ENVIRONMENTAL CHEMICAL ANALYSIS

Chapters 24-27

C. Baird and M. Cann, *Environmental Chemistry*, Freeman and Co.: New York, 2005 (3rd ed.)

Ion chromatograph: Image available at http://water.metrohm.com/images/water/

OUTLINE

- **Analysis of water and wastewater** — *Chapter 24*
  - **New developments in analytical chemistry**
  - **Methods of Analysis**
- **Analysis of wastes and solids** *- Chapter 25*
- **Analysis of air and other gases** *- Chapter 26*
- **Analysis of biological materials and xenobiotics** — *Chapter 27*

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Chapter 24

Chemical Analysis of Water and Wastewater

New developments in analytical chemistry

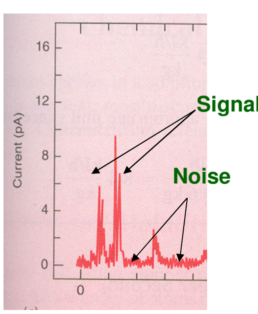
New and improved analytical techniques

- Better ***sensitivity***

  Between 2 techniques, the one that gives a better signal for a certain level of an analyte is the ***more sensitive method***

- Better ***detection limits*** (also **LOD**, for limit of detection)

  Lowest analyte concentration that can be measured above the noise level with a specified degree of confidence



NOTE: The term ***analyte*** pertains to the chemical species being analyzed

New developments in analytical chemistry, Cont.

Better sensitivity and lower LODs:

- ***Consequence***: Pollutants that escaped detection before are now detectable
  - Poses questions in the setting of ***maximum allowable limits*** (MAL) of various pollutants

Example: Arsenic's MAL in drinking water has been lowered from 50 ppb (or ug/L) to 10 ppb [effective Feb. 2002] due to better instrumentation for detecting this element and the known toxicity of As and its compounds.

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Methods of Analyzing Water and Wastewater

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Chemical parameters commonly determined in water

Chemical species	*Significance in water*	*Methods of Analysis*
Acidity	Indicates industrial pollution; acidic mine drainage	
Alkalinity	Water treatment; algal productivity	
Hardness (Ca^{2+}; Mg^{2+})	Water quality; Water treatment	
Metals (Like Pb, Cd, Hg, As, Cr)	Toxic pollutants	)
Anions (Like NO_3^- and PO_4^{3-})	Algal productivity; Toxicity; Water quality	

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Chemical parameters … (Cont.)

Chemical species (Cont.)	*Significance in water*	*Methods of Analysis*
Organic carbon	Indicates organic pollution	
Organic contaminants	Indicates organic pollution	
Oxygen demand, BOD (Biochemical)	Water quality and pollution	
Oxygen demand, COD (Chemical)	Water quality and pollution	
Pesticides	Water pollution	

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Types of Chemical Analysis

Based on information desired:

1) Qualitative = **identifies** the analyte(s)

2) Quantitative = determines the **concentration** of an analyte

Based on method:

1) Classical techniques (also called wet-chemical methods)

- Utilizes a chemical reaction with the analyte; reaction stoichiometry is used to quantify the analyte
- Examples: ***Titration, Gravimetric analysis***

2) Instrumental methods = use of modern analytical instruments to quantify and/or identify analytes

- Examples: ***Spectroscopy, Chromatography***

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Parameters that are determined using wet-chemical methods in the chemical analysis of water and wastewater

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Acidity

Why test for acidity?

- Indicates industrial pollution or acid mine drainage

Method: **Titration with a base**

- **Methyl orange endpoint** (pH 4.5) gives "***free acidity***" due to strong acids like HCl and H_2SO_4
- **Phenolphthalein endpoint** (pH 8.3) gives "***total acidity***" due to all titratable acids

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Alkalinity

Why? Alkalinity indicates algal productivity; need for water treatment

Method: Total alkalinity is determined by **titration with sulfuric acid** to the methyl orange endpoint (pH 4.5)

Example of reaction involved:

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_{2(g)}$$

bicarbonate (HCO_3^-) ***acid titrant*** (H^+)

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Alkalinity - Cont.

HCO_3^-	+	H^+	$\longrightarrow$	H_2O + $CO_{2(g)}$
bicarbonate		*acid titrant*		

Problem: A 200-mL sample of water required 25.12 mL of 0.0100 M standard H_2SO_4 for titration to the methyl orange end point. What was the total alkalinity of the water sample?

Hint: How many moles of H^+ is produced per mole of H_2SO_4?

Answer: Alkalinity = 2.5×10^{-3} M

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Dissolved Oxygen, DO

Significance in water

- Adequate dissolved oxygen is necessary for ***good water quality***. Oxygen is a necessary element to all forms of life.
- As DO levels in water drop **below 5.0 mg/l**, aquatic life is put under ***stress***. The lower the concentration, the greater the stress.
- O_2 levels that remain **below 1-2 mg/l** for a few hours can result in large ***fish kills***.

http://www.state.ky.us/nrepc/water/wcpdo.htm

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Dissolved Oxygen, DO – Cont.

Determined by the ***Winkler titration*** (below) = a 3-step reaction

Step 1: **Precipitation** of O_2 with manganese ions

$$2\ \mathbf{Mn^{2+}} + 4\ OH^- + O_2 \longrightarrow 2\ MnO_{2\,(s)} + 2\ H_2O$$

Step 2: Reaction of MnO_2 with iodide

$$2\ MnO_{2\,(s)} + 4\ \mathbf{I^-} + 8\ H^+ \longrightarrow 2\ Mn^{2+} + 2\ I_2 + 4H_2O$$

Step 3: Reduction of molecular iodine by thiosulfate ions

$$2\ I_2 + 4\ \mathbf{S_2O_3^{2-}} \longrightarrow 2\ S_4O_6^{2-} + 4\ I^-$$

thiosulfate

Overall stoichiometry: **1 mol O_2 : 2 mol I_2 : 4 mol $S_2O_3^{2-}$**

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Dissolved Oxygen, DO – *Cont.*

Problem: A 25.00-mL aliquot of a surface water sample was titrated using the Winkler method for dissolved oxygen content. The aliquot required 1.15 mL of a 0.0275 M thiosulfate. Determine the amount of **DO** in terms of **mg O_2/L** water. Is there sufficient DO to support aquatic life?

Overall stoichiometry: **1 mol O_2 : 2 mol I_2 : 4 mol $S_2O_3^{2-}$**

Work: mol $S_2O_3^{2-}$ = (0.00115 L)(0.00275 mol/L) = 3.16 x 10^{-5}

mol O_2 = (mol $S_2O_3^{2-}$)/4 = 7.91 x 10^{-6} $[O_2]$ = (7.91 x 10^{-6})/(0.02500 L) = 3.16 x 10^{-4} mol/L

$[O_2]$ in mg/L = (3.16 x 10^{-4} mol/L)(32.0 g O_2/mol)(1000 mg/g) = ***10.8 mg O_2/L*** water

Yes. **DO**

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Dissolved Oxygen, DO – *Cont.*

The volunteer on the left is titrating a water sample, while the other volunteer is "fixing" another sample (photo by K. Register).

Figure 9-4. *Titration of a reagent into a water sample.*

Image available at http://www.epa.gov/owow/estuaries/monitor/chptr09.html 17

Biochemical oxygen demand, BOD

Significance of BOD

- BOD directly affects the amount of ***dissolved oxygen*** in estuaries.
- The ***greater the BOD***, the ***more rapidly oxygen is depleted***. This means less oxygen is available to aquatic organisms.
- BOD measures the ***amount of oxygen that microorganisms consume*** while decomposing organic matter.

http://www.epa.gov/owow/estuaries/monitor/chptr09.html 18

Significant BOD Levels *(from Campbell and Wildberger, 1992).*

Type of Water	BOD (mg/l)
Unpolluted, natural water	<5
Raw sewage	150-300
Wastewater treatment plant effluent	8-150*

*Allowable level for individual treatment plant specified in discharge permit

SOURCE: http://www.epa.gov/owow/estuaries/monitor/chptr09.html

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BOD – Cont.

BOD measurement

BOD is measured by ***incubating*** a sealed sample of water for ***5 days*** followed by *measuring the* ***loss of O_2*** from the beginning to the end of the test. It uses the same method for determining DO.

An automated BOD analyzer. Image available at http://www.esi.info/detail.cfm/Skalar/SP100-biological-oxygen-demand-robotic-analyser/_/R-34115_YO196NA

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Chemical oxygen demand, COD

COD measures the ***total amount of O_2*** *needed to* *oxidize all organic matter* into CO_2 and water.

- COD does not differentiate between biologically available and inert organic matter

Thermo Scientific Orion Thermo/COD165 reactor. Image available at http://www.coleparmer.com/buy/product/91900-thermo-scientific-orion-thermo-cod165-reactor.html

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COD - Cont.

- **COD measurement** using a *closed reflux titration unit*.

(1) Digestion: Boil and reflux sample solution with chromic and sulfuric acids in the presence of excess potassium dichromate.

(2) Titration: After digestion, unreacted dichromate is ***titrated*** with ferrous ammonium sulfate (FAS)

- Determines the amount of dichromate consumed
- Oxidizable organic matter is then calculated in terms of the oxygen equivalent.

http://mollie.berkeley.edu/~bacteria/protocol%205.pdf

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

where:

A = mL FAS used for blank

B = mL FAS used for sample

M = molarity of FAS, and

8000 = milliequivalent weight of oxygen X 1000 mL/L

http://mollie.berkeley.edu/~bacteria/protocol%205.pdf

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Total Organic Carbon, TOC

Significance of TOC

- Organic matter affects a number of processes in aquatic systems, including:
    - Nutrient cycling
    - Biological activity
    - Chemical transport and interactions

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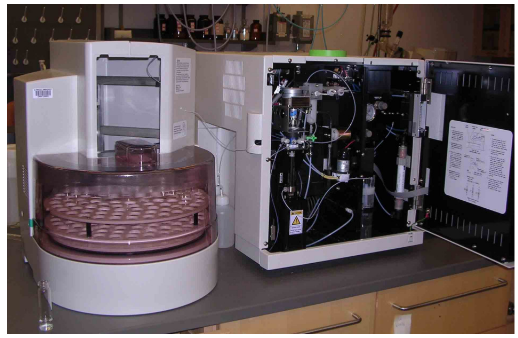
Measurement of TOC

TOC-TN Analyzer. Image available at http://www.ecs.umass.edu/eve/facilities/images/TOCTNcr1vvs.jpg

based on the high-temperature combustion method



1. Water samples are heated to 680℃ in an O_2-rich environment inside combustion tubes filled with a platinum catalyst. Here, all carbon compounds are completely oxidized to CO_2.

The CO_2 generated is detected using an **infrared** gas analyzer (NDIR). *These steps yield the total carbon,* ***TC****.*

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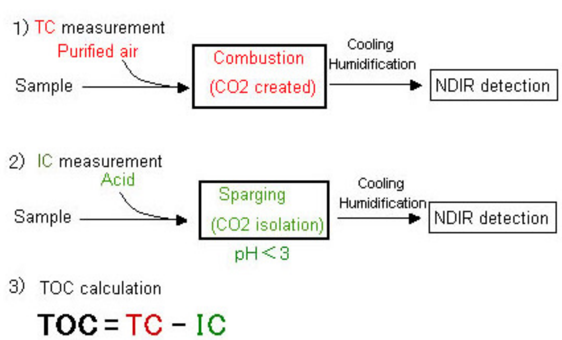
Measurement of TOC – *Cont.*

2) The oxidized sample further undergoes sparging, converting inorganic carbon, **IC,** in the sample to CO_2, which is detected with the NDIR.

3) The **TOC** concentration is then calculated by subtracting the IC concentration from the obtained TC concentration.



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Reference: http://www.shimadzu.com/an/toc/lab/toc-l4.html