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Appendices

Appendix A

Standard methods for the examination of water and wastewater

1. Chemical oxygen demand (COD)

1.1 Introduction

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variety of samples, and ease of manipulation. Oxidation of most organic compounds is 95 to 100% of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Ammonia, present either in the waste or liberated from nitrogen-containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions.

1.2 Closed reflux with titrimetric method

1.2.1 Principle

Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent. Keep ratios of reagent weight, volumes, and strengths constant when sample volumes other than 50 ml are used. The standard 2 hr reflux time may be reduced if it has been shown that a shorter period yields the same results.

1.2.2 Interferences and limitations

Volatile organic compounds are more completely oxidized in the closed system because of longer contact with oxidant. Before each use inspect culture-tube caps for breaks in the TFE liner. Select culture-tube size for the degree of sensitivity desired. Use the 25 mm x 150 mm tube for samples with low COD content because a larger volume sample can be treated.

1.2.3 Apparatus

1. Digestion vessels preferably use borosilicate culture tubes, 16 mm x 100 mm, 20 mm x 150 mm, or 25 mm x 150 mm, with TFE-lined screw caps. Alternatively, use borosilicate ampules, 10 ml capacity, 19 to 20 mm diameter.
2. Heating block, cast aluminium, 45 to 50 mm deep, with holes sized for close fit of culture tubes or ampules.

3. Block heater or oven, to operate at 150 ± 2 °C. 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 hr exposure at 150 °C will not damage the caps.
4. Ampule sealer: Use only a mechanical sealer to insure stronger, consistent seals.

1.2.4 Reagents

1. Standard potassium dichromate digestion solution, 0.0167M: Add to about 500 ml distilled water 4.913 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103 °C for 2 hr, 167 ml concentrated H_2SO_4 and 33.3 g $HgSO_4$. Dissolve, cool to room temperature and dilute to 1000 ml.
2. Sulfuric acid reagent.
3. Ferroin indicator solution.
4. Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10M: Dissolve 39.2 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml concentrated H_2SO_4 , cool, and dilute to 1000 ml. Standardize solution daily against standard $K_2Cr_2O_7$ digestion solution.

$$\text{Molarity of FAS solution} = \frac{\text{Volume } 0.0167M \text{ } K_2Cr_2O_7 \text{ solution titrated ml}}{\text{Volume FAS used in titration ml}} \times 0.10 \quad (A-1)$$

5. Sulfamic acid.
6. Potassium hydrogen phthalate standard.

1.2.5 Procedure

Wash culture tubes and caps with 20% H₂SO₄ before first use to prevent contamination. Refer to Table A. 1 for proper sample and reagent volumes. Place sample in culture tube or ampule and add digestion solution. Carefully run sulfuric acid reagent down inside of vessel so an acid layer is formed under the sample digestion solution layer. Tightly cap tubes or seal ampules, and invert each several times to mix completely.

CAUTION: Wear face shield and protect hands from heat produced when contents of vessels are mixed. Mix thoroughly before applying heating heat to prevent local heating of vessel bottom and possible explosive reaction.

Place tubes or ampules in block digester or oven preheated to 150 °C and reflux for 2 hr. Cool to room temperature and place vessels in test tube rack. Remove culture tubes caps and add small TFE-covered magnetic stirring bar. If ampules are used, transfer contents to a larger container for titrating. Add 0.05 to 0.10 ml (1 to 2 drops) ferroin indicator and stir rapidly on magnetic stirrer while titrating with 1.10M FAS. The end point is a sharp color change from blue-green to reddish brown, although the blue-green may reappear within minutes. In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.

1.2.6 Calculation

$$COD \text{ as } mg/L \text{ of } O_2 = \frac{(A - B) \times M \times 8000}{ml \text{ sample}} \quad (A-2)$$

where:

A = Volume of FAS used for blank (ml),

B = Volume of FAS used for sample (ml), and

M = Molarity of FAS

Table A-1 Sample and reagent quantities for various digestion vessels

Digestion vessel	Sample (ml)	Digestion solution (ml)	Sulfuric acid reagent (ml)	Total final volume (ml)
Culture tubes;				
16 mm x 100 mm	2.5	1.5	3.5	7.5
20 mm x 150 mm	5.0	3.0	7.0	15.0
25 mm x 150 mm	10.0	6.0	14.0	30.0
Standard 10 ml ampules				
	2.5	1.5	3.5	7.5

1.2.7 Precision and Bias

Sixty synthetic samples containing potassium hydrogen phthalate and NaCl were tested by six laboratories. At an average COD of 195 mg O₂/L in the absence of chloride, the standard deviation was ± 11 mg O₂/L (coefficient of variation, 5.6%). At an average COD of 208 mg O₂/L and 100 mg Cl⁻/L, the standard deviation was ± 10 mg O₂/L (coefficient of variation, 4.8 %).

2. Total organic carbon (TOC)

2.1 Introduction

The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes, and the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) may be used to characterize these fractions. The presence of organic carbon that does not respond to either the BOD or COD test makes them unsuitable for the measurement of total organic carbon. Total organic carbon (TOC) is a more convenient and direct expression of total organic content than either BOD or COD, but does not provide the same kind of information. If a repeatable empirical relationship is established between TOC and BOD or COD, then TOC can be used to estimate the accompanying BOD or COD. This relationship must be established independently for each set of matrix conditions, such as various points in a treatment process. Unlike BOD or COD, TOC is independent of the oxidation state of the organic matter and

does not measure other organically bound elements such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by BOD and COD. TOC measurement does not replace BOD and COD testing.

To determine the quantity of organically bound carbon, the organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measured quantitatively. TOC methods utilize heat and oxygen, ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide (CO_2). The CO_2 may be measured directly by a nondispersive infrared analyzer, it may be reduced to methane and measured with a flame ionization detector, or CO_2 may be titrated chemically.

2.2 Combustion-infrared Method

The combustion-infrared method has been used for a wide variety of samples, but its accuracy is dependent on particle size reduction because it uses small-orifice syringes.

2.2.1 Principle

The sample is homogenized and diluted as necessary and a microportion is injected into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The water is vaporized and the organic carbon is oxidized to CO_2 and H_2O . The CO_2 from oxidation of organic and inorganic carbon is transported in the carrier gas streams and is measured by means of a non-dispersive infrared analyzer.

Because total carbon is measured, IC must be measured separately and TOC obtained by difference.

Measure IC by injecting the sample into a separate reaction chamber packed with phosphoric acid coated quartz beads. Under the acidic conditions, all IC is converted to CO_2 , which is measured. Under these conditions organic carbon is not oxidized and only IC is measured.

Alternatively, convert inorganic carbonates to CO_2 with acid and remove the CO_2 by purging before sample injection. The sample contains only the NPOC fraction of total carbon; a VOC determination also is necessary to measure true TOC.

2.2.2 Interference

Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration, although necessary to eliminate particulate organic matter when only DOC is to be determined, can result in loss or gain of DOC, depending on the physical properties of the carbon-containing compounds and the adsorption of carbonaceous material on the filter, or its desorption from it. Check filters for their contribution to DOC by analyzing a filtered blank. Note that any contact with organic material may contaminate a sample. Avoid contaminated glassware, plastic containers, and rubber tubing. Analyze treatment, system, and reagent blanks.

2.2.3 Minimum detectable concentration

1 mg carbon/L this can be achieved with most combustion-infrared analyzers although instrument performance varies. The minimum

detectable concentration may be reduced by concentrating the sample, or by increasing the portion taken for analysis.

2.2.4 Sampling and storage

Collect and store samples in amber glass bottles with TFE-lined cap. Before use, wash bottles with acid, seal with aluminum foil, and bake at 400 °C for at least 1 h. Wash TFE septa with detergent, rinse repeatedly with organic-free water, wrap in aluminum foil, and bake at 100 °C for 1 h. Preferable use thick silicone rubber-backed TFE septa with open ring caps to produce a positive seal. Because the detection limit is relatively high, less rigorous cleaning may be acceptable; use bottle blanks with each set of samples. Use a Kemmerer or similar type sampler for collecting samples from a depth exceeding 2 m. Preserve samples that cannot be examined immediately by holding at 4 °C with minimal exposure to light and atmosphere. Acidification with phosphoric or sulfuric acid to a pH ≤ 2 at the time of collection is especially desirable for unstable samples, and may be used on all samples; acid preservation, however, requires that inorganic carbon subsequently is purged before analysis.

2.2.5 Apparatus

1. Total organic carbon analyzer, Shinadzu TOC-5050A.
2. Syringes: 0 to 50 μl , 0 to 200 μl , 0 to 500 μl , and 0 to 1 ml capacity.
3. Sample blender or homogenizer.
4. Magnetic stirrer and TFE-coated stirring bars.
5. Filtering apparatus and 0,45- μm -pore-diameter filters.

2.2.6 Reagents

1. Reagent water, prepare blanks and standard solutions from carbon-free water; preferable use carbon-filtered, redistilled water.
2. Concentrated phosphoric acid, H_3PO_4 . Alternatively use sulfuric acid, H_2SO_4 , but not hydrochloric acid.
3. Organic carbon stock solution: dissolve 2.1254 g anhydrous potassium biphthalate, $\text{C}_8\text{H}_5\text{KO}_4$, in carbon free water and dilute to 1000 ml; 1.00 ml = 1.00 mg carbon. Alternatively, use any other organic carbon-containing compound of adequate purity, stability, and water solubility. Preserve by acidifying with H_3PO_4 or H_2SO_4 to $\text{pH} \leq 2$.
4. Inorganic carbon stock solution: dissolve 4.4122 g anhydrous sodium carbonate, Na_2CO_3 , in water, add 3.497 g anhydrous sodium bicarbonate, NaHCO_3 , and dilute to 1000 ml; 1.00 ml = 1.00 mg carbon. Alternatively, use any other inorganic carbonate compound of adequate purity, stability, and water solubility. Keep tightly stoppered.
5. Carrier gas: purified oxygen or air, CO_2 -free and containing less than 1 ppm hydrocarbon (as methane).
6. Purging gas: Any gas free of CO_2 and hydrocarbons.

2.2.7 Procedure

1. Instrument operation: Follow manufacturer's instructions for analyzer assembly, testing, calibration, and operation. Adjust to optimum combustion temperature (900 °C) before using instrument; monitor temperature to insure stability.
2. Sample treatment: If a sample contains gross solids or insoluble matter, homogenize until satisfactory replication is obtained.

Analyze a homogenizing blank consisting of reagent water carried through the homogenizing treatment.

If inorganic carbon must be removed before analysis, transfer a representative portion of 10 to 15 ml to a 30 ml beaker, add conc H_3PO_4 to reduce pH to 2 or less, and purge with gas for 10 min. Do not use plastic tubing. Inorganic carbon also may be removed by stirring the acidified sample in a beaker while directing a stream of purified gas into the beaker. Because volatile organic carbon will be lost during purging of the acidified solution, report organic carbon as total nonpurgeable organic carbon.

If the available instrument provides for a separate determination of inorganic carbon (carbonate, bicarbonate, free CO_2) and total carbon, omit decarbonation and proceed according to the manufacturer's directions to determine TOC by difference between TC and IC.

If dissolved organic carbon is to be determined, filter sample through 0.45- μ m-pore-diameter filter with vacuum; analyze a filtering blank.

3. Sample injection: Withdraw a portion of prepared sample using a syringe fitted with a blunt-tipped needle. Select sample volume according to manufacturer's direction. Stir samples containing particulates with a magnetic stirrer. Select needle size consistent with sample particulate size. Inject samples and standards into analyzer according to manufacturer's directions and record response. Repeat injection until consecutive peaks are obtained that are reproducible to within $\pm 10\%$.

4. Preparation of standard curve: Prepare standard organic and inorganic carbon series by diluting stock solutions to cover the expected range in samples, Inject and record peak height or area of these standards and a dilution water blank. Plot carbon concentration in milligrams per liter against corrected peak height or area on rectangular coordinate paper. This is unnecessary for instruments provided with a digital readout of concentration. If desirable, prepare a standard curve having concentrations of 1 to 10 mg/L by making appropriate dilutions of the standards.

With most TOC analyzers, it is not possible to determine separate blanks for reagent water, reagents and the entire system. In addition, some TOC analyzers produce a variable and erratic blank that cannot be corrected reliably. In many laboratories, reagent water is the major contributor to the blank value. Correcting only the peak heights of standards (which contain reagent water + reagents + system blank) creates a positive error, while also correcting samples (which contain only reagents and system blank contributions) for the reagent water blank creates a negative error. Minimize errors by using reagent water and reagents low in carbon.

Inject samples and procedural blanks (consisting of reagent water taken through any pre-analysis steps-values are typically higher than those for reagent water) and determine sample organic carbon concentrations by comparing corrected peak heights to the calibration curve.

2.2.8 Calculations

1. When reagent water is a major portion of the total blank:

- Calculate corrected peak height of standards by subtracting the reagent-water blank peak height from the standard peak heights

- Prepare a standard curve of corrected peak height vs. TOC concentration.

- Subtract the procedural blank from each sample peak height and compare to the standard curve to determine carbon content.

NOTE: There will be a positive error if the TOC of the reagent water is significant in comparison to the TOC of the sample. Make a special effort to obtain carbon-free reagent water.

- Apply the appropriate dilution factor when necessary.

- Subtract the inorganic carbon from the total carbon when TOC is determined by difference.

2. When reagent water is a minor portion of the total blank:

- Calculate corrected peak height of standards and samples by subtracting the reagent-water blank peak height from the standard and sample peak heights.

- Prepare a standard curve of corrected peak height vs. TOC concentration.

- Subtract the procedural blank from each sample peak height and compare to the standard curve to determine the carbon content. Values

will have a negative error equal to the blank contribution from the reagent water.

- Apply the appropriate dilution factor when necessary.
- Subtract the inorganic carbon from the total carbon when TOC is determined by difference.

NOTE: If the TOC analyzer design permits isolation of each of the contributions to the total blank, apply appropriate blank corrections to peak heights of standards (reagent blank, water blank, system blank) and sample (reagent blank and system blank).

Appendix B

Sample of calculations

1. Chemical oxygen demand (COD)

$$\text{COD as mg/L of } O_2 = \frac{(A - B) \times M \times 8000}{\text{ml sample}}$$

Given

Volume of FAS used for blank (A)	3.25 ml
B = Volume of FAS used for sample (B)	0.30 ml
Molarity of FAS (M)	0.043 M
Volume of sample	0.50 ml

$$\begin{aligned}\text{COD as mg/L of } O_2 &= \frac{(3.25 - 0.30) \times 0.043 \times 8000}{0.50} \\ &= 2,029.6 \text{ mg/L}\end{aligned}$$

2. COD removal efficiency

$$\text{COD removal efficiency} = \frac{\text{COD}_i - \text{COD}_t}{\text{COD}_i} \times 100$$

Given

Initial COD of solution (COD_i) 314 mg/L

COD at 24 hr (COD_{24}) 121 mg/L

$$\begin{aligned} \text{COD removal efficiency} &= \frac{314 - 121}{314} \times 100 \\ &= 61.5 \% \end{aligned}$$

3. TOC removal efficiency

$$\text{TOC removal efficiency} = \frac{\text{TOC}_i - \text{TOC}_t}{\text{TOC}_i} \times 100$$

Given

Initial TOC of solution (TOC_i) 314 mg/L

TOC at 24 hr (TOC_{24}) 121 mg/L

$$\begin{aligned} \text{TOC removal efficiency} &= \frac{142 - 56}{142} \times 100 \\ &= 60.6 \% \end{aligned}$$

4. IrO₂ film thickness

$$\text{IrO}_2 \text{ film thickness} = \frac{\text{Wt. of IrO}_2 \text{ coated Si wafer} - \text{Wt. of Si wafer}}{\text{Si wafer surface area} \times \text{IrO}_2 \text{ density}} \times 10,000$$

Given

Width of Si wafer	0.873 cm
Length of Si wafer	0.987 cm
Density of IrO ₂	11.7 g/cm ³
Weight of Si wafer	0.11920 g
Weight of IrO ₂ -coated Si wafer	0.11934 g

$$\begin{aligned} \text{IrO}_2 \text{ film thickness} &= \frac{0.11934 - 0.11920}{0.873 \times 0.987 \times 11.7} \times 10,000 \\ &= 0.139 \text{ micron} \end{aligned}$$

5. IrO₂ film growth rate

$$\text{IrO}_2 \text{ film growth rate} = \frac{\text{IrO}_2 \text{ film thickness}}{\text{Deposition time}} \times 1,000$$

Given

IrO ₂ film thickness	0.139 micron
Deposition time	300 min

$$\begin{aligned} \text{IrO}_2 \text{ film growth rate} &= \frac{0.139}{300} \times 1,000 \\ &= 0.46 \text{ nm/min} \end{aligned}$$

6. Ir film thickness

$$\text{Ir film thickness} = \frac{\text{Wt. of Ir coated Si wafer} - \text{Wt. of Si wafer}}{\text{Si wafer surface area} \times \text{Ir density}} \times 10,000$$

Given

Width of Si wafer	0.819 cm
Length of Si wafer	0.878 cm
Density of Ir	22.65 g/cm ³
Weight of Si wafer	0.10177 g
Weight of Ir-coated Si wafer	0.10185 g

$$\begin{aligned} \text{Ir film thickness} &= \frac{0.10185 - 0.10177}{0.819 \times 0.878 \times 22.65} \times 10,000 \\ &= 0.049 \text{ micron} \end{aligned}$$

7. Ir film growth rate

$$\text{Ir film growth rate} = \frac{\text{Ir film thickness}}{\text{Deposition time}} \times 1,000$$

Given

Ir film thickness 0.049 micron

Deposition time 270 min

$$\begin{aligned} \text{Ir film growth rate} &= \frac{0.049}{270} \times 1,000 \\ &= 0.18 \text{ nm/min} \end{aligned}$$

8. SnO₂ film thickness

$$\text{SnO}_2 \text{ film thickness} = \frac{\text{Wt. of SnO}_2 \text{ coated Si wafer} - \text{Wt. of Si wafer}}{\text{Si wafer surface area} \times \text{SnO}_2 \text{ density}} \times 10,000$$

Given

Width of Si wafer 0.690 cm

Length of Si wafer 0.755 cm

Density of SnO₂ 7 g/cm³

Weight of Si wafer 0.07444 g

Weight of SnO₂-coated Si wafer 0.07536 g

$$\begin{aligned}\text{SnO}_2 \text{ film thickness} &= \frac{0.07536 - 0.07444}{0.690 \times 0.755 \times 7} \times 10,000 \\ &= 2.52 \text{ micron}\end{aligned}$$

9. SnO₂ film growth rate

$$\text{SnO}_2 \text{ film growth rate} = \frac{\text{SnO}_2 \text{ film thickness}}{\text{Deposition time}} \times 1,000$$

Given

SnO ₂ film thickness	2.52 micron
Deposition time	120 min

$$\begin{aligned}\text{SnO}_2 \text{ film growth rate} &= \frac{2.52}{120} \times 1,000 \\ &= 21 \text{ nm/min}\end{aligned}$$

10. Power required

$$\text{Power required} = \frac{\text{Applied current} \times \text{Cell voltage}}{\text{Flow rate} \times 1,000}$$

Given

Applied current	0.016 A
Cell voltage	14.9 V
Flow rate	9×10^{-6} L/hr

$$\begin{aligned}
 \text{Power required} &= \frac{0.016 \times 14.9}{9 \times 10^{-6} \times 1,000} \\
 &= 26.5 \text{ kW-hr/m}^3
 \end{aligned}$$

11. Treatment cost

$$\text{Treatment cost} = \text{Power required} \times \text{Electricity cost}$$

Given

Power required	26.5 kW-hr/m ³
Electricity cost	2.5 Baht/kW-hr

$$\begin{aligned}
 \text{Treatment cost} &= 26.5 \times 2.5 \\
 &= 66.25 \text{ Baht/m}^3
 \end{aligned}$$

Biography

Mr. Songsak Klamklang was born on March 12, 1975 in Chainat province, Thailand. He got his Bachelor of Engineering in Chemical Engineering from Department of Chemical Engineering, Faculty of Engineering, Kasetsart University in 1998. He got his Master of Science in Chemical Technology from Department of Chemical Technology, Faculty of Science, Chulalongkorn University in 2000. Then, he had further persuade study and got his Doctor of Philosophy in Chemical Technology from Chulalongkorn University in 2006.