The Science of
CHEMICAL OXYGEN DEMAND
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Contents   Page

I. INTRODUCTION

Recent advances in oxygen demand research have expanded the number of options available for testing. The purpose of this technical bluebook is to 1) provide background information on oxygen demand testing, and 2) discuss the comparative advantages of methods currently available, including the new Hach Manganese III COD Method designed to eliminate hazardous heavy metals waste.

Background on Oxygen Demand Testing

Oxygen demand is an important parameter for determining the amount of organic pollution in water. The test has its widest application in measuring waste loadings of treatment plants and in evaluating the efficiency of treatment processes. Other applications include testing lake and stream water samples for organic pollution. Oxygen demand testing does not determine the concentration of a specific substance; rather, it measures the effect of a combination of substances and conditions. Because oxygen demand is not a pollutant, it poses no direct threat to fish or other life. It can, however, pose an indirect threat to living organisms by reducing the level of dissolved oxygen.
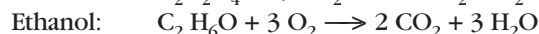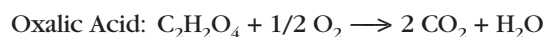
There are three widely-used methods of measuring oxygen demand. Two measure oxygen demand directly: Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). A third method—Total Organic Carbon (TOC)—measures oxygen demand indirectly.

BOD Test

Of the three test methods that determine oxygen demand (BOD, COD and TOC), the BOD test most closely models aerobic waste treatment and the aquatic ecosystem. In this test, microorganisms consume organic compounds for food while consuming oxygen at the same time. The standard BOD test measures the amount of oxygen consumed in a sample over a five-day period. Due to the length of time required to complete the test, results provide historical data only and do not facilitate rapid water quality assessment or optimal process control. The test is limited in some applications such as industrial wastewaters, which often contain heavy metal ions, cyanides, and other substances toxic to microorganisms. When microorganisms become poisoned by toxic substances, they are unable to oxidize waste, in which case the BOD test becomes an ineffective measure of organic pollution.

TOC Test

The Total Organic Carbon (TOC) test uses heat, ultraviolet light, and a strong chemical oxidant (or a combination of these three) to oxidize organic compounds to CO_2 and H_2O. Oxygen demand is measured indirectly by determining the amount of CO_2 produced using infrared spectroscopy, conductivity, or coulometry (an electrochemical technique). The test can take several minutes to several hours to complete, and information obtained from TOC analysis is less useful than information obtained from BOD and COD analysis. Also, the TOC test does not differentiate between compounds with the same number of carbon atoms in different stages of oxidation and will thus produce different oxygen demand results. Because BOD and COD tests directly measure the amount of oxygen required to stabilize a waste sample, results reflect the original oxidation state of the chemical pollutants. This is demonstrated using the following example, where two compounds with the same number of carbon atoms in different oxidation states are oxidized to CO_2 and H_2O.

Oxalic Acid: $C_2H_2O_4 + 1/2\ O_2 \longrightarrow 2\ CO_2 + H_2O$
Ethanol: $C_2H_6O + 3\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$

While TOC results are identical for both compounds, the oxygen demand of ethanol is six times greater than oxalic acid, and will thus have a much greater effect on the dissolved oxygen content of a receiving water.

COD Test

The Chemical Oxygen Demand (COD) test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO_2 and H_2O. By definition, chemical oxygen demand is "a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant."[*] Oxygen demand is determined by measuring the amount of oxidant consumed using titrimetric or photometric methods. The test is not adversely affected by toxic substances, and test data is available in 1-1/2 to 3 hours, providing faster water quality assessment and process control.

COD test results can also be used to estimate the BOD results on a given sample. An empirical relationship exists between BOD, COD and TOC. However, the specific relationship must be established for each sample. Once correlation has been established, the test is useful for monitoring and control. Table 1 compares the attributes of BOD, COD and TOC tests.

Parameter	COD	BOD	TOC
Table 1: Comparison of COD, BOD and TOC Tests			
Oxidant Used	K_2Cr_2O7 $Mn_2(SO_4)_3$	Oxidation by microorganisms	• O_2 • $K_2S_2O_8$ • Heat • Combination of the above with various catalysts
Most Suitable Use	Rapid and frequent monitoring of treatment plant efficiency and water quality	Modeling treatment plant process and the effects of organic compounds on the dissolved oxygen content of receiving waters	Measures amount of total organic carbon in samples
Test Completion Time	1-1/2 to 3 hours	5 days (for standard BOD test)	Several minutes to hours
Accuracy and Precision	5 - 10% relative standard deviation; may be higher when samples contain suspended solids; sample homogenization can be important	15% relative standard deviation; not considered highly accurate	5 - 10% relative standard deviation; may be higher when samples contain suspended solids; sample homogenization can be important
Advantages	• Correlates with BOD on waste with constant composition. • Toxic materials do not affect oxidant. • Changes in the COD value between influent and effluent may parallel BOD content and supplement BOD results • Short analysis time	• Most closely models the natural environment when used with the proper "seed"	• Correlates with BOD on waste with constant composition, but not as closely as COD • Short analysis time
Disadvantages	• Interference from chloride ions • Some organic compounds are not oxidized completely	• Toxic materials kill microorganisms • Microorganisms do not oxidize all materials present in waste • Inaccuracies when used with improper "seed" • Lengthy test period	• Requires expensive equipment • Some organic compounds are not oxidized completely • Measures Total Organic Carbon and not oxygen demand

Oxidants Used for COD Testing

Analysts have attempted to use many different oxidants in the COD test procedure. Hach laboratories have experimented with permanganate (in both acidic and basic solutions), cerate, persulfate, periodate, iodate, bromate, perbromate, hypochlorite, perchlorate, ferrate, bismuthate, hydrogen peroxide, ozone, oxygen, hydroxyl radical, vanadate, ultraviolet light, bomb colorimetry, combinations of several oxidants and electrochemical techniques. These approaches have not been suitable due to difficulties in reagent preparation, reagent stability, photosensitivity, low oxidation potential, poor oxidation efficiency, expense, and user protocols that proved too complex.

Several oxidants, however, have proven to overcome most of these difficulties. The most widely used oxidant is potassium dichromate and more recently manganese III sulfate. Table 2 summarizes the attributes of oxidants not widely used for COD testing.

Table 2: Major Oxidants Other than $K_2Cr_2O_7$ and $Mn_2(SO_4)_3$ Used in COD Determinations		
Oxidant	**Advantages**	**Disadvantages**
$KMnO_4$	• Stable for several months, MnO_2 must be excluded • Is used in acidic, neutral and basic media • Manganese is a non-hazardous metal	• Relatively slow-acting and is not quantitative • Results may depend upon sample size • Does not oxidize volatile acids or amino acids • Incomplete oxidation of many organic compounds • Unstable in solution: Forms MnO_2 precipitate which catalyzes reagent decomposition.
$Ce(SO_4)_2$	• More complete oxidation of organic compounds than $KMnO_4$ • More stable than $KMnO_4$	• Incomplete oxidation of many organic compounds • Poor reproducibility • Photometric measurement at 320 nm where incompletely oxidized organic compounds interfere • Relatively expensive
K_2S_2O	• Oxidizes many organic nitrogen-containing compounds more completely than other oxidants • Widely used with TOC instrumentation	• Requires elaborate equipment • More labor intensive • Relatively unstable
KIO_3	• Strong oxidant	• Difficult to use • Questionable accuracy
O_2	• Oxygen consumption measured directly	• Elaborate equipment required

The oxidants described in Table 2 have a number of limitations which are eliminated when $K_2Cr_2O_7$ are used as an oxidant.

II. DICHROMATE CHEMICAL OXYGEN DEMAND

Dichromate has been used to oxidize organic matter for more than 70 years. It has been preferred over other oxidants because of its superior oxidizing ability on a large variety of samples, and for its ease of use. The test measures the oxygen equivalent of the amount of organic matter oxidized by potassium dichromate in a 50% sulfuric acid solution. Generally, a silver compound is added as a catalyst to promote the oxidation of certain classes of organic compounds. A mercuric compound may be added to reduce the interference from oxidation of chloride ions.

There are two digestion methods used in the COD test: the older Macro Digestion Method, and the Micro Digestion Method. The Macro Digestion Method requires a considerable amount of space, equipment and volume of reagents for each test. Each set-up includes a flask, a glass condenser with hose, a hot plate, a laboratory stand, and clamps. Sample volumes are also relatively large. Because of these inconveniences, the macro method has been virtually replaced by the micro method. The Micro Digestion Method minimizes reagent consumption and reduces the required space and equipment to one reactor block that will digest up to 25 samples at one time. Each test set-up is a self-contained disposable vial, which is inserted into a block heater. Reagent and sample volumes are considerably smaller, which decreases reagent cost and waste volume.

The two-hour digestion time can be reduced if caution is observed. Many types of waste are digested completely in 30 minutes or less at 150 °C, the normal operating temperature. The time of complete digestion can be recognized through experience, or by using a colorimetric reading with the micro method discussed later. In this approach, many consecutive readings are taken on a single sample, allowing a final determination of when the reaction is complete.

After the oxidation step is completed, the amount of dichromate consumed is determined titrimetrically or colorimetrically. Either the amount of reduced chromium (trivalent) or the amount of unreacted dichromate (hexavalent) can be measured. End products of the reaction are carbon dioxide, water, and various states of the chromium ion.

The micro method has several advantages over the macro method, including the capture of volatile organics, small sample size, elimination of cumbersome equipment, and a reduction in the volume of expensive and hazardous reagents.

Dichromate COD Chemistry

When organic matter is oxidized by dichromate in sulfuric acid, most of the carbon is converted to CO_2. Hydrogen present is converted to H_2O. The reaction is illustrated using the primary standard, potassium acid phthalate (KHP), as an example:

$$2\ KC_8H_5O_4 + 10\ K_2Cr_2O_7 + 41\ H_2SO_4 \longrightarrow$$
$$16\ CO_2 + 46\ H_2O + 10\ Cr_2(SO_4)_3 + 11\ K_2SO_4$$
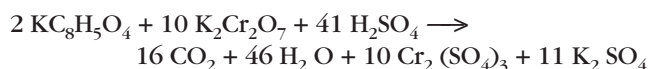
Dichromate ions ($Cr_2O_7^{-2}$) form orange-colored solutions. When dichromate is reduced to chromic ion (Cr^{+3}), the solution becomes green. Intermediate valence states may also occur. The standard reduction potential, E° (25 °C vs. Normal Hydrogen Electrode, pH = 0) is about 1.36 volts. The actual potential will vary with temperature, pH, and the ratio of dichromate to chromic ion concentrations according to the following equation:

$$E = E° + \frac{0.0001983\ T}{6}\ \log\ \frac{[H^+]\ [Cr_2O_7^{2-}]}{[Cr^{+3}]^2}$$

Precision and Accuracy

A number of samples have been tested using Hach's High Range, Low Range, and Ultra Low Range Dichromate COD vials. Results are given in Table 3 below.

	Table 3: Dichromate COD Precision and Accuracy			
Sample	Dichromate COD mg/L	Standard Deviation mg/L	Relative Standard Deviation %	Number of Tests n
500 mg/L COD	500[1]	1.7	0.3	3
500 mg/L COD + 500 mg/L Chloride	508[1]	1.0	0.1	3
Wastewater Influent	245[1]	6	2.4	5
Wastewater Effluent	45[2]	4.7	2.6	5
Textile Industry	176[1]	4.6	2.6	5
ASTM Synthetic Wastewater Sample	1018[1]	14	1.3	3
Swimming Pool	13[3]	0.6	4.6	3

[1]Hach High Range Dichromate COD Vial
[2]Hach Low Range Dichromate COD Vial
[3]Hach Ultra Low Range Dichromate COD Vial

Pros and Cons of Dichromate

Pros
- Dichromate accomplishes a complete oxidation when used with a catalyst and a two-hour digestion period.
- Dichromate is stable at room temperature when protected from exposure to light.

Cons
- Some organic compounds are only partially oxidized.
- Some organic compounds, such as pyridine, are not oxidized.
- There can be interference from inorganic pollutants, mainly chloride ions.
- Reaction temperature is limited by thermal decomposition of the oxidant.
- Dichromate is classified as a carcinogen.

Improving the Dichromate COD Test

Through careful research, many of the disadvantages to the COD test have been overcome or reduced in significance. Incomplete oxidation of aliphatic hydrocarbons, organic acids or alcohols have been improved by using silver ion as a catalyst. Some compounds are not oxidized even with the catalyst. Disposal considerations play an increasingly important role in chemical testing. Although the micro method minimizes the volume of waste generated, the dichromate COD does contain hexavalent chromium, which must be treated as hazardous wastes and mercury.

III. MANGANESE III REAGENT DEVELOPMENT AND CHEMISTRY

A newly developed COD test using Mn III COD oxidizes organic compounds in water without the disposal problems associated with the other method. The chemistry behind the Manganese III COD is unique and not widely known. The following paragraphs discuss the various facets and challenges presented by Mn III chemistry and the process which led to the successful development of the Manganese III COD reagent for wastewater analysis.

Manganese III salts participate in a number of complex chemical equilibria which are largely dependent on acid type and strength. Metastable solutions have been prepared containing up to 40 g/L Mn III. These solutions do not reach equilibrium for several weeks to several months. At equilibrium, the maximum reported level is about 1.6 g/L Mn III in 11 N H_2SO_4 (saturated with $MnSO_4$). Initial experiments with the reagent contained up to 1.1 g/L Mn III.

After several weeks, purple, planar, diamond-shaped crystals were formed. The crystals have been identified as manganosulfuric acid, $H_2[Mn_2(SO_4)_4] \bullet 8 H_2O$. Over time the percentage of vials observed with crystals increased dramatically. The reagent was heated in a reactor block at 150 °C in an attempt to dissolve the crystals which had formed. Reconstitution of the reagent was incomplete, requiring the reformulation of the reagent using a lower concentration of manganese III. The suitability of Mn III for use as a COD test reagent is dependent upon the ability to stabilize Mn III at a concentration high enough to oxidize organic compounds and provide a useful test range.

The solubility of Mn III in sulfuric acid is optimal at a normality of 11. However, for effective oxidation of organic compounds, the normality should be above 12. As the acid strength increases above 11 N, the solubility of Mn III decreases. The optimum reagent composition must balance these two factors: manganese III solubility and reagent acid strength.

The Manganese III COD reagent is stabilized by complex-ation in sulfuric acid solution where there are several possible Mn III complexes. The predominant species in 11 N H_2SO_4 are $Mn_2(SO_4)_3$ and two hydrated species, $[Mn(H_2O)_5HSO_4]^{2+}$ and $[Mn(H_2O)_5(HSO_4)_2]^+$.

Reagent stability is also affected by the disproportionation reaction as shown below.

$$2 Mn^{3+} \longleftrightarrow Mn^{4+} + Mn^{2+}$$

The addition of excess Mn II provides additional stability by forcing the above equilibrium towards Mn III. Consideration must also be given to the decrease in the oxidation potential of the Mn III/Mn II couple due to excess Mn II.

Once reagent strength and stability are determined, reagent and sample volumes can be adjusted. Consideration must be made for optimum sample volume, reagent dilution, and the desired test range.

Reagent Preparation

Reagent preparation methods can be divided into three groups: methods based on chemical oxidation of Mn II; methods based on electrochemical oxidation of Manganese II; and methods based upon dissolution of solid Mn III. In our laboratories, the most frequently used method for laboratory-scale preparations has been the oxidation of manganous sulfate with potassium permanganate, as described by the following equation:

$$2 KMnO_4 + 8 MnSO_4 + 8 H_2SO_4 \longrightarrow$$
$$5 Mn_2(SO_4)_3 + K_2SO_4 + 8 H_2O$$
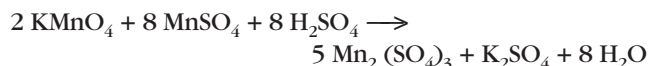
The Manganese III COD solution has a broad absorption band in the region of 420 to 600 nm, with a maximum absorbance at 510 nm. For comparison, potassium per-manganate is an oxidant that has a visual appearance somewhat similar to the Manganese III COD. Both solutions are purple in color, but the spectra are quite different. See Figure 1.
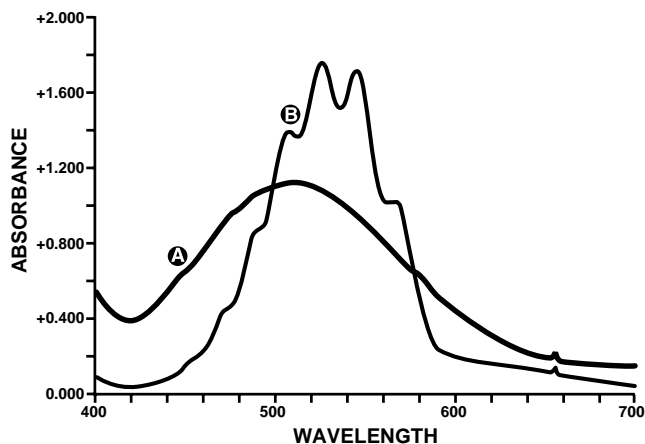
Figure 1.
A: Mn III Reagent blank solution, approximately 0.008 N Mn III
B: Potassium Permanganate solution, approximately 0.001 N, in deionized water.

The Mn III COD Reagent calibration is linear over the range from 0 to 1000 mg/L COD. The working range of the test is 20 to 1000 mg/L COD. The calibration slope is negative. (See the calibration graph in Figure 2.) The reagent has an oxidation efficiency of about 80% for standards prepared from KHP and for typical wastewater samples. When standards and samples have the same oxidation efficiencies, the sample COD recoveries will be 100%. When samples contain components not oxidized to the same extent as KHP, standards can be prepared from reference materials which more closely match the sample. No oxygen demand test will oxidize all organic compounds with 100% efficiency. An alternate approach for difficult-to-oxidize samples is to

Figure 2.
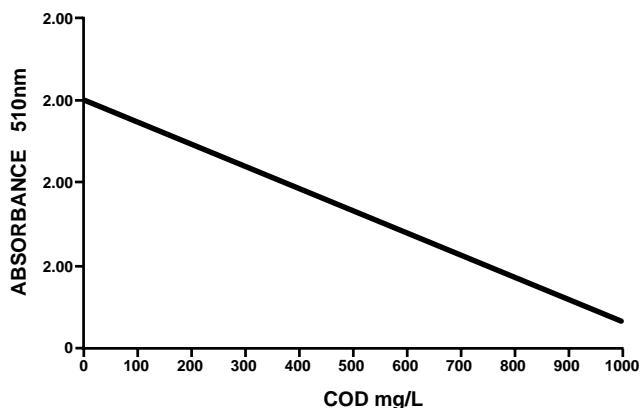**Maganese III COD Reagent Calibration, Hach DR/3000 at a wavelength of 510 nm and using a Hach Mn III COD Reagent vial as the sample cell (path length = 13.5 mm). The slope is -0.0013 Abs/mg/L; the x-axis intercept is 1185 mg/L; and the correlation coefficient is 0.9997.**

increase the digestion time (which can be extended up to 4 hours), so long as a blank is also digested for the same period of time.

The reaction occurring in the Mn III COD reagent vial is best represented by the following equation, where the reagent is reacted with KHP:

$$2\ KC_8H_5O_4 + 30\ Mn_2(SO_4)_3 + 24\ H_2O \longrightarrow$$
$$16\ CO_2 + 60\ MnSO_4 + 28\ H_2SO_4 + 2\ KHSO_4$$
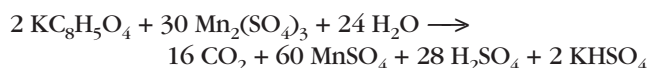
Precision and Accuracy

A number of samples have been tested and the precision and accuracy of these results determined. Table 4 contains representative sample results. The 800 mg/L COD standard was tested using the Mn III COD procedure without chloride removal, while the remaining samples were tested using the Mn III COD with the chloride removal procedure.

| Table 4: Precision of Mn III COD Test				
Sample	Mn III COD mg/L	Standard Deviation mg/L	Relative Standard Deviation %	Number of Tests *n*
800 mg/L COD	797	13	1.6	7
500 mg/L COD + 500 mg/L Chloride	508	3	0.6	4
ASTM Wastewater Influent Reference	1008	7	0.7	4
Wastewater Influent	463	13	2.8	3

Comparative Advantages
- The one-hour digestion period is shorter than other methods.
- Correlates very well with Dichromate COD and BOD test results.
- Is not photosensitive.
- Is stable at room temperature.
- The reagent contains no hazardous metals and generates no hazardous metal waste.

There are three factors that should be noted about the Manganese III COD Procedure. It oxidizes approximately 80% oxidation of most organic compounds. There is interference from some inorganic compounds, mainly chloride ions. And the reaction temperature is limited by thermal decomposition of the oxidant.

IV. THEORETICAL OXYGEN DEMAND AND COD TEST CALIBRATION

Theoretical Oxygen Demand of Potassium Acid Phthalate (KHP) - The Industry Standard
COD testing is based upon the theoretical amount of oxygen required to oxidize organic compounds to CO_2 and H_2O. The most commonly used standard is potassium hydrogen phthalate (KHP). The theoretical oxygen demand of KHP is stated by the following equation:

$$KC_8H_5O_4 + 7.5\ O_2 \longrightarrow 8\ CO_2 + 2\ H_2O + KOH$$
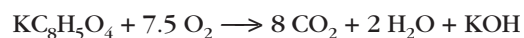
Seven and one-half molecules of oxygen consume one molecule of KHP. On a weight basis, the theoretical oxygen demand for KHP is 1.175 mg O_2 per mg KHP. To prepare a 2000 mg/L stock COD standard solution from KHP, the standard concentration is divided by the theoretical oxygen demand, resulting in the amount of KHP to be dissolved in one liter of deionized water. The equation below demonstrates this for a 2000 mg/L COD standard solution.

$$\frac{2000\ mg/L\ COD\ (O_2)}{1.175\ mg\ O_2\ /\ mg\ KHP} = 1,702\ mg\ KHP/L$$

Additional standards can be made by preparing serial dilutions of this stock solution. Test results are expressed as mg/L COD or mg/L O_2. These expressions are equivalent.

Calibrations based upon reference materials other than KHP
Occasionally, samples contain a major sample component which is incompletely oxidized, and results will be lower than expected. It may be beneficial for COD results to closely match the theoretical oxygen demand of the sample. In this situation, calibration standards can be prepared from that sample component. For example: An industrial wastewater sample contains acetone as a major sample component and acetone is incompletely oxidized.

To obtain better results on this sample, a calibration curve can be prepared using acetone as the reference material. To prepare the standard solution, first calculate the theoretical oxygen demand of acetone.

$$C_3H_6O + 4\,O_2 \longrightarrow 3\,CO_2 + 3\,H_2O$$
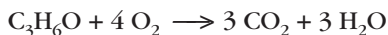
Four molecules of oxygen consume one molecule of acetone and, on a weight basis, the theoretical oxygen demand for acetone is calculated as follows:

$$\frac{4\,(32\ mg/mM\ O_2)}{58\ mg\ /\ mM\ acetone} = \frac{2.21\ mg\ O_2}{mg\ acetone}$$

A 1000 mg/L COD standard can be prepared from acetone as follows:

$$\frac{1000\ mg/L\ COD}{2.21\ mg\ O_2\ /\ mg\ acetone} = 452.5\ \ mg\ acetone\ /L$$

Serial dilutions can be made for additional standards.

Theoretical Oxygen Demand of Nitrogen-Containing Compounds

Most nitrogen-containing compounds yield nitrogen as ammonia after oxidation. This includes heterocyclic nitrogen-containing compounds, and is demonstrated using pyrrole in the example below:

$$C_4H_5N + 4\text{-}1/2\,O_2 \longrightarrow 4\,CO_2 + H_2O + NH_3$$
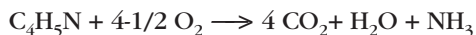
Four and one half molecules of oxygen consume one molecule of pyrrole. On a weight basis, the theoretical oxygen demand for pyrrole is 2.149 mg O_2 per mg pyrrole.

Heterocyclic compounds containing two or more atoms of nitrogen in a molecule are also easily oxidized. Generally, part of the nitrogen is split off as ammonia and part is split off as diatomic nitrogen. This is demonstrated using Imidazole in the following example:

$$C_3H_4N_2 + 3\,1/4\,O_2 \longrightarrow 3\,CO_2 + 1/2\ \ H_2O + NH_3 + N_2$$

Three and one quarter molecules of oxygen consume one molecule of imidazole. On a weight basis, the theoretical oxygen demand for imidazole is 1.507 mg O_2 per mg imidazole.

Oxidation Efficiency of Organic Compounds

The oxidation efficiency for a given organic compound can be easily determined. A COD standard is prepared from the compound of interest and is tested. The result of the test is then divided by the standard value and multiplied by 100 to determine the percent recovery or oxidation efficiency.

The dichromate COD procedure will oxidize most organic compounds with 90 - 100% efficiency. However, some compounds are not oxidized and others are only partially oxidized, such as benzene, toluene, and ethylamines. Examples of compounds that resist oxidation are pyridine, pyridine derivatives and methylamines.

V. CATALYSTS

Straight-chain aliphatic compounds are not effectively oxidized without a catalyst. Several metals that have multiple valence states are generally effective as a catalyst with dichromate. Silver, manganese, mercury, nickel, iron, cobalt and copper have all demonstrated catalytic activity. Silver is the most effective catalyst for the greatest variety of organic compounds, and manganese is reported to have a catalytic activity comparable to silver on some compounds.

The catalytic activity of silver is diminished through the formation of insoluble silver halides when halides are present. These precipitates are partially oxidized, but there is a significant loss of free silver ion which must be available for catalytic activity. When sample chloride is complexed with mercury or removed through other techniques, silver will be an effective catalyst.

Catalysts have not produced significant improvement in recoveries of Manganese III COD and also increase reagent cost. High silver concentrations increase recoveries partially, but not significantly, and disposal problems increase.

VI. INTERFERENCES

Reduced inorganic materials may be oxidized by the COD reagent and constitute a positive interference when present in significant amounts.

Chloride is the most common interference and has the greatest effect on test results. The theoretical oxygen demand of chloride is expressed by the following equation:

$$4\,Cl^- + O_2 + 4\,H^+ \longrightarrow 2\,H_2O + 2\,Cl_2$$
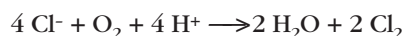
One molecule of oxygen consumes 4 molecules of chloride ions. On a weight basis, the theoretical oxygen demand for chloride is 0.226 mg O_2 per mg Cl^-. A sample containing 1000 mg/L chloride will have a theoretical oxygen demand of 226 mg/L COD. Pure chloride solutions are oxidized quantitatively by COD reagents which do not contain a silver catalyst or a chloride masking agent. Silver ions partially mask chloride ions through the formation of insoluble silver chloride. This results in erratic oxidation of chloride and diminishes the ability of silver to function as a catalyst. When organic matter and chloride are both present in a sample, the oxidation of chloride may also be erratic. This is why the technique of determining the chloride concentration by a separate technique and adjusting the COD result does not always provide accurate results.

When chloride is present with high concentrations of ammonia, organic amines, or nitrogenous matter, the interference is severe. This is due to a series of cyclic changes from chlorine to chloride through the formation of chloramine intermediates. Ammonia, organic amines,

or nitrogenous matter do not interfere when chloride is absent. Organic amines and nitrogenous matter are a source of ammonia nitrogen after oxidation by the COD reagent. The easiest remedy to this problem is to remove sample chloride.

Mercuric sulfate is the most widely used reagent for masking chloride interference and is most effective when the ratio of mercuric sulfate to chloride is 10:1. For example, a 2 mL sample containing 2000 mg/L chloride (4 mg Cl⁻) will require 40 mg mercuric sulfate to effectively mask the chloride interference. In some instances, mercuric sulfate may not mask chloride well enough to prevent the combined interference of chloride and high concentrations of ammonia or other nitrogenous compounds. This occurs more often in strong dichromate solutions (high range reagents). One solution to this problem is to dilute the sample to a level where it can be tested using a weaker dichromate solution (low range reagent). The combined interference will usually not be observed with the lower-strength reagent.

Hach Dichromate COD Reagents contain enough mercuric sulfate to eliminate the interference up to 2000 mg/L chloride. The Ultra High Range COD Procedure will eliminate up to 20,000 mg/L chloride, because the sample size used is 0.20 mL rather than the standard 2.00 mL.

When samples do not contain a significant amount of chloride, it is not necessary for the COD reagent to contain mercuric sulfate. Hach's Dichromate COD2 Reagent vials do not contain mercuric sulfate and can be used for this sample type.

Mercury is very toxic and disposal usually is not a legal option. The only legal method for waste mercury handling is recycling, which can be expensive.

A recent technique for chloride removal was developed in conjunction with the Manganese III COD reagent. The sample is pretreated to remove chloride using a Chloride Removal Cartridge. A Vacuum Pretreatment Device (VPD) controls sample flow rate (see photo). An acidified sample is transferred to the Chloride Removal Cartridge, where a vacuum draws the sample through a glass fiber filter, then through a chloride removal reagent bed, and into a Manganese III COD vial. The filter captures any suspended solids that may be present in the sample. These solids often contain oxidizable organic material and must be returned to the COD vial. Also, if suspended solids are allowed into the reagent reservoir, they will interfere with chloride removal. The reagent bed contains the solid, non-water soluble oxidant, sodium bismuthate. Chloride removal is optimized through the Chloride Removal Cartridge system, while minimizing any effect the oxidant may have on other sample components. The Chloride Removal Cartridge system will remove up to 1000 mg/L chloride.

Vacuum Pretreatment Device

Chloride Removal Cartridge

An historical method for chloride removal is the addition of a reagent to precipitate chloride. This precipitate is separated from the solution by settling, centrifuging or filtration, and a sample aliquot is taken for testing. While chloride is effectively removed from the sample, suspended solids are also removed. These solids often contain oxidizable organic material. The resulting COD is some fraction of the total and is referred to as soluble COD. The most common reagent used for precipitation of chloride is a silver salt.

Nitrite nitrogen interferes with the test and has a theoretical oxygen demand of 1.1 mg O_2 per mg NO_2 - N. Concentrations rarely exceed 1 to 2 mg/L and the interference is considered insignificant. When NO_2 - N concentrations are present at higher levels, the interference can be eliminated by the addition of 10 mg sulfamic acid per mg NO_2 - N. A separate blank must also be prepared containing the same concentration of sulfamic acid.

Other reduced species such as sulfide, or ferrous iron, are usually not present in significant amounts. If necessary, a correction can be made for these interferences. After determining the species concentration using a separate method, there are several ways to make corrections: 1) Determine the theoretical oxygen demand of the species and apply a mathematical correction to the COD result; 2) Prepare a standard from the species of interest, perform a COD test on the standard, and apply a mathematical correction to the result; 3) Spike the sample with the interfering species, perform a COD test on this sample, and apply a mathematical correction to the COD result.

VII. COMPARATIVE STUDIES OF COD TEST RESULTS

Comparison of Mn III COD and Dichromate COD Tests

Wastewater samples were tested using both the dichromate and Mn III COD procedures.
Sample data is presented in Table 5.

Sample	Sample	Manganese III COD mg/L	Dichromate COD mg/L	Ratio Mn III COD/ Cr COD
WWTP Influent #1	1	428	488	0.88
WWTP Influent #2	1	463	510	0.91
Industrial Influent #1	1	153	169	0.90
Industrial Influent #2	1	234	248	0.94
Industrial Influent #3	1	220	250	0.88
WWTP Influent #3	Day 1	345	523	0.66
	Day 2	316	496	0.64
	Day 3	312	512	0.61
	Day 4	334	443	0.75
	Day 5	344	501	0.69
	Day 6	349	468	0.75
WWTP Effluent #3	Day 1	56	62	0.90
	Day 2	64	63	1.02
	Day 3	62	51	1.22
	Day 4	55	57	0.96
	Day 5	58	63	0.92
	Day 6	59	62	0.95
WWTP Influent #4	Day 1	365	452	0.81
	Day 2	411	553	0.74
	Day 3	406	515	0.79
	Day 4	280	400	0.70
	Day 5	346	478	0.72
	Day 6	348	457	0.76
	Day 7	374	482	0.78
WWTP Effluent #4	Day 1	11*	41	N/A
	Day 2	13*	43	N/A
	Day 3	6*	10	N/A
	Day 4	5*	29	N/A
	Day 5	6*	31	N/A
	Day 6	27	38	0.71
	Day 7	31	35	0.88
Paper Mill Effluent	Day 1	437	465	0.94
	Day 2	421	450	0.94
	Day 3	444	457	0.97
	Day 4	430	444	0.97
	Day 5	429	412	1.04
	Day 6	414	438	0.95
Paper Mill Clarifier Samples	Day 1	881	913	0.96
	Day 2	931	1110	0.84
	Day 3	1174	1268	0.93
	Day 4	775	856	0.91
	Day 5	900	906	0.99
	Day 6	996	1052	0.95

*This data is below the valid test range of the Mn III COD. It is reported here for consistency.

Correlation of the Mn III COD and BOD Tests

An empirical relationship exists between COD and BOD, but the correlation must be established for a specific sample. Once this correlation has been done, COD test results can be used to estimate BOD test results, BOD test dilutions, and BOD performance in the plant. In Table 6 below, Mn III COD (with chloride removal) results are used to estimate BOD test results. The estimated BOD test results are compared to actual BOD test data.

Table 6: Comparison Between Estimated BOD (from COD results) and Actual BOD Test Data			
Sample	**Mn III COD Result mg/L**	**Estimated BOD Result mg/L**	**Actual BOD Result mg/L**
Influent #1 - Day 1	365	199	207
Influent #1 - Day 2	411	209	206
Influent #1 - Day 3	406	208	236
Influent #1 - Day 4	280	181	203
Influent #1 - Day 5	346	195	192
Influent #1 - Day 6	348	196	149
Influent #1 - Day 7	374	201	198

Effluent #1 - Day 1	11*	10	11
Effluent #1 - Day 2	11*	13	10
Effluent #1 - Day 3	6*	10	9
Effluent #1 - Day 4	5*	10	10
Effluent #1 - Day 5	6*	10	11
Effluent #1 - Day 6	27	9	8
Effluent #1 - Day 7	31	8	9

Influent #2 - Day 1	345	210	174
Influent #2 - Day 2	316	193	200
Influent #2 - Day 3	312	190	214
Influent #2 - Day 4	334	204	189
Influent #2 - Day 5	344	210	272
Influent #2 - Day 6	349	213	171

Effluent #2 - Day 1	56	15	13
Effluent #2 - Day 2	64	17	14
Effluent #2 - Day 3	62	16	16
Effluent #2 - Day 4	55	14	13
Effluent #2 - Day 5	58	15	18
Effluent #2 - Day 6	59	15	17

*This data is below the valid Mn III COD test range; however, a reasonable BOD test estimate was obtained.

COD Results on Selected Synthetic Organic Compounds

Synthetic compounds were used to prepare standard solutions of known theoretical oxygen demand. The solutions were tested using the dichromate COD and Mn III COD (without chloride removal) test procedures . Five replicates were tested on each compound using each COD procedure. Results are presented in Table 7 below.

Sample	Theoretical COD mg/L	Manganese III COD		Dichromate COD	
		Result mg/L	Std. Deviation	Result mg/L	Std. Deviation
Glycine	500	458	15	512	2
Glucose	500	517	10	495	3
Glutamic Acid	500	418	7	475	2
Dextrin	500	483	6	477	2
Nicotinic Acid	500	10	3	60	3
Tannic Acid	500	422	9	442	1
Acetic Acid	500	122	9	491	2
Lauryl Sulfate Sodium Salt	500	495	6	488	2
Benzoquinone	500	445	3	485	2
Humic Acids Sodium Salt*	100	97	9	104	2

Table 7:
COD Results on Synthetic Compounds

*Estimated theoretical oxygen demand of 1 mg O_2 per mg Humic Acids

VIII. CHEMICAL OXYGEN DEMAND PROCEDURES

Sample Handling and Preservation

Samples must be representative of the environment or treatment process of interest. Collect samples in clean glass bottles or plastic bottles known to be free of contamination. Biologically active samples should be tested as soon as possible. When settleable or suspended solids are present, the sample should be homogenized prior to testing. Homogenization reduces the size of solids and creates a more uniform sample solution. It may also be helpful to stir the sample, using a magnetic stir plate and stir bar, while taking sample aliquots for analysis. Some loss of volatile sample components may occur during homogenization, but in most samples this is insignificant. The benefits of testing a homogenous sample are significant. Homogenization should be done prior to acid preservation. If this is not possible, necessary safety precautions should be taken. Samples not immediately tested should be preserved with concentrated sulfuric acid to a pH of 2 or less. This will require about 2 mL of concentrated sulfuric acid per liter of sample. Acid-preserved samples are stable for up to 28 days when refrigerated at 4 °C. When the sample COD exceeds the range of the COD procedure used, run the test with COD vials of the appropriate range or dilute the sample into the range of the test. Dilution water should be high quality deionized water free of organic compounds. Dilution water quality becomes increasingly important at lower COD concentrations.

DIGESTION PROCEDURES

There are two COD digestion procedures: the micro digestion method and the macro digestion method. The macro digestion procedure requires large volumes of reagent, bulky glassware, and considerably more space for sample digestion. Because the classic technique is described in other sources, it will not be discussed further here.

COD reagents contain strong oxidants (hexavalent chromium, manganese III sulfate) in strong sulfuric acid solution. During the course of digestion, these reagents oxidize organic carbon compounds to CO_2 and H_2O.
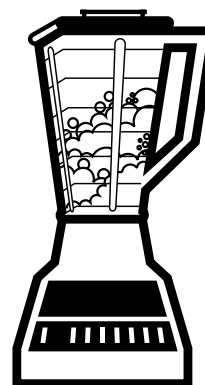
The Micro COD Digestion

Apparatus used in the micro digestion method consists of a COD Reactor with a 25-vial capacity. A typical COD reactor is shown in Figure 3. Using this digestion technique, it is possible to test 25 samples while using a minimum of laboratory bench space. The Hach COD Reactor will maintain a temperature of 150 ± 2 °C, which is more accurate than most laboratory ovens. Hach Company strongly recommends that digestions be performed only in the COD reactor. Please note that, "Severe damage of most culture tube closures from oven digestion introduces a potential source of contamination and increases the probability of leakage. Use an oven for culture-tube digestion only when it has been determined that 2-hour exposure at 150 °C will not damage caps."* Caps on Hach COD Reagent vials are specially designed to provide a positive seal when used in the COD Reactor. They will not withstand temperatures above 120 °C, which will be present if an oven is used for digestion. The caps reach a temperature of about 85 °C when used with the COD Reactor, even though the digestion mixture maintains 150 °C. This temperature difference provides the refluxing action necessary for the recovery of volatile organics.

Micro digestion has the following advantages:

- Small reagent volumes mean lower cost for reagent disposal.
- Recovery of volatile compounds is uniform and higher because of the closed container.
- Prepared vials are easy to handle and take a minimum of time to use.

FIGURE 3.
Hach COD Reactor

- Digestion requires minimum space and equipment.
- Requires less analyst attention.
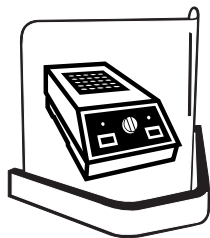
Micro Digestion Method

1. Turn on the COD Reactor and preheat to 150 °C.

2. Homogenize 100 ml of sample for 30 seconds in a blender.

3. Remove the cap of a COD Reagent vial and transfer the appropriate amount of sample into the vial.

The Dichromate Ultra Low Range, Low Range, and High Range COD products require 2.00 mL of sample. The Dichromate High Range Plus COD requires 0.20 mL and the Manganese III COD reagent uses 0.50 mL of sample (0.60 mL with the Chloride Removal Cartridge).

4. Replace the vial cap tightly. Hold the vial by the cap and invert several times over a sink to mix. (CAUTION! Dichromate COD vials will become very hot during mixing.)

5. Place the vials into the pre-heated COD Reactor. Heat the vials for 1 hour (Mn III COD Reagent) or 2 hours (Dichromate COD Reagents).

6. Remove the vials from the reactor and cool to room temperature.

7. Determine COD results either colorimetrically or by titration.

Note: See the Dichromate COD or Manganese III COD Procedures for specific details pertaining to the digestion procedure.

Safety Notes for the Micro Digestion Method

The micro digestion method is relatively safe for the following reasons:

- Small quantities of reagent are used.
- The apparatus is compact and durable.
- Pipetting and measurement of hazardous reagents has been eliminated.
- The Hach COD Reactor is safety-fused to shut down at 180 °C. This will ensure that sample and reagent will not overheat.
- The reacted sample is measured directly in the COD vial, eliminating the need for sample/reagent transfer.

As with any procedure involving chemical analysis, the analyst should observe certain precautions when using the micro digestion method:

- Use the exact volume of sample called for in the procedure. A larger sample will dilute the acid concentration and lower the boiling point in the mixture. This will increase the pressure in the vial and may cause it to burst or leak. The vials have been tested using pure water at 185 °C (about 20 to 30 times greater pressure than the normal reaction mixture) for seven hours without damage, but they cannot be guaranteed as pressure vessels.
- Place a safety shield in front of the reactor while heating the vials. In the unlikely event of vial breakage, this precaution will minimize any resulting hazard.
- **WEAR SAFETY GLASSES OR GOGGLES.** When mixing the sample and reagent, hold the vial away from the face and body. A great deal of heat is generated, which can crack even borosilicate glass in some instances.

*Standard Methods for the Examination of Water and Wastewater, 15th Edition, p5-14

14

COLORIMETRIC DETERMINATION
Procedures for COD measurement

The measurement of COD test results is done using colorimetric and titrimetric procedures. Colorimetric procedures are easier and quicker to run and are generally more accurate. However, when samples are turbid or colored, or if a spectrophotometer is not available, a titrimetric procedure should be used. Titrimetric procedures require a higher degree of operator skill and take longer to perform.

Colorimetric Procedures

The micro COD test vial used for this digestion also serves as a cuvette for colorimetric measurement. Use with a test tube adapter in a Hach spectrophotometer or other comparable model. Tests have shown that the optical properties of COD vials are very good. The variation in vial absorbance from batch to batch is less than 0.004 units. A Hach DR/4000 and test tube adapter are shown in Figure 4.
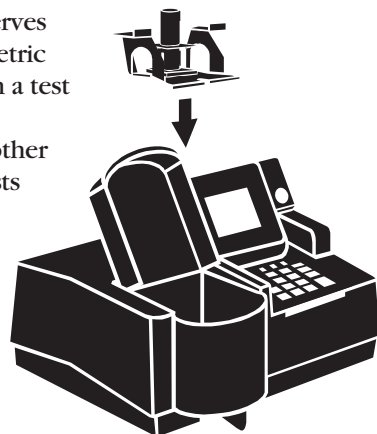
**Figure 4.
Hach DR/4000 and Test Tube Adapter**

Colorimetric measurements allow the digestion to be monitored periodically for completeness. This means that easy-to-digest samples can be analyzed with confidence in a short period of time. Typical time study curves are shown in Figure 5. They clearly demonstrate that COD determinations made for process control purposes can be conducted in a shorter digestion time than specified in the procedure. For samples which are difficult to oxidize, the digestion time can be extended up to four hours if a blank is also run for the same period of time.
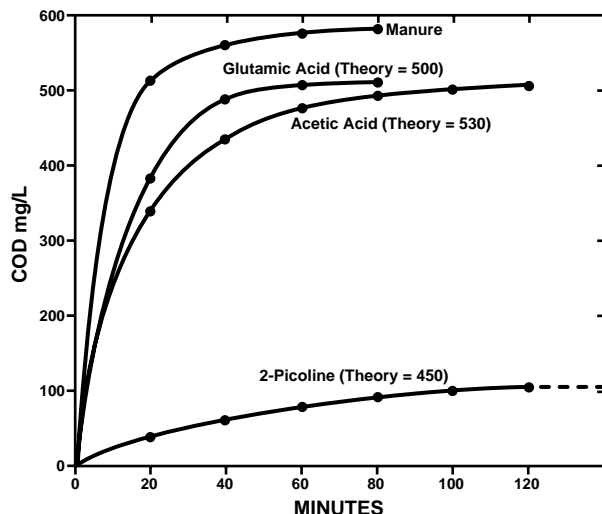
A reagent blank must be prepared from each new lot of vials. This is done by carrying a sample of high-purity deionized water through the digestion process. The blank is used to zero the spectrophotometer and can be reused until a new lot of reagent is introduced. It must, however, be monitored for degradation. To monitor the blank, fill a clean, empty COD vial with 5 mL of deionized water. Set the instrument to absorbance mode and the appropriate wavelength. Zero the instrument with the deionized water blank and measure the reagent blank absorbance. When the absorbance changes by approximately 0.010 from its initial value, a new blank must be run. Dichromate COD Reagent blanks are photosensitive and must be stored in the dark. Manganese III COD Reagent blanks are not photosensitive.

Hach provides Dichromate COD vials in four ranges, Ultra Low Range (0-40 mg/L), Low Range (0-150 mg/L), High Range (0-1500 mg/L), and High Range Plus (0-15,000 mg/L). The Manganese III COD is available in the 20-1000 mg/L range.

Dichromate COD Tests
Colorimetric Measurement for the
Ultra Low Range COD (0-40 mg/L Range)
(Using a Hach DR/4000)

The Hach Ultra Low Range COD test is the lowest range and highest sensitivity COD test available. Results are measured at a wavelength of 350 nm. The maximum sensitivity is at 345 nm, but the test measurement is made at 350 nm for instrumentation considerations. The calibration line for this test has a negative slope. The amount of hexavalent chromium remaining after digestion is measured and it decreases as the COD concentration increases. High quality, organic-free, deionized water is required for blanks and dilution water with this test range. Figure 6 shows several scan overlays of COD standards at various concentrations tested.
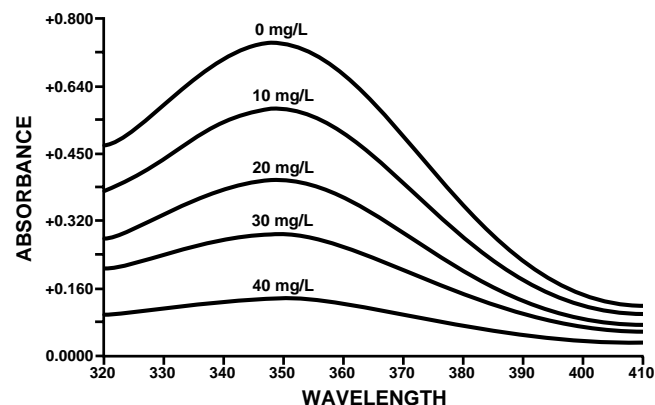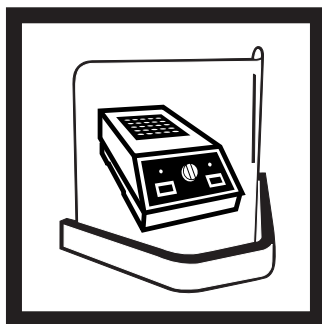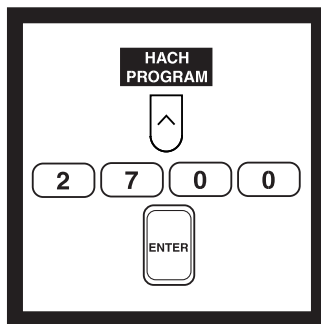
Figure 6. Ultra Low Range COD scan using standards at 0, 10, 20, 30, 40 mg/L COD.

Figure 5. Typical Digestion Curves - COD vs. Time

Colorimetric Measurement for the Ultra Low Range COD Test (0-40 mg/L)
An example of a completely illustrated, easy-to-follow procedure from Hach.

1. Perform the digestion according to given instructions.

2. Press the soft key under HACH PROGRAM. Select the stored program number for ultra low range COD by pressing 2700 with the numeric keys.
Press: ENTER

3. The display will show: HACH PROGRAM: 2700 COD, ULR. The wavelength (λ), 350 nm, is automatically selected.

4. Insert the Test Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

5. Clean the outside of the blank with a towel.

6. Place the blank into the adapter with the Hach logo facing the front of the instrument. Close the light shield.
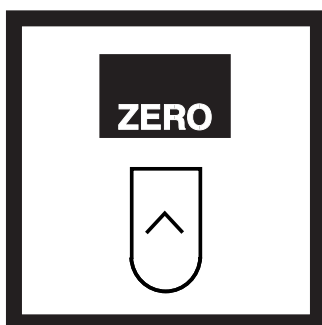
7. Press the soft key under ZERO. The display will show: 0.0 mg/L COD.

8. Clean the outside of the sample vial with a towel.

9. Place the sample vial into the adapter. Close the light shield. Results in mg/L COD (or chosen units) will be displayed.

Accuracy Check
Standard Solution Method.
Check the accuracy of the 0 to 40 mg/L range with a 30 mg/L standard. Using Class A glassware, prepare a 1000-mg/L solution by diluting 850 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1000 mL of organic-free deionized water. Prepare a 30 mg/L dilution by diluting 3.00 mL of this solution into a 100.0 mL volumetric flask. Dilute to volume with deionized water, stopper, and invert 10 times to mix.

Method Performance Precision
Standard: 30.0 mg/L COD

Program	95% Confidence Limits
2700	29.9 - 30.1 mg/L COD

Estimated Detection Limit

Program	EDL
2700	0.2 mg/L COD

Sensitivity
Program Number: 2700

Portion of Curve	ΔAbs	$\Delta Concentration$
Entire Range	0.010	-0.52 mg/L

COLORIMETRIC MEASUREMENT FOR THE LOW RANGE COD (0-150 mg/L RANGE)
(Using a Hach DR/4000: Please note—procedure is fully illustrated with icons in the instrument manual.)

The Hach Low Range COD is measured at 420 nm. The test range is 0-150 mg/L COD. The COD concentration increases as the concentration of hexavalent chromium decreases. This results in a calibration line with a negative slope. The optimum test range is about 20 to 150 mg/L COD.

Procedure
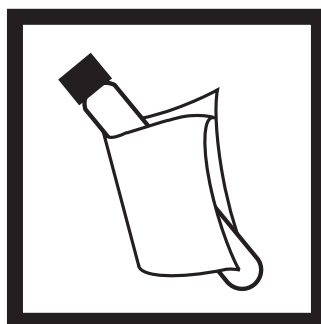**1.** Perform the digestion according to given instructions.

2. Press the soft key under HACH PROGRAM. Select the stored program number for Low Range COD by pressing 2710 with the numeric keys. Press: ENTER

3. The display will show: HACH PROGRAM: 2710 COD, LR. The wavelength (λ), 420 nm, is automatically selected.

4. Insert the Test Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

5. Clean the outside of the blank with a towel.

6. Place the blank into the adapter with the Hach logo facing the front of the instrument. Close the light shield.

7. Press the soft key under ZERO. The display will show: 0.0 mg/L COD.

8. Clean the outside of the sample vial with a towel.

9. Place the sample vial into the adapter. Close the light shield. Results in mg/L COD (or chosen units) will be displayed.

Accuracy Check
Standard Solution Method
Check the accuracy of the 0 to 150 mg/L range with a 100 mg/L KHP standard. Prepare by dissolving 85 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1 liter of deionized water. Use 2 mL as the sample volume. Or dilute 10 mL of 1000-mg/L COD Standard Solution to 100 mL to produce a 100-mg/L standard.

To adjust the calibration curve using the reading obtained with the 100-mg/L standard solution, press the soft keys under OPTIONS< MORE then STD:OFF. Press ENTER to accept the displayed concentration, the value of which depends on the selected units. If an alternate concentration is used, enter the actual concentration and press ENTER to return to the read screen.

Method Performance Precision
Standard: 100.0 mg/L COD

Program	95% Confidence Limits
2710	99.4 - 100.6 mg/L O_2

Estimated Detection Limit

Program	EDL
2710	1.1 mg/L COD

Sensitivity
Program Number: 2710

Portion of Curve	ΔAbs	$\Delta Concentration$
Entire Range	0.010	3.45 mg/L

COLORIMETRIC MEASUREMENT FOR THE HIGH RANGE COD (0-1500 mg/L RANGE) AND HIGH RANGE PLUS (0-15000 mg/L RANGE)
(Using a Hach DR/4000: Please note—procedure is fully illustrated with icons in the instrument manual.)

Hach's High Range and High Range Plus COD are the highest test ranges available from Hach Company. The chemistry and calibration data are identical for both tests. High Range Plus COD is designed to eliminate the dilution step normally required for COD samples which have concentrations from 1500 mg/L up to 15,000 mg/L. When the High Range Plus vial is manufactured, dilution water is added directly to the High Range COD Reagent to accomplish a 1 to 10 dilution when 0.20 mL of sample is added to the reagent vial. The results are measured at 620 nm, and the calibration line has a positive slope. The amount of trivalent chromium is measured, and its concentration increases as the COD concentration increases.

Procedure

1. Perform the digestion according to given instructions.

2. Press the soft key under HACH PROGRAM. Select the stored program number for High and High Range Plus COD by pressing 2720 with the numeric keys. Press: ENTER

3. The display will show: HACH PROGRAM: 2720 COD, HR, HR Plus. The wavelength (λ), 620 nm, is automatically selected.

4. Insert the Test Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

5. Clean the outside of the blank with a towel.

6. Place the blank into the adapter with the Hach logo facing the front of the instrument. Close the light shield.

7. Press the soft key under ZERO. The display will show: 0.0 mg/L COD.

8. Clean the outside of the sample vial with a towel.

9. Place the sample vial into the adapter. Close the light shield. Results in mg/L COD (or chosen units) will be displayed. When High Range Plus COD vials are used, multiply the displayed value by ten.

Accuracy Check

Standard Solution Method

0-1500 mg/L range: Check the accuracy of the 0 to 1,500 range by using either a 300 mg/L or 1000 mg/L COD Standard Solution. Use 2 mL of one of these solutions as the sample volume; the expected result will be 300 or 1000 mg/L COD respectively.

Or, prepare a 500-mL standard by dissolving 425 mg of dried (120 °C, overnight) KHP in 1000 mL of deionized water.

To adjust the calibration curve using the reading obtained with the 100-mg/L standard solution, press the soft keys under OPTIONS< MORE then STD:OFF. Press ENTER to accept the displayed concentration, the value of which depends on the selected units. If an alternate concentration is used, enter the actual concentration and press ENTER to return to the read screen.

0-15,000 mg/L range: Check the accuracy of the 0 to 15,000 mg/L range by using a 10,000 mg/L COD Standard Solution. Prepare the 10,000 mg/L solution by dissolving 8.500 g of dried (120 °C, overnight) KHP in 1 liter of deionized water. Use 0.2 mL of this solution as the sample volume; the expected result will be 10,000 mg/L COD (display x 10).

To adjust the calibration curve using the reading obtained with 1000 mg/L COD Standard Solution, press the soft keys under OPTIONS< MORE then STD:OFF. Press ENTER to accept the value and return to the screen. The instrument will only allow adjustment if the entered concentration is within 10% of the measured concentration.

Method Performance Precision
0-1500 mg/L range
Standard: 1000 mg/L COD

Program	95% Confidence Limits
2720	998 - 1002 mg/L COD

0-15,000 mg/L range
Standard: 10,000 mg/L COD

Program	95% Confidence Limits
2720	9980 - 10,020 mg/L COD

Estimated Detection Limit

Program	EDL
2720 (0 - 1500 mg/L)	3 mg/L COD
2720 (0 - 15,000 mg/L)	30 mg/L COD

Sensitivity
Program Number: 2720

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	-23.5 mg/L

MANGANESE III COD TEST
Colorimetric Measurement for the Manganese III COD (20 to 1000 mg/L COD)
(Using a Hach DR/4000: Please note—procedure is fully illustrated with icons in the instrument manual.)

The Hach Manganese III COD Procedure can be run with or without the chloride removal pretreatment. If chloride is absent or does not present a significant interference, the pretreatment steps can be omitted. The working range of the test is 20 to 1000 mg/L COD. The test is measured at 510 nm, and the calibration line has a negative slope. When manganese III is measured spectrophotometrically, its concentration decreases as the COD concentration increases. High quality, organic-free deionized water is required for blanks and dilution water. Figure 7 shows scans of COD standards tested using the Mn III COD Reagent.
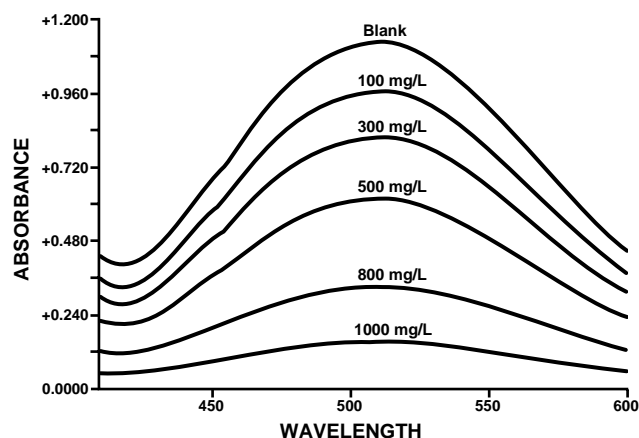

Figure 7. Overlay scans of standards with concentrations of (blank) 0, 100, 300, 500, 800, and 1000 mg/L COD, which were tested using the Mn III COD Reagent.

Manganese III COD Procedure without Chloride Removal Pretreatment

(Using a Hach DR/4000: Please note—procedure is fully illustrated with icons in the instrument manual.)

Procedure

1. Press the soft key under HACH PROGRAM. Select the stored program number for Manganese III COD by pressing 2730 with the numeric keys.

2. The display will show: HACH PROGRAM: 2730 COD, Mn III. The wavelength (λ), 510 nm, is automatically selected.

3. Homogenize 100 mL of sample for 30 seconds in a blender.

4. Pipet 0.50 mL of sample into a Mn III COD vial. Cap and invert several times to mix.

5. Prepare a blank by substituting 0.50 mL of deionized water for the sample. Cap and invert several times to mix.

6. Place the vials in the COD reactor which has been preheated to 150 °C. Digest for 1 hour.

7. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about 3 minutes.

8. Remove the vials from the water and wipe with a clean, dry paper towel.

9. Insert the COD Vial Adapter into the sample cell module of the DR/4000 by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

10. Place the blank into the sample cell compartment. Close the light shield.

11. Press the soft key under ZERO. The display will show: 0 mg/L COD

12. Place the sample vial in the adapter. Close the light shield. Results in mg/L COD will be displayed.

MANGANESE III COD WITH CHLORIDE REMOVAL PRETREATMENT

(Using a Hach DR/4000 Instrument: Please note—procedure is fully illustrated with icons in the instrument manual.)

The Manganese III COD procedure with chloride removal is nearly identical to the procedure without chloride removal. However, there are some differences. To remove chloride from samples using the Chloride Removal Cartridge and Vacuum Pretreatment Device, it is necessary to make the sample solution acidic prior to filtering through the Chloride Removal Cartridge. This process results in a small but consistent volume change. The change does not alter the calibration line slope, but does cause a slight offset. This makes it necessary to prepare a separate blank to zero the instrument for all tests where the chloride removal pretreatment is used.

Procedure

1. Press the soft key under HACH PROGRAM. Select the stored program number for Manganese III COD by pressing 2730 with the numeric keys.

2. The display will show: HACH PROGRAM: 2730 COD, Mn III. The wavelength (λ), 510 nm, is automatically selected.

3. Homogenize 100 mL of sample for 30 seconds in a blender.

4. Using a TenSette® Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell.

5. Using an automatic dispenser or TenSette Pipet, add 1.0 mL of concentrated sulfuric acid to the mixing cell.

6. Cap the cell tightly and invert it several times. The solution will become hot. Cool to room temperature before proceeding.

7. Prepare a blank by repeating steps 4 - 6 above, using deionized water for the sample.

8. If not already on, turn on the COD Reactor and heat to 150 °C.

9. Label each Mn III COD vial and remove the cap. Place the vials in one of the numbered holes in the Vacuum Pretreatment Device base.

10. Place the VPD top on the base. Insert a fresh Chloride Removal Cartridge directly above each Mn III COD vial. Plug any open holes in the Vacuum Pretreatment Device top using the stoppers provided.

11. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the Vacuum Pretreatment Device top until the internal gauge reads 20 inches of water column (WC).

12. Pipet 0.60 mL of each acidified sample into a Chloride Removal Cartridge. Pipet 0.60 mL of acidified blank into another Chloride Removal Cartridge. It should take 30 to 45 seconds to draw liquid through the Chloride Removal Cartridge into each vial.

13. Close the vacuum regulator valve completely to achieve full vacuum. (Full vacuum is 20 to 25 inches of mercury and must be read on a separate gauge, usually one attached directly to the vacuum pump.) After one minute of full vacuum, open the regulator valve to release the vacuum.

14. Turn the pump off. Remove the Vacuum Pretreatment Device top and set it beside the base.

15. Use forceps to remove the filter from the top of each Chloride Removal Cartridge. Place the filter in the corresponding Mn III COD vial.

16. Remove the Mn III COD vial from the vacuum chamber and replace the original cap tightly. Invert several times to mix.

17. Place the vials in the COD reactor, which has been preheated to 150 °C. Digest for 1 hour.

18. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about 3 minutes.

19. Remove the vials from the water and wipe with a clean, dry paper towel.

20. Insert the COD Vial Adapter into the sample cell module of the DR/4000 by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

21. Place the blank into the sample cell compartment. Close the light shield.

22. Press the soft key under ZERO. The display will show: 0 mg/L COD

23. Place the sample vial in the adapter. Close the light shield. Results in mg/L COD will be displayed.

Accuracy Check
Standard Solution Method
Prepare an 800 mg/L COD Standard Solution by adding 0.6808 g of dried (120 °C, overnight) potassium acid phthalate (KHP) to one liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be 800 ± 24 mg/L COD. An 800 mg/L COD Standard Solution can also be purchased directly from Hach.

To adjust the calibration curve using the reading obtained with the 800 mg/L COD Standard Solution, press the soft keys under OPTIONS MORE then STD:OFF. Press ENTER to accept the value and return to the read screen. The instrument will only allow adjustment if the entered concentration is within 10% of the measured concentration.

Method Performance Precision
(data is for Manganese III COD without the chloride removal procedure)

Standard: 500 mg/L COD

Program	95% Confidence Limits
2730	497 - 503 mg/L COD

Estimated Detection Limit
Program	EDL
2730	4 mg/L COD

Sensitivity
Program Number: 2730

Portion of Curve	Abs	Concentration
Entire range	0.010	8 mg/L

Titration Methods
Two titrimetric techniques are widely used in COD testing: the macro and micro techniques. Because macro techniques have limitations similar to those of the macro digestion procedures, they will not be considered further.

The titration procedure is well established for use with the Dichromate COD Reagent. Hach has adapted this procedure for use with the Low Range (0 to 150 mg/L), High Range (0 to 1500 mg/L), and the High Range Plus (0 to 15,000 mg/L) COD Reagents.

When titration is used for measurement, the amount of hexavalent chromium remaining after digestion is determined. There are two ways of doing this. In both cases, the initial amount of hexavalent chromium must be known. The final hexavalent chromium level is then subtracted from the initial level to determine the amount of hexavalent chromium reduced during the digestion. This difference is used to calculate the COD. The initial amount is known either through calculation (because primary grade potassium dichromate is readily available) or by standardizing the bulk solution before running the individual tests.

The amount of dichromate is usually determined by direct titration using ferrous ammonium sulfate (FAS) as the titrant and ferroin (1,10 phenanthroline ferrous sulfate) as the indicator. The apparatus used with the macro procedure is shown in Figure 8.
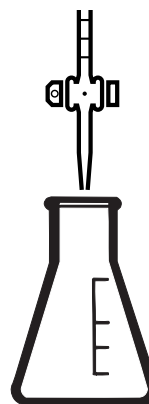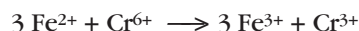

Figure 8. Apparatus Used with Macro Procedure

During the course of the titration, the titrant (Fe^{2+}) reacts instantly with hexavalent chromium (Cr^{6+}) to form trivalent chromium (Cr^{3+}) and ferric ion (Fe^{3+}), as shown below:

$$3\ Fe^{2+} + Cr^{6+} \longrightarrow 3\ Fe^{3+} + Cr^{3+}$$

At the end of the titration, there is no hexavalent chromium present for this reaction to occur and the titrant reacts with the indicator to form an orange-brown color. The indicator, 1,10 phenanthroline, forms an intense color with Fe^{2+} (ferrous ion), but does not react with Fe^{3+} (ferric ion). This end point could also be detected using a potentiometric system.

Other titrants and indicators have been used. One of these titrants is hydroquinone with diphenylamine indicator.

Back titration techniques are also used to determine the amount of hexavalent chromium consumed in the COD digestion. With this technique, a measured amount of reducing agent ions, such as Fe^{2+} or I^-, are added to the digested mixture. The reducing agent consumes the remaining hexavalent chromium after digestion, and excess or unreacted reducing agent titrated. This technique indirectly determines the amount of hexavalent chromium left in the digested solution. Several combinations of reducing agent and titrant have been used with this technique, including ferrous ion with potassium permanganate, iodide with thiosulfate, and oxalate or formate with permanganate.

Micro Titration Procedure

Micro titration procedures use small reagent volumes, require a minimum of space, and are easy to perform. They offer an alternative to colorimetric measurement procedures when samples are highly colored or turbid, or when a spectrophotometer is not available. The test requires more operator skill and a greater amount of time to perform than colorimetric procedures.

Micro Buret Titration

1. After digestion, cool the vial to room temperature. Carefully remove the cap of a vial. Rinse the inside wall with less than 1 mL of deionized water.

2. Add a small Teflon stirring bar and one drop of the appropriate Ferroin Indicator Solution. When using the Low Range COD Digestion Reagent Vials, use Low Range Ferroin Indicator Solution. When using High Range or High Range Plus COD Digestion Reagent Vials, use High Range Ferroin Indicator Solution.

3. Place the vial on the titration stand. Turn on the magnetic stirrer.

4. Titrate with the appropriate Ferrous Ammonium Sulfate Solution (FAS) until the sample color changes sharply from greenish-blue to orange-brown. When using the Low Range COD Digestion Reagent Vials, use 0.0125 N FAS. When using High Range or High Range Plus COD Digestion Reagent Vials, use 0.125 N FAS. Record the mL of titrant required. The mL required for the prepared sample is value B. The mL required for the blank is value A.

5. Pipet 2.00 mL of Potassium Dichromate Standard Solution into an empty vial. When using the Low Range COD Digestion Reagent Vials, use a 0.025 N solution. When using High Range or High Range Plus COD Digestion Reagent Vials, use a 0.25 N solution. Add 3 mL of concentrated sulfuric acid to the vial. Swirl to mix. Wait for the solution to cool until the vial is comfortable to touch.

6. Add one drop of Ferroin Indicator Solution selected in step 2.

7. Add a stir bar and titrate with Ferrous Ammonium Sulfate Standard Solution selected in step 4 until the color changes from greenish-blue to orange-brown. Record the number of mLs required. This is value C.

8. Determine the mg/L COD according to the following equation:

$$COD\ mg/L = \frac{(A - B) \times 2000 \times M}{C}$$

Where:

A= mL used in titration of reagent blank

B= mL used in titration of prepared sample

C= mL used in titration of standard solution in step 7

M= 0.1 when using Low Range COD Digestion Reagent Vials

M= 1 when using High Range COD Digestion Reagent Vials

M= 10 when using High Range Plus COD Digestion Reagent Vials

For example, when using Low Range COD Reagent vials:

A=3.95 mL

B=2.00 mL

C=4.00 mL

M=0.1

$$COD\ mg/L = \frac{(3.95-2.00) \times 2000 \times 0.1}{4.00} = 97.5$$

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