# Comprehensive Organic Parameters in Water Quality Monitoring

# Chemical Oxygen Demand ( COD)

**What is COD ?**

**oxygen equivalent of amount of organics oxidizable by a strong chemical oxidant (dichromate)**

# Method of measuring COD

- The reaction of potassium dichromate with organic compounds :

$$2Cr_2^{6+}O_7^{2-} + 16H^+ + 3C(\text{代表有机物}) \xrightarrow{\text{硫酸银}} 4Cr^{3+} + 8H_2O + 3CO_2\uparrow$$

- Measurement of excess: The excess potassium dichromate is titrated with ferrous ammonium sulfate (FAS) until all of the excess oxidizing agent has been reduced to $Cr^{3+}$.

$$Cr_2^{6+}O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

**The oxidation-reduction indicator Ferroin is added during this titration step as well. Once all the excess dichromate has been reduced, the Ferroin indicator changes from blue-green to reddish-brown.**

# Inorganic interference

- What is the most prevalent inorganic species that interferes with the COD analysis, and how is this interference dealt with?
- ----Chloride
- How it interfere?

$$Cr_2^{6+}O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 3Cl_2 \uparrow + 2Cr^{3+} + 7H_2O \uparrow$$

- How to eliminate the chloride interference ?

$$Hg^{2+} + 4Cl^- \rightarrow [HgCl_4]^{2-}$$

**Indicate whether COD results would probably be higher, lower, or the same as the true value under the following conditions, and briefly explain why:**

- **(a) mercuric sulfate was not added;**
- **----higher**
- **(b) silver sulfate was not added;**
- **----lower**
- **(c) the ferrous ammonium sulfate was assumed to have the same normality as it did 2 weeks prior to the current analysis.**
- **----higher**

# Calculation of COD

- **What is the theoretical COD of samples containing 300 mg/L of ethanol ?**

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2\uparrow + 3H_2O$$

46 96

300 COD

**COD = (300*96)/46 = 626 (mg/L)**

# Some Organics Resistant to Oxidation by dichromate

- some volatile organics
  - especially straight chain volatile organics
  - Ag catalyzes their oxidation
- other organics
  - Aromatic hydrocarbons
  - Pyridine

# Closed Reflux (micro) Method

- heat closed vial
- less sample, chemicals, apparatus
- no loss of volatile organics
- relatively safer
- heat in oven
- measure color at 600 nm or 420 nm

# Biochemical Oxygen Demand ( BOD)

**What is BOD ?**

**Biochemical oxygen demand is usually defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions.**

**The BOD test is widely used to determine the pollutional strength of domestic and industrial wastes in terms of the oxygen that they will require if discharged into natural watercourses in which aerobic conditions exist.**

# Method of measuring BOD

- The dilution method of measuring BOD is based upon the fundamental concept that the rate of biochemical degradation of organic matter is directly proportional to the amount of unoxidized material existing at the time.
- According to this concept, the rate at which oxygen is used in dilutions of the waste is in direct ratio to the percent of waste in the dilution, provided that all other factors are equal.
- For instance, a 10 percent dilution uses oxygen at one-tenth the rate of a 100 percent sample.

**List five requirements of a satisfactory dilution water for BOD work.**

- (1) freedom from toxic materials
- (2) favorable pH and osmotic conditions
- (3) presence of available accessory nutrient elements
- (4) standard temperature
- (5) presence of a significant population of mixed organisms of soil origin

## Why do the COD and BOD analyses usually give different results for the same waste?

- BOD is similar in function to COD, in that both measure the amount of organic compounds in water.
- During the determination of COD, organic matter is converted to carbon dioxide and water regardless of the biological assimilability of the substances. As a result, COD values are greater than BOD values and may be much greater when significant amounts of biologically resistant organic matter is present.

- **What could be inferred from the following analytical results concerning the relative ease of biodegradability of each waste?**

| waste | $BOD_5$ mg/L | COD mg/L |
|---|---|---|
| A | 240 | 300 |
| B | 100 | 500 |
| C | 120 | 240 |

- In determining the $BOD_5$ of a sample, an analyst added 0, 20.0, 40.0, and 100.0 mL of sample and diluted into 800 mL seperately. Dissolved –oxygen (DO) measurements were made on the samples before and after incubation at 20℃ for 5 days. The results are shown in the table. What is the $BOD_5$ for the sample?

| Sample volume, mL | DO on day 0, mg/L | DO on day 5, mg/L | $BOD_5$ mg/L |
|---|---|---|---|
| 0 | 8.16 | 7.98 | |
| 20.0 | 7.91 | 6.34 | |
| 40.0 | 7.80 | 5.66 | |
| 100.0 | 7.69 | 2.40 | |

$$BOD_5\ (mg/L) = [\ (C_1-C_2) - (B_1-B_2)f_1] / f_2$$

$B_1-B_2 = 8.16 - 7.98 = 0.18$ mg/L

| Sample volume, mL | DO on day 0, mg/L | DO on day 5, mg/L | $C_1-C_2$ mg/L | $BOD_5$ mg/L |
|---|---|---|---|---|
| 0 | 8.16 | 7.98 | 0.18 | 0.18 |
| ~~20.0~~ | ~~7.91~~ | ~~6.34~~ | ~~1.57~~ | |
| 40.0 | 7.80 | 5.66 | 2.14 | 39 |
| 100.0 | 7.69 | 2.40 | 5.29 | 41 |

**final $BOD_5$ result of the sample: (39 + 41) /2 = 40 mg/L**