 1 g MgSO_4 + 1 g $\text{Al}_2(\text{SO}_4)_3$ + 15 ml Ag_2SO_4 solution
- 8" 1 g MgSO_4 + 1 g $\text{Fe}_2(\text{SO}_4)_3$ + 15 ml Ag_2SO_4 solution
- 9" 1 g $\text{Fe}_2(\text{SO}_4)_3$ + 1 g $\text{Al}_2(\text{SO}_4)_3$ + 1 ml Ag_2SO_4 solution

were used in the last step. The evaluation of the above catalysts with the ten different organic compounds showed that 15 ml of silver sulfate solution in combination with MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, or $\text{Fe}_2(\text{SO}_4)_3$ gave reasonable higher COD values as compared to the first three combination catalysts as shown in Table 4. The data in Table 4 indicate that comparable COD values are obtained for most of the above ten compounds when 15 ml of silver sulfate solution plus one gram of MgSO_4 are used to replace the 70 ml of silver sulfate solution required as the catalyst in the standard COD procedure. The magnesium sulfate-silver sulfate suggested replacement catalyst combination for silver sulfate does not substantially oxidize pyridine or aromatic hydrocarbons. These results are similar to one obtained using 70 ml of silver sulfate solution in the standard procedure. However, preliminary studies, Table 6, indicated that the COD values for aromatic hydrocarbons are materially increased by substituting a dry ice cooled condenser filled with crushed ice in place of a Friedrich's condenser. The selection of the best possible cooling mixture for a dry ice condenser in COD determinations should justify further study.

The results of the oxidation of these compounds showed that formaldehyde is oxidized by 74% when 70 ml of silver sulfate solution is used and 69% when 15 ml of silver sulfate solution is used in the standard procedure, acetic acid is 99% oxidized and 92% oxidized when 15 ml of silver sulfate solution is used as a catalyst (see in Table 1).

For high molecular weight organic compounds, viz., toluene, oleic acid, benzene, certain of the new catalysts gave higher oxidation values than 70 ml of silver sulfate solution. For example, toluene is oxidized by ferric oxide (70.5%), and benzene is oxidized by aluminum sulfate (38.7%), whereas silver sulfate gave respective oxidation values of 38.1%, 32.2%, 37.6% for toluene, oleic acid, and benzene (see Table 3).

Tabular data for effect of time of heating on COD values of acetic acid are shown in Table 5. Typical data were obtained for other compounds that are readily oxidized in boiling dichromate sulfuric acid solution, which indicate that such compounds are generally and substantially oxidized within the recommended 2-hour digestion period.

Typical data of the carbon content of stock sample solutions using the total carbon analyzer described above under Apparatus are reported in Table 7. These measurements were carried out to verify and test the comparative accuracy of the revised procedure.

Statistical treatment of certain data obtained in this study was carried out as described by Laitinen and Harris (9). Eleven replicate measurements of COD values for acetic acid, reported in Table 8 using the revised method proposed in this study gave a mean of 489 with a standard deviation of two COD units. The 95% confidence interval of the mean and the standard deviation are 489 ± 1 to 8, respectively.

The data obtained in this phase of the study show that among the catalysts studied, silver sulfate is generally the best catalyst for carrying out COD determinations. However, substantially the same results could be obtained using 15 ml of silver sulfate solution in combination with 1 g magnesium sulfate. Thus, based on the data obtained in this study, the already described procedure is proposed for carrying out chemical oxygen demand determinations in the high level concentration range, thereby obtaining essentially the same COD values as those of the standard Moore method at less expense.

PHASE II

Inasmuch as the Moore method using silver sulfate as a catalyst has generally been accepted as a standard method for carrying out COD determinations, this procedure was selected for the studies reported herein. The primary emphasis in this study was to find a recommended replacement catalyst in the low level COD range of 5 to 50 mg of sample, for silver sulfate because of the extremely high cost of this catalyst.

The concentration effect of silver sulfate catalyst using the standard Moore method on eleven different organic compounds that might be found in certain wastes are shown in Table 9. These tabular data indicate that 20 ml of silver sulfate solution gives COD values fairly close to the ones obtained for 70 ml of silver sulfate solution for most of the compounds. Based upon exploratory tests, the 5 catalysts (MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, CaSO_4 and ZrOSO_4) were selected for detail study using eleven organic substances. These studies were carried out by placing accurately weighed samples of approximately 50 mg of each organic compound in separate 1 liter volumetric flasks and diluting the volume with deionized water. The data for these studies are shown in Table 10. Among the catalysts employed, MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ generally gave fairly high COD value; however, none of the 5 catalysts were effective in oxidizing acetic acid.

In an attempt to ascertain the additive catalytic effect of the aforementioned 5 selected catalysts, these catalysts were grouped in pairs giving rise to ten possible combinations. The pair combination catalytic effect of these catalysts are shown in Table 2. The MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ generally gave the highest COD value.

The effect of silver sulfate concentration on COD values in the presence of one gram each of aluminum sulfate and magnesium sulfate are reported in Table 12. Correlation of these tabular data with the ones reported in Table 9, with the exception of acetic acid, show that 20 ml of silver sulfate solution in combination with aluminum sulfate and magnesium sulfate generally gave COD values fairly comparable to the ones obtained using 70 ml of silver sulfate solution.

Tabular data reported in Table 13 for true samples taken from selective sites locations in the Houston Ship Channel and adjoining wastewaters show that the COD values obtained using the revised procedure proposed in this study are comparable to the one determined using the standard procedure.

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TABLE 1. EFFECT OF SILVER SULFATE USING MOORE METHOD FOR
DETERMINING OXYGEN CONSUMED

Compounds	Volume of Silver Sulfate Solution COD Values, mg/l (% of Recovery)							
	0	5	10	15	20	35	50	70
Acetic acid	36.0(6.8)	364(68.3)	436(81.8)	490(91.9)	528(99.0)	530(99.4)	532(99.8)	530(99.4)
Benzene	37.8(2.5)	98.0(6.4)	208(13.5)	304(19.8)	185(12.0)	83.3(5.3)	81.5(5.3)	578(37.6)
Tert-Butyl alcohol	223(34.4)	467(72.0)	542(83.6)	571(88.0)	584(90.0)	607(93.6)	616(95.0)	646(99.6)
Ethyl alcohol	346(33.2)	650(62.3)	759(72.7)	824(79.0)	887(85.0)	942(90.3)	950(91.0)	946(90.7)
Formaldehyde	308(57.8)	331(62.1)	347(65.1)	370(69.4)	312(58.5)	293(55.0)	300(56.3)	396(74.3)
3-Hydroxypyridine	844(37.1)	966(42.5)	838(36.9)	834(36.7)	954(42.0)	954(42.0)	952(41.9)	846(37.2)
Oleic acid	141(19.5)	174(24.1)	214(29.6)	289(40.0)	362(50.0)	407(56.3)	403(55.7)	407(56.3)
Pyridine	- -	10.0(0.7)	10.0(0.7)	18.0(1.2)	15.0(1.0)	27.7(1.9)	- -	- -
Sucrose	- -	559(99.6)	526(93.8)	526(93.8)	559(99.6)	556(99.1)	554(98.8)	553(98.6)
Toluene	427(27.3)	244(15.6)	262(16.7)	306(19.6)	246(15.7)	211(13.5)	185(11.8)	594(38.0)

TABLE 2. EFFECT OF DIFFERENT VOLUMES OF SULFURIC ACID ON COD* VALUES
USING 15 ml OF SILVER SULFATE CATALYST

Compounds	Volume of H ₂ SO ₄ , ml COD Values, mg/l (% of Recovery)				
	10	20	30	40	55
Acetic acid	304(57.0)	324(60.8)	352(66.0)	364(68.3)	490(91.9)
Benzene	92(6.0)	148(9.6)	360(23.4)	450(29.2)	304(19.8)
Tert-Butyl alcohol	224(34.5)	388(59.8)	396(61.1)	468(72.2)	571(88.0)
Ethyl alcohol	356(34.1)	352(33.7)	352(33.7)	360(34.5)	824(79.0)
Formaldehyde	368(69.0)	380(71.3)	372(69.8)	376(70.5)	370(69.4)
3-Hydroxypyridine	784(34.5)	788(34.7)	808(35.5)	844(37.1)	834(36.7)
Lactic acid	220(41.3)	208(39.0)	236(44.3)	256(48.0)	480(90.0)
Oleic acid	28(3.9)	36(5.0)	180(24.9)	215(29.7)	289(40.0)
Sucrose	504(89.8)	516(92.0)	524(93.4)	528(94.1)	526(93.8)
Toluene	60(3.8)	153(9.8)	380(24.3)	470(30.0)	306(19.6)

*Each COD value was calculated from triplicate determinations

TABLE 3. EFFECT OF DIFFERENT SUBSTITUTE CATALYSTS FOR SILVER
SULFATE FOR DETERMINING OXYGEN CONSUMED

Catalysts*	COD Values, mg/l (% of Recovery)					
	NONE	Ag ₂ SO ₄	MgSO ₄	MgO	Mg(NO ₃) ₂	Fe ₂ (SO ₄) ₃
<u>Compounds</u>						
Acetic acid	36.0(6.8)	520(97.5)	27.9(5.2)	27.9(5.2)	35.9(6.7)	69.7(13.1)
Benzene	37.7(2.5)	578(37.6)	74.8(4.9)	257(16.7)	121(7.9)	154(10.0)
Tert-Butyl alcohol	446(68.8)	646(99.6)	472(72.8)	444(68.5)	464(71.5)	496(76.5)
Ethyl alcohol	346(33.2)	936(89.7)	560(53.7)	571(54.7)	556(53.3)	560(53.7)
Formaldehyde	308(57.8)	396(74.3)	381(71.5)	381(71.5)	388(72.8)	369(69.2)
3-Hydroxypyridine	842(86.9)	847(87.5)	846(87.4)	852(88.0)	848(87.0)	988(102)
Oleic acid	143(19.8)	233(32.2)	246(34.0)	210(29.0)	536(74.1)	468(64.7)
Pyridine	- -	- -	- -	- -	- -	- -
Sucrose	522(98.0)	532(95.0)	540(96.0)	508(101)	- -	572(102)
Toluene	492(31.4)	596(38.1)	772(49.3)	756(48.3)	294(18.8)	282(18.0)

TABLE 3 (continued)

Catalysts	COD Values, mg/l (% of Recovery)					
	Fe ₂	MnO ₂	Al ₂ (SO ₄) ₃	CuO	ZnSO ₄	CdSO ₄
<u>Compounds</u>						
Acetic acid	43.8(8.2)	35.9(6.7)	39.8(7.5)	49.8(9.3)	8.0(1.5)	43.5(8.2)
Benzene	416(27.0)	304(19.8)	596(38.7)	79.4(5.2)	28.0(1.8)	404(26.3)
Tert-Butyl alcohol	512(78.9)	409(63.2)	627(96.7)	419(64.6)	409(63.0)	544(83.9)
Ethyl alcohol	567(54.3)	450(43.7)	600(57.5)	564(54.0)	400(38.3)	364(34.9)
Formaldehyde	360(67.7)	376(70.5)	361(67.7)	380(71.3)	374(70.2)	386(72.4)
3-Hydroxypyridine	843(87.1)	797(82.3)	840(86.7)	988(102)	826(85.3)	957(98.8)
Oleic acid	575(79.5)	274(37.9)	421(58.1)	189(26.1)	392(41.7)	333(46.0)
Pyridine	- -	- -	- -	- -	- -	- -
Sucrose	556(99.0)	368(66.4)	568(101)	- -	560(99.8)	548(97.7)
Toluene	183(11.7)	- -	132(8.4)	460(29.4)	79.0(5.0)	88.9(5.7)

*In Tables IIIa, IIIb and IIIc, seventy milliliters of Ag₂SO₄ solution or in the other cases 1 gram of the specified catalyst was used, except that only 0.1 gram of any platinum element compound was employed.

TABLE 4. EFFECT OF DIFFERENT COMBINATION CATALYSTS
FOR DETERMINING OXYGEN CONSUMED

Compounds	COD Values, mg/l (% of Recovery)			
	$\text{Fe}_2(\text{SO}_4)_3 + \text{Al}_2(\text{SO}_4)_3$	$\text{MgSO}_4 + \text{Al}_2(\text{SO}_4)_3$	$\text{MgSO}_4 + \text{Fe}_2(\text{SO}_4)_3$	$\text{MgSO}_4 + 15 \text{ ml. Ag}_2\text{SO}_4$
Acetic acid	23.8(4.5)	59.5(11.2)	71.4(13.4)	514(96.4)
Benzene	317(20.6)	460(29.9)	339(22.0)	603(39.2)
Tert-Butyl alcohol	395(60.9)	532(82.0)	442(68.1)	608(93.7)
Ethyl alcohol	325(31.1)	331(31.7)	363(34.8)	1,017(97.5)
Formaldehyde	323(60.6)	532(99.8)	385(72.2)	405(76.0)
3-Hydroxypyridine	819(84.6)	835(89.3)	887(91.6)	857(88.5)
Oleic acid	631(87.2)	675(93.3)	417(57.6)	- -
Pyridine	6.0(0.5)	29.8(2.4)	37.7(3.0)	43.6(3.4)
Sucrose	516(92.0)	552(98.4)	561(100)	181(11.6)

TABLE 4 (continued)

Compounds	COD Values*, mg/l (% of Recovery)				
	$\text{Al}_2(\text{SO}_4)_3 +$	$\text{Fe}_2(\text{SO}_4)_3 +$	$\text{MgSO}_4 + \text{Fe}_2(\text{SO}_4)_3$	$\text{Fe}_2(\text{SO}_4)_3 +$	$\text{MgSO}_4 + \text{Al}_2(\text{SO}_4)_3$
	15 ml. Ag_2SO_4	15 ml. Ag_2SO_4	15 ml. Ag_2SO_4	15 ml. Ag_2SO_4	+ 15 ml. Ag_2SO_4
Acetic acid	444(83.3)	440(82.6)	474(88.9)	476(89.3)	520(97.5)
Benzene	577(37.5)	567(36.9)	672(43.7)	469(30.5)	612(40.0)
Tert-Butyl Alcohol	573(88.3)	546(84.1)	593(91.4)	558(86.0)	624(96.2)
Ethyl Alcohol	923(88.4)	859(82.3)	913(87.5)	722(69.2)	871(83.5)
Formaldehyde	373(70.0)	371(69.6)	383(86.5)	344(64.5)	371(69.6)
3-Hydroxy- pyridine	752(77.7)	954(98.5)	838(86.5)	836(86.3)	834(86.1)
Oleic acid	- -	- -	466(64.4)	539(74.5)	352(48.7)
Pyridine	19.8(1.4)	15.9(1.1)	37.7(2.6)	38.7(2.7)	19.8(1.4)
Sucrose	- -	556(99.0)	552(98.4)	515(91.8)	555(98.9)
Toluene	143(9.1)	105(6.7)	162(10.4)	156(10.0)	120(7.7)

*In each case one gram of each catalyst plus 15 ml of Ag_2SO_4 solution was used.

TABLE 5. EFFECT OF TIME OF HEAT ON COD VALUES OF ACETIC ACID
USING THE REVISED MOORE METHOD

<u>Time, Minutes</u>				<u>Mean COD* Value, mg/l</u>	<u>% of Recovery</u>
1)	After 30 Minute Shaking			20.0	3.8
2)	Before Boiling Point			68.0	12.8
3)	5 Minute After Boiling			236	44.3
4)	10	"	"	244	45.8
5)	15	"	"	300	56.3
6)	20	"	"	316	59.3
7)	25	"	"	328	61.5
8)	30	"	"	340	63.8
9)	35	"	"	412	77.3
10)	40	"	"	448	84.0
11)	60	"	"	460	86.3
12)	80	"	"	476	89.3
13)	100	"	"	496	93.0
14)	140	"	"	504	94.5
15)	180	"	"	504	94.5
16)	220	"	"	508	95.3
17)	340	"	"	508	95.3

*Mean COD values were determined from triplicate determinations using the recommended revised Moore procedure.

TABLE 6. COMPARISON OF CERTAIN COD VALUES USING REVISED METHOD
FRIEDRICH'S CONDENSER VS. DRY-ICE CONDENSER

<u>Compound</u>	<u>Mean COD,** mg/l</u>	<u>Mean COD* Value, mg/l(%)</u>
1) Sodium Stearate***	604(44.9)	792(58.8)
2) Glutamic Acid	448(78.4)	460(80.5)
3) Isobutyric Acid	592(65.1)	888(97.7)
4) Acetic Acid	490(91.9)	500(93.8)
5) Toluene	306(19.6)	748(47.8)
6) Benzene	304(19.8)	792(51.5)

**COD values determined using a Friedrich's condenser

*COD values determined using a dry ice condenser filled with crushed ice-water mixture

***Sodium stearate's low value appears to result partially from incomplete oxidation

TABLE 7. CARBON CONTENT OF STOCK SAMPLE SOLUTIONS USING
TOTAL CARBON ANALYZER

<u>Organic Compound</u>	<u>Carbon Taken, mg/l</u>	<u>Carbon Found, mg/l</u>	<u>% Error</u>
Formaldehyde	200.0	193.9	3.1
Benzene	461.0	451.4	2.1
Toluene	456.0	448.1	1.7
Acetic Acid	200.0	192.1	4.0
Sucrose	210.5	205.7	2.3
Ethyl Alcohol	260.8	268.5	3.0
Oleic Acid	382.9	390.6	2.0
T-butyl Alcohol	324	317.8	2.0
3-Hydroxypyridine	316	308.4	2.3
Lactic Acid	200	207.0	4.0
Pyridine	380	385.2	1.5

TABLE 8. STATISTICAL ANALYSIS FOR ACETIC ACID
USING 15 ml Ag_2SO_4 + 1gr MgSO_4

Mean COD Value, Mg/l (% of Recovery)

488(91.5)
492(92.3)
492(92.3)
488(91.5)
488(91.5)
488(91.5)
488(91.5)
488(91.5)
488(91.5)
492(92.3)
488(91.5)

Mean 489

Sd. dev. ± 1.87

Coeff. of
Var. .4%

Theoretical
Value 533

% Recovery 91.7

TABLE 9. EFFECT OF SILVER SULFATE USING MOORE METHOD FOR
DETERMINING OXYGEN CONSUMED

Compounds	Volume of Silver Sulfate Solution COD Values, mg/l (% of Recovery)							
	0	5	10	15	20	35	50	70
Acetic acid	28.3(53.1)	31.5(59.1)	33.0(62.0)	35.5(66.6)	37.7(70.7)	45.6(85.5)	51.8(97.1)	52.2(98.0)
Benzene	19.4(12.6)	13.7(8.9)	12.8(8.3)	6.2(4.0)	14.0(9.1)	10.0(6.5)	75.5(49.1)	66.5(43.2)
Tert-Butyl alcohol	53.1(41.0)	60.5(46.6)	65.6(50.6)	68.3(52.7)	71.9(55.4)	74.9(57.7)	76.7(59.1)	77.4(57.7)
Ethyl alcohol	36.8(35.3)	80.8(77.4)	87.8(84.1)	98.8(88.0)	93.4(89.5)	95.8(91.8)	98.2(94.1)	98.5(94.4)
Formaldehyde	34.8(65.3)	37.0(69.4)	36.4(69.3)	31.5(59.1)	37.7(70.7)	33.0(61.9)	51.8(97.2)	47.2(88.6)
3-Hydroxypyridine	83.2(85.9)	86.6(39.1)	84.4(37.1)	90.9(93.9)	91.2(94.2)	93.3(96.3)	94.0(97.1)	89.0(91.1)
Lactic acid	44.0(82.5)	45.6(85.5)	47.6(89.3)	48.4(90.7)	49.0(92.0)	51.6(96.8)	51.8(97.1)	51.9(97.3)
Oleic acid	30.1(20.9)	13.3(9.2)	11.2(7.7)	29.2(20.2)	19.8(13.7)	46.8(32.4)	26.9(18.6)	33.9(23.4)
Pyridine	0.8(0.6)	0.8(0.6)	0.9(0.7)	1.2(0.9)	3.5(2.8)	9.2(7.2)	13.9(11.0)	14.3(11.3)
Sucrose	49.1(87.5)	53.2(94.9)	52.4(93.4)	50.1(89.3)	50.4(89.9)	50.7(90.4)	52.2(93.0)	53.6(95.5)
Toluene	53.5(34.2)	42.3(27.0)	24.0(15.3)	10.9(7.0)	12.4(7.9)	7.3(4.7)	20.8(13.3)	14.5(9.3)

TABLE 10. EFFECT OF DIFFERENT CATALYSTS ON COD VALUES
FOR DIFFERENT ORGANIC COMPOUND

Compounds	COD Values, mg/l (% of Recovery)				
	$\text{Al}_2(\text{SO}_4)_3$	CaSO_4	MgSO_4	$\text{Fe}_2(\text{SO}_4)_3$	ZrOSO_4
Acetic acid	10.0(18.8)	6.3(11.8)	8.0(15.0)	2.0(3.8)	5.2(9.8)
Benzene	20.2(13.1)	11.0(7.2)	25.5(16.6)	27.9(18.1)	12.0(7.8)
Tert-Butyl alcohol	60.6(46.7)	61.0(47.0)	59.0(45.5)	48.1(37.1)	54.0(41.6)
Ethyl alcohol	51.5(49.4)	20.5(19.6)	52.3(50.1)	48.3(46.0)	30.0(28.8)
Formaldehyde	36.0(67.4)	41.0(76.9)	35.5(65.9)	35.2(65.9)	48.0(90.0)
3-Hydroxypyridine	74.3(76.7)	97.0(100.2)	76.4(78.9)	76.0(78.5)	- -
Lactic acid	41.6(78.0)	43.0(80.6)	41.6(78.0)	25.5(47.8)	51.5(96.6)
Oleic acid	25.5(17.6)	28.0(19.4)	10.1(7.0)	39.6(27.4)	32.8(22.7)
Pyridine	0.8(0.6)	0	2.0(1.6)	.40(3.2)	5.2(4.1)
Sucrose	51.7(92.2)	- -	52.5(93.6)	51.7(92.2)	66.0(101.5)
Toluene	44.4(28.4)	33.0(21.0)	19.8(12.7)	25.1(16.0)	56.0(35.8)

TABLE 11. EFFECT OF COMBINATIONS CATALYSTS ON COD VALUES
FOR DIFFERENT ORGANIC COMPOUNDS

Compounds	COD Values, mg/l (% of Recovery)				
	$\text{Al}_2(\text{SO}_4)_3 + \text{MgSO}_4$	$\text{Al}_2(\text{SO}_4)_3 + \text{CaSO}_4$	$\text{Al}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_3$	$\text{Al}_2(\text{SO}_4)_3 + \text{ZrOSO}_4$	$\text{Fe}_2(\text{SO}_4)_3 + \text{ZrOSO}_4$
Acetic acid	29.6(55.5)	8.5(15.9)	8.4(15.8)	7.0(13.1)	9.2(17.3)
Benzene	46.8(30.4)	6.4(4.2)	17.4(11.3)	5.5(3.6)	12.0(7.8)
Tert-Butyl alcohol	79.2(61.0)	29.0(22.3)	49.6(38.2)	34.1(26.3)	74.8(57.7)
Ethyl alcohol	55.6(53.3)	31.0(29.7)	51.5(49.4)	40.5(38.8)	76.0(72.0)
Formaldehyde	42.0(78.8)	42.0(78.8)	38.8(72.8)	37.3(70.0)	55.0(103.3)
3-Hydroxypyridine	77.2(79.7)	107 (110.5)	78.0(80.5)	- -	- -
Lactic acid	45.6(85.5)	31.0(58.1)	36.4(68.3)	45.0(84.4)	55.6(104.2)
Oleic acid	31.2(21.6)	46.0(31.8)	24.8(17.2)	28.2(19.5)	54.2(37.5)
Pyridine	6.8(5.40)	3.1(2.4)	5.6(4.4)	1.4(1.1)	4.8(3.8)
Sucrose	51.2(91.3)	61.0(108.6)	56.1(100)	54.3(96.7)	- -
Toluene	50.4(32.2)	3.7(2.4)	16.4(10.5)	7.8(5.0)	38.0(24.3)

TABLE 11 (continued)

Compounds	COD Values, mg/l (% of Recovery)				
	$\text{Fe}_2(\text{SO}_4)_3 + \text{MgSO}_4$	$\text{Fe}_2(\text{SO}_4)_3 + \text{CaSO}_4$	$\text{MgSO}_4 + \text{CaSO}_4$	$\text{MgSO}_4 + \text{ZrOSO}_4$	$\text{CaSO}_4 + \text{ZrOSO}_4$
Acetic acid	7.0(13.1)	8.7(16.3)	7.5(14.0)	6.0(11.3)	12.4(23.3)
Benzene	10.5(6.8)	4.1(2.7)	5.0(3.2)	6.0(4.0)	4.3(2.8)
Tert-Butyl alcohol	49.3(38.0)	37.5(29.0)	31.3(24.1)	39.6(30.5)	31.0(24.0)
Ethyl alcohol	52.7(50.5)	36.0(34.5)	33.0(31.6)	38.0(36.4)	37.0(35.5)
Formaldehyde	33.8(63.4)	45.0(84.4)	46.0(86.3)	42.8(80.3)	33.0(62.0)
3-Hydroxypyridine	71.8(74.1)	- -	96.0(99.1)	- -	102.0(105.3)
Lactic acid	32.2(60.4)	53.0(99.4)	37.0(69.4)	40.0(75.0)	36.0(67.5)
Oleic acid	32.6(22.5)	47.0(38.9)	27.0(18.7)	23.6(16.3)	42.0(29.0)
Pyridine	5.1(4.00)	3.0(2.4)	2.0(1.6)	0	2.4(2.0)
Sucrose	14.4(25.7)	60.5(107.8)	63.0(112.2)	59.2(105.5)	58.0(103.3)
Toluene	12.4(7.9)	10.0(6.4)	8.5(5.4)	5.6(3.6)	5.1(3.2)

TABLE 12. EFFECT OF SILVER SULFATE ON COD VALUES IN THE
PRESENCE OF ALUMINUM AND MAGNESIUM SULFATES

		Volume of Silver Sulfate Solution COD Values, mg/l (% of Recovery)							
Compounds		0	5	10	15	20	35	50	70
Acetic acid	29.6(55.5)	35.6(66.8)	39.9(74.9)	44.0(82.6)	46.0(86.3)	50.1(93.9)	50.8(95.3)	51.5(96.6)	
Benzene	46.8(30.4)	41.5(27.0)	50.1(32.6)	50.4(32.8)	54.6(35.5)	66.1(43.6)	71.2(46.3)	69.9(45.4)	
Tert-Butyl alcohol	79.2(61.0)	85.0(65.5)	88.4(68.2)	91.9(71.0)	98.5(73.99)	100.1(77.2)	107.9(83.2)	109.3(84.3)	
Ethyl alcohol	55.6(53.3)	84.4(81.0)	87.1(83.5)	95.0(91.0)	94.1(90.2)	98.4(94.3)	98.4(94.3)	95.6(91.6)	
Formaldehyde	42.0(78.8)	43.1(80.9)	41.5(77.9)	41.9(98.6)	48.3(90.6)	51.7(97.0)	51.7(97.0)	52.8(99.1)	
3-Hydroxy-pyridine	77.2(79.7)	79.1(81.7)	80.3(82.9)	86.4(89.2)	86.9(89.7)	90.1(93.1)	95.0(98.1)	91.5(94.5)	
Lactic acid	45.6(85.5)	47.2(88.5)	47.0(88.1)	48.2(90.4)	49.9(93.6)	51.1(95.9)	52.5(98.4)	52.9(99.2)	
Oleic acid	31.2(21.6)	18.9(13.1)	17.4(12.0)	31.5(21.8)	27.5(19.0)	51.3(35.5)	43.1(29.8)	50.2(34.7)	
Pyridine	6.8(5.4)	7.0(5.5)	7.2(5.7)	7.5(5.9)	7.9(6.2)	8.7(7.0)	9.5(7.5)	10.7(9.5)	
Sucrose	51.2(91.3)	51.7(92.2)	52.4(93.4)	53.3(95.0)	53.8(95.4)	53.5(95.4)	54.0(96.3)	54.6(97.3)	
Toluene	50.4(32.2)	51.5(32.9)	52.8(33.7)	54.5(34.8)	58.4(37.3)	69.2(44.2)	76.7(49.0)	77.9(49.8)	

TABLE 13. THE EFFECT OF DIFFERENT CATALYST OR CATALYST COMBINATIONS ON COD FOR ACETIC ACID

<u>Catalyst</u>	<u>COD, mg/l (% of Recovery)</u>
1g $\text{Al}_2(\text{SO}_4)_3$	10.0(18.8)
1g MgSO_4	8.0(15.0)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$	29.6(55.5)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$ + 5 ml Ag_2SO_4 Solution	35.6(66.8)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$ + 10 ml Ag_2SO_4 "	39.9(74.9)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$ + 15 ml Ag_2SO_4 "	44.0(82.6)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$ + 20 ml Ag_2SO_4 "	46.0(86.3)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$ + 50 ml Ag_2SO_4 "	50.8(95.3)
1g MgSO_4 + 1g $\text{Al}_2(\text{SO}_4)_3$ + 70 ml Ag_2SO_4 "	51.5(96.6)

TABLE 14. STANDARD METHOD VS. REVISED METHOD USING
HOUSTON AREA WATER SAMPLES

Sample Site Location	Mean COD, mg/l		Revised Method Standard Method X100
	Standard Method	Revised Method	
1 - Buffalo Bayou-Franklin at U.S. Post Office	34.0	45.6	134
2 - Allen's Landing at Main	26.8	28.4	106
3 - First Southwest Downfall	20.4	58.0	284
4 - Buffalo Bayou at Eastex Freeway	30.8	49.5	161
5 - Brown & Root	32.0	34.6	108
6 - Buffalo Bayou at Lockwood	40.8	50.6	124
7 - Northside Sewage Treatment Plant	89.6	69.6	78
8 - Ship Channel Turning Basin	95.6	105.5	110
9 - 610 Bridge	116.4	144.8	124
10 - Sims Bayou at Ship Channel	99.6	120.4	121
11 - Olins Downfall #1 on Ship Channel	135.2	155.6	115
12 - Bouy #139 in Ship Channel	152.4	164.45	108
			Av. 131

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT <p>This study was made to find a catalyst to replace silver sulfate in the COD method in order to reduce the cost of the determination. The results show that comparable results to the standard method for concentration of 50-500 mg/l could be obtained using a reduced amount of silver sulfate in combination with magnesium sulfate. Another procedure is described for determining COD in the range of 5-50 mg/l using a combination of silver sulfate, aluminum sulfate and magnesium sulfate to replace silver sulfate.</p>		
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