

Manganese III Chemical Oxygen Demand Technical Paper

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INTRODUCTION

The Chemical Oxygen Demand Procedure (COD) is widely used in the wastewater industry to measure the organic loading of a waste stream. For samples from a specific source, COD can be related empirically to Biochemical Oxygen Demand (BOD), organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. By definition, COD 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."¹ The dichromate reflux method has been preferred over procedures using other oxidants because of superior oxidizing ability with a wide variety of samples, and ease of manipulation. However, the dichromate COD reagent contains the following hazardous materials: potassium dichromate (oxidant) silver sulfate (catalyst), and mercuric sulfate (masking agent), in a 50% sulfuric acid medium. Silver, chromium and mercury are regulated heavy metals. Mercury is poisonous and with no disposal option must be recycled.²

If waste disposal is an issue it would be advantageous to replace the dichromate COD with a COD procedure which does not contain mercury, chromium or silver and which will provide the analyst with data comparable to the dichromate COD. Method continuity should be maintained for current wastewater treatment monitoring and control, water pollution studies, and for historical reference.

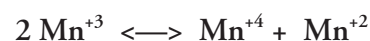
Analysts have attempted to use many different oxidants in the COD test procedure. Our laboratories have experimented with permanganate (in both acidic and basic solutions), cerate, persulfate, periodate, iodate, bromate, perbromate, hypochlorite, perchlorate, ferrate, bismuthate, hydrogen peroxide, ozone, oxygen, hydroxyl radical, vanadate, ultraviolet light, bomb calorimetry, 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 ease of use.

One viable reagent, not widely used but a very suitable oxidant, is manganese III sulfate in sulfuric acid media. The reagent is a strong oxidant, is stable, is not photosensitive, and has a desirable spectrum for colorimetric measurement.

REAGENT DEVELOPMENT

Manganese III (Mn III) salts participate in a number of complex chemical equilibria which are largely dependent upon 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 H₂SO₄ (saturated with MnSO₄).³ Initial experiments with the reagent contained up to 1.1 g/L Mn III. After several weeks the formation of purple, planar, diamond-shaped crystals was observed. Over a period of time the percentage of vials observed with crystals increased dramatically. These crystals were identified by Gorbechev, et al³ as manganosulfuric acid, H₂[Mn₂(SO₄)₄] • 8 H₂O. Heating these solutions in a reactor at 150 °C did not dissolve all crystals. 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. Complexation of Mn III with sulfate or bisulfate provides stability to the Mn III reagent. Reagent stability is also affected by disproportionation as shown below.



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 the addition of 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 CHEMISTRY

Reagent preparation methods can be divided into three groups: methods based upon chemical oxidation of Mn II, methods based upon electrochemical oxidation of Mn II, and methods based upon dissolution of solid Mn III. Details of these formulations are present in the literature references

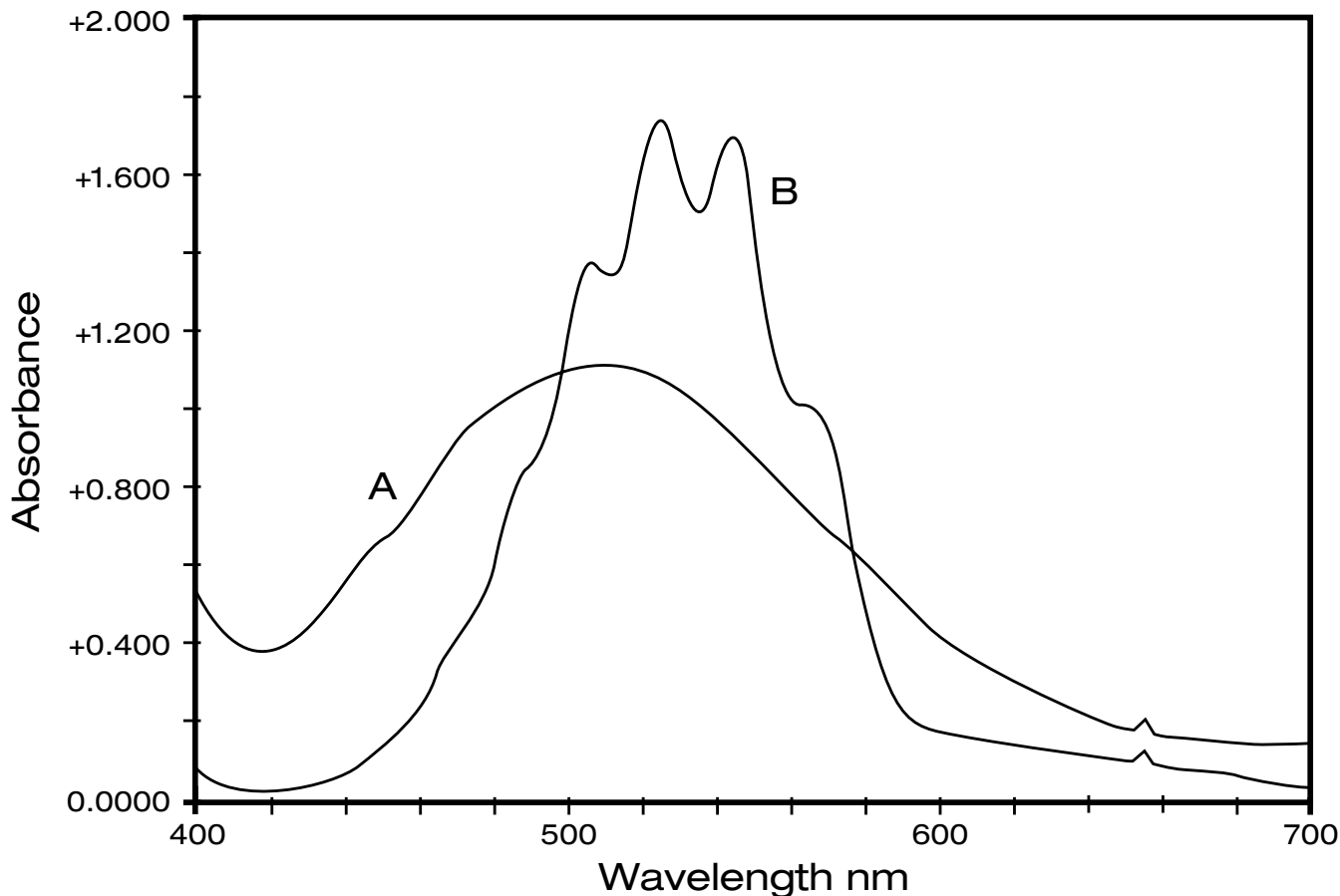
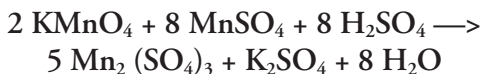


Figure 1. Spectra obtained on a Hewlett Packard 8452A Spectrophotometer using a 1-cm path length.
 A: Mn III Reagent blank solution, approximately 0.008 N Mn III.
 B: Potassium Permanganate solution, approximately 0.001 N, in deionized water.

provided.⁴⁻¹⁰ In our laboratory 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:

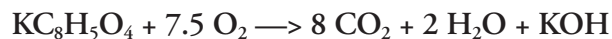


In sulfuric acid solution there are several possible Mn III species. Gorbechev et al³ reports the predominant species in 11 N H₂SO₄ as Mn₂(SO₄)₃. Barek et al⁴ reports the presence of two hydrated species, Mn(H₂O)₅HSO₄²⁺ and [Mn(H₂O)₅(HSO₄)₂]⁺.

The Mn III COD (U.S. Patent # 5,556,787) solution has a broad absorption band in the region from 420 to 600 nm, with a maximum absorbance at 510 nm. For comparison, potassium permanganate is an oxidant which has a visual appearance somewhat similar to the Mn III COD. Both solutions are purple colored but the spectra are quite different. See Figure 1.

CALIBRATION

COD testing is based upon the theoretical amount of oxygen required to oxidize organic compounds to CO₂ and H₂O. Test results may be expressed as mg/L COD or mg/L O₂. Standards are prepared based upon this reaction. The most commonly used standard is potassium hydrogen phthalate (KHP) and the theoretical oxygen demand is stated by the following equation.



Seven and one-half molecules of oxygen consume one molecule of potassium hydrogen phthalate. On a weight basis, the theoretical oxygen demand for KHP is 1.175 mg O₂ per mg KHP. Preparation of a 1000 mg/L COD standard from KHP follows:

$$\frac{1000 \text{ mg/L COD}}{1.175 \text{ mg O}_2/\text{mg KHP}} = 851 \text{ mg/L KHP}$$

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.

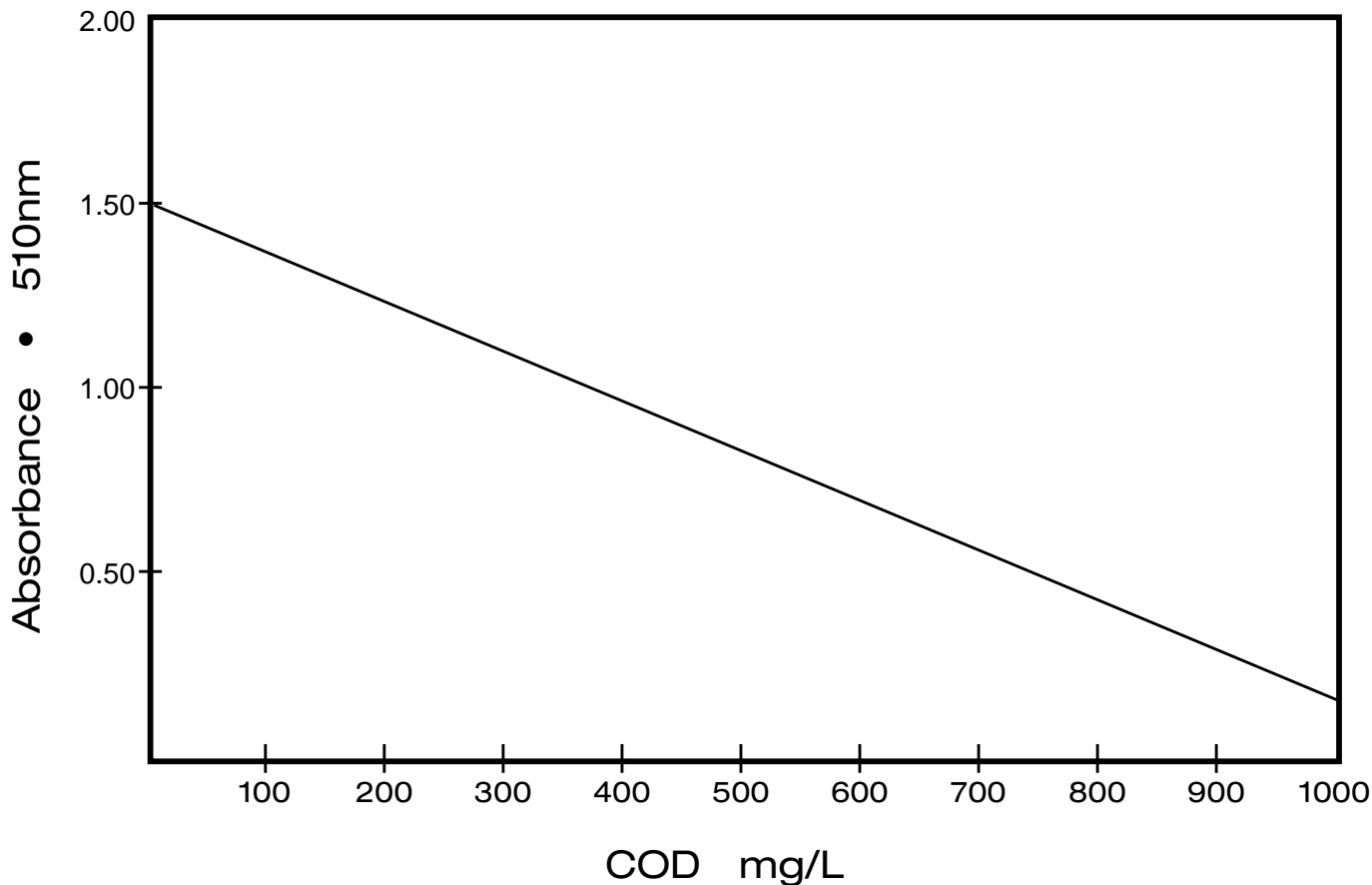
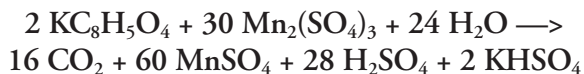


Figure 2. Mn III COD Reagent Calibration. Hach DR/3000 at a wavelength of 510 nm and using a Hach Mn III COD Reagent vial as the sample cell, (path length = 13.5 mm). The slope is -0.0013 Abs/mg/L, the x-axis intercept is 1185 mg/L, and the correlation coefficient is 0.9997.

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



INTERFERENCES

Inorganic materials may be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Species such as nitrite, sulfide or ferrous iron are usually not present in significant amounts. If necessary, these interferences can be corrected for. After determining their concentration with a separate method, the theoretical oxygen demand of that species can be used to correct the COD result, or a standard can be prepared from the interfering species and the COD result from the interference standard used to correct the final COD concentration.

Chloride is the most common interference. The theoretical oxygen demand of chloride is 0.226 mg

O_2 per mg Cl^- .^{11,12} A sample containing 2000 mg/L chloride has a theoretical COD of 452 mg/L. With typical sample COD values ranging from 100 to 1000 mg/L, the magnitude of this interference is severe. Mercuric sulfate is the most effective and widely used means of masking the chloride interference. The ratio of $\text{HgSO}_4 : \text{Cl}^-$ should be 10 : 1 for effective masking of chloride.¹² For example, a 2-mL sample having a chloride concentration of 2000 mg/L (4 mg Cl^-) will require 40 mg HgSO_4 to effectively mask the chloride interference. When a large number of samples are tested the amount of waste mercury accumulates. Mercury is very toxic and legal disposal is not an option. The only acceptable option for handling mercury waste is recycling which is expensive.

Elimination of mercury from industrial use will reduce cost by eliminating the expense of mercury recycling, will reduce the potential exposure of the analyst to a hazardous material, and is an environmentally sound practice for both the user and the manufacturer.

ALTERNATIVES TO MERCURY FOR CHLORIDE REMOVAL

Chloride removal schemes can be divided into two groups, internal (formulations) and external (pretreatment techniques).

Formulations were evaluated which contained a number of metals or combinations of metals which, when added to the COD reagent, would eliminate the chloride interference. Some of these metals were toxic, such as mercury, others were necessary in concentrations high enough to become regulated waste and some provided no significant benefit. COD reagents can also be formulated to reduce the oxidation potential of the solution to a level below that required to oxidize chloride to chlorine (about - 1.36 volts). This is effective for preventing the oxidation of chloride but the oxidation of most organic compounds is drastically reduced and the formulation has little value as a COD reagent.

A number of sample pretreatment techniques have been tested. Techniques where chloride is precipitated from solution followed by settling, filtration or centrifugation will remove chloride but suspended solids, which often contain a significant contribution to the COD of the sample, are also removed from the solution. A total COD value must include suspended solids. Precipitation reagents, such as silver, may also be regulated. Ion-selective or ion-exchange resins are partially effective for chloride removal, but resins are leached by the sample solution resulting in a COD contribution from the resin which is unacceptable. Electrochemical oxidation of chloride is possible, but it is relatively expensive, time consuming, non-selective and some loss of solids was observed in our experiments. Chemical oxidation of chloride prior to oxidation of the sample is a technique, which when performed under controlled conditions, is very effective.

When samples containing chloride are exposed to a chemical oxidant of sufficient oxidation potential, chloride is oxidized to chlorine. If the time the sample is exposed to the oxidant is controlled, a degree of selectivity can be obtained which will allow oxidation of one sample component, chloride, and have minimal effect on organic sample components. Sodium bismuthate is a strong oxidant which is not soluble in aqueous solutions and when present as a solid will affect some constituents in solution. When contained in a cartridge, exposure of an acidified

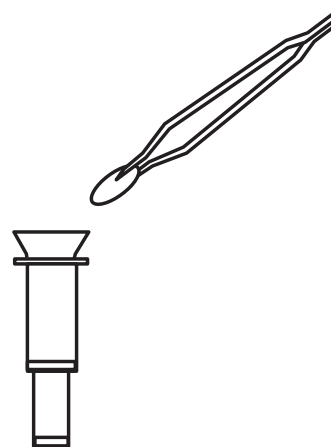
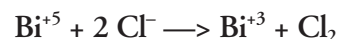


Figure 3. Chloride Removal Cartridge with top glass fiber filter being removed with forceps.

sample to the oxidant can be controlled to maximize chloride oxidation and removal, but minimize the effect of the oxidant on organic sample components. The reaction of bismuth with chloride is represented by the following equation:



The Chloride Removal Cartridge (patent pending) is composed of two halves. Both halves are open at the top and have pie-shaped grid openings at the bottom. The lower half contains a reagent reservoir for the solid oxidant, sodium bismuthate (patent pending). Glass fiber filters, above and below the reagent reservoir, hold the sodium bismuthate in place. The glass fiber filter is binder free and contributes no oxidizable organic compounds to the final COD result.

The upper half of the cartridge contains a small glass fiber filter, which is placed on top of the grid. The upper cartridge is fitted into the top portion of the lower cartridge to create one unit—the Chloride Removal Cartridge.

Sample is dispensed into the upper cartridge reservoir and a low vacuum draws the sample through the Chloride Removal Cartridge at a controlled rate into a COD vial, which is placed beneath the cartridge. Any suspended solids present in the sample are captured by the top glass fiber filter. Allowing suspended solids into the reagent reservoir would interfere with the removal of chloride. In addition, suspended solids are often composed of significant amounts of organic material which contribute to the sample COD.

After the sample has passed through the cartridge, the top glass fiber filter, which may have captured

suspended solids, is transferred to the COD vial (See Figure 3). In the absence of suspended solids, the filter does not need to be transferred to the vial.

ANALYTICAL PROCEDURE

The procedure can be run with or without the chloride removal pretreatment. If chloride is not present in significant amounts, the chloride removal procedure is not necessary.

Procedure without chloride removal

Samples containing suspended solids are first homogenized. A sample volume of 0.50 mL is transferred to a Mn III COD vial. The vials are capped, mixed, and heated for 60 minutes at 150 °C. Following digestion the vials are cooled to room temperature and results are read on a spectrophotometer.

Procedure with chloride removal

When the chloride removal procedure is used, 1.00 mL of concentrated sulfuric acid is dispensed into a mixing bottle containing 9.00 mL of sample and the mixture is cooled to room temperature. A Chloride Removal Cartridge is placed into an opening in the Vacuum Pretreatment Device (patent pending; see Figure 4). A low vacuum level of 20 inches of water is established and 0.60 mL of the sample-acid mixture is transferred into the Chloride Removal Cartridge (see Figure 5). (The 0.60 mL sample volume is necessary due to the acid dilution step and a slight loss of sample in the Chloride Removal Cartridge. The calibration slope is unaffected and a slight offset is accounted for when the reagent blank is used to zero the instrument.)

The sample requires 30 to 45 seconds to pass through the cartridge and into the Mn III COD vial, which is directly below the cartridge. The vacuum level is then increased to 20 to 25 inches of mercury to pull any sample which remains inside the cartridge reagent bed. The vacuum is released and the top of the Vacuum Pretreatment Device is removed and set beside the base. The glass fiber, which has captured sample suspended solids, is removed using a pair of needle nose forceps and placed into the Mn III COD vial.

The vial is capped, mixed and heated for 60 minutes at 150 °C. Following digestion the vials are cooled to room temperature and results are read on a spectrophotometer (see Figure 6).

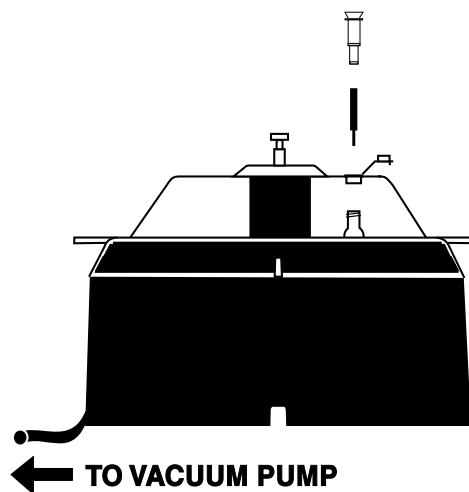


Figure 4. Insertion of the Chloride Removal Cartridge into the Vacuum Pretreatment Device.

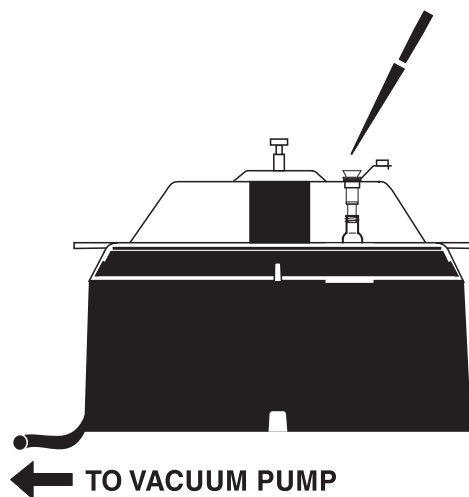


Figure 5. Transferring 0.60 mL of acidified sample into the Chloride Removal Cartridge.



Figure 6. Reading COD results on a DR/2010 Spectrophotometer.

PRECISION

A number of samples have been tested and the precision of these results determined. Table 1 contains representative sample results. The 800 mg/L COD standard was tested using the Mn III COD procedure only, while the remaining samples were tested using the Mn III COD with the Chloride Removal procedure.

MN III COD COMPARABILITY TO DICHROMATE COD

Samples were tested using both the dichromate COD procedure and the Mn III COD procedure. Sample data is presented in Table 2.

Table 1 — Precision

Sample	Mn III COD mg/L	Standard Deviation mg/L	RSD %	Replicates 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

Table 2 — Manganese III COD Comparability to Dichromate COD

Sample	Manganese III COD mg/L	Dichromate COD mg/L	Ratio Mn III COD/ Cr COD
Domestic WWTP Influent #1	428	488	0.88
Domestic WWTP Influent #2	463	510	0.91
Industrial Influent #1	153	169	0.90
Industrial Influent #2	234	248	0.94
Industrial Influent #3	220	250	0.88

CONCLUSION

The Mn III COD procedure is a fast, reliable COD procedure which will provide the analyst with data that is comparable to the dichromate COD procedure for most wastewater samples. The reagent contains no hazardous metals and generates no hazardous metal waste. This will reduce disposal or recycling cost, will reduce exposure of the analyst to hazardous materials, and is an environmentally sound practice. The reagent system uses existing reactor blocks and spectrophotometers which are common in most laboratories.

Acknowledgments

I would like to acknowledge Don Miller and Scott Brayton, the inventors of the Manganese III COD Reagent and Chloride Removal Cartridge.

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Lit. No. 7057

F71 Printed in U.S.A.

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