LEC-5

Water Analysis

INTRODUCTION TO ENVIRONMENTAL CHEMICAL ANALYSIS

- chemical analysis are essential to environmental chemistry.
- The knowledge scientists' seek to get about pollutants :
  - a) identities and
  - b) quantities
- In different type of environmental samples:
  - a) water,
  - b) Air
  - c) soil
  - d) biological systems

The general aspects of environmental chemical analysis

<u>**analysis of**</u>

1) water
2) wastewater
3) analysis of wastes and solids
4) air and gas analysis
5) analysis of biological materials
6) xenobiotic substances

Water Analysis

Why analysis of water is very important?

1- Water is playing a major part in our lives.

2- To know types and amounts of water pollutants.

3- To know the water quality.

4- To know pollutant water sources.

5- To select the best water treatment method.

Water Analysis

1. Sampling

2. Physical investigation

3. Chemical analysis

4. Biological testing

Water Sampling and Storage Procedures

- Correct sampling and storage procedures are essential to get meaningful data about the samples.
- Preservation techniques differ significantly for different analysis ➔separate samples must be collected for chemical and biological analysis.
- The shorter the time interval between sample collection and analysis, the more accurate the analysis will be.
- Some analyses must be performed in the field within minutes of sample collection.

Water Sampling and Storage Procedures

Some analyses should performed on the body of water itself directly such as analyses of :

1) Temperature
2) pH (water pH may change within a few minutes after collection,)
3) Dissolved gases:
   a) O_2, CO_2, H_2S (hydrogen sulfide), Cl_2 (chlorine) may be lost,
   b) O_2, CO_2, may be absorbed from the atmosphere.
4) Calcium and total hardness (changes in the pH-alkalinity-cause precipitation of calcium carbonate)

Water Sampling and Storage Procedures

Other analyses that are preferred to be performed directly :

1) Redox reactions if anaerobic water sample is exposed to atmospheric oxygen cause errors in analysis of :
   a) soluble Fe^{2+} and Mn^{2+} which are oxidized to insoluble Fe^{3+} and Mn^{7+} (as MnO_4^-) compounds.
   b) I^- and CN^- frequently are oxidized.
   c) Cr^{6+} in solution may be reduced to insoluble Cr^{3+}.

Water Sampling and Storage Procedures

<u>**Other analyses that are preferred to be performed directly :**</u>

2) Microbial activity can
   a) decrease phenol or
   b) decrease biological oxygen demand(BOD) values,
   c) change the nitrate-nitrite-ammonia balance,
   d) alter the relative proportions of sulfate and sulfide.
3) silicate, and boron are leached from glass container walls.

Water Sample Preservation

Method of sample preservation

1) Refrigeration to 4°C (most general).

(Note: Freezing should be avoided because of precipitates formation of and loss of gas).

2) Acidification is commonly applied to metal samples:
   a) prevent their precipitation
   b) slows microbial action.

(Note: the samples should be filtered before adding acid to enable determination of dissolved metals.

Water Sample Preservation

various additives and treatment techniques can be employed to minimize sample deterioration.

These methods are summarized in the Table :

Preservative or technique used	Effect on sample	Type of samples for which the method is employed
Nitric acid	Keeps metals in solution	Metal-containing samples
Sulfuric acid	Bactericide	Biodegradable samples containing organic carbon, oil, or grease
	Formation of sulfates with volatile bases	Samples containing amines or ammonia
Sodium hydroxide	Forms sodium salts from volatile acids	Samples containing volatile organic acids or cyanides
Chemical reaction	Fix a particular constituent	Samples to be analyzed for dissolved oxygen using the Winkler method

Water Sample Preservation

Method of sample preservation

To ensure meaningful results, then sample holding times:

1) zero for parameters such as:
   b) temperature or
   c) dissolved oxygen measured by a probe,
2) Less than 24 hours for:
   b) acidity,
   c) alkalinity,
   d) nitrogen or
   e) phosphorus,
3) 6 months for metals.

Note: Details on water sample preservation are found in standard references on water analysis.

Physical Properties Measured in Water

Chemical substances in water samples are

1) suspended, or
2) dissolved

➔ are classified physically as:

1) Total,
2) Filterable,
3) Non-filterable, or
4) Volatile

➔ the total concentration of dissolved ionic material is measured using specific conductance (it measures the degree to which water conducts alternating current).

Physical Properties Measured in Water

The commonly determined physical properties of water are:

1) color,
2) residue (solids),
3) odor,
4) temperature,
5) specific conductance, and
6) turbidity.

Chemical Analysis

1) Total dissolved solids (TDS)
2) Acidity by pH meter
3) Determination of total alkalinity of water
4) Determination of chloride in water
5) Determination of water total hardness by EDTA
6) Separation and detection of anions by ion chromatography
7) Detection of metal ions by (ICP, AA, AE, ...)

CLASSICAL METHODS OF WATER ANALYSIS

- **Titrations (The most common classical methods for water analysis):**

1) <u>Acidity</u> is determined by titrating H^+ with base:

a) "free acidity" due to strong acids (HCl, H_2SO_4): using methyl orange endpoint (pH 4.5).

b) "total acidity" accounts for all acids except those weaker than HCO_3^-: phenolphthalein endpoint (pH 8.3).

2) <u>Alkalinity</u>

a) by titration with H_2SO_4 to pH 8.3 to neutralize bases as strong as, or stronger than: $CO_3^{2-} + H+ <==> HCO_3^-$

b) "total alkalinity" by titration to pH 4.5 to neutralize bases weaker than CO_3^{2-} or stronger than HCO_3^-:

$$HCO_3^- + H+ <==> H_2O + CO_2(g)$$

CLASSICAL METHODS OF WATER ANALYSIS

water hardness: a measure of the total concentration of Ca^{2+} and Mg^{2+} in water(titrated at pH 10 with a solution of EDTA):

Ca^{2+}(or Mg^{2+}) + H_2Y^{2-} <==> CaY^{2-} (or MgY^{2-}) + $2H^+$

1) H_2Y^{2-} = partially ionized EDTA chelating agent.
2) Eriochrome Black T is indicator (requires Mg^{2+} presence that forms a wine-red complex).

INSTRUMENTAL METHODS OF WATER ANALYSIS

Absorption Spectrophotometer

Molecular Absorption Spectrophotometer (UV/Vis):

It is useful for a number of common analytes measured in water including water pollutants some of these are:

1) **Surfactants:** The UV/vis method is based on: their reaction with methylene blue to form blue salt.
2) **Tannin and lignin :** The UV/vis method is based on: Blue color from tungstophosphoric and molybdophosphoric acids.

INSTRUMENTAL METHODS OF WATER ANALYSIS

Atomic Spectrophotometric Analysis of Water

- are favored for determination of most metals in water.

1) Flame atomic absorption: useful for a variety of metals whose concentrations are not too low.

2) Flameless (graphite furnace) atomic absorption:

- useful for metals with much lower detection limits.
- It is particularly useful for Cd, Pb, and Cr.

3) Cold vapor atomic absorption:

- It is useful for Hg, Se, and Sb
- They are measured at very low levels by reduction in solution.

INSTRUMENTAL METHODS OF WATER ANALYSIS

Inductively coupled plasma atomic emission (ICP-AES or ICP-OES) and mass spectroscopy (ICP-MS)

- **They extend the scope and speed of elemental analysis by atomic spectrometric means.**

Advantage of ICP-MS and ICP-OES

1) **Its multielement capability (up to 30 elements can be measured at once).**
2) **They can also measure some nonmetals.**

INSTRUMENTAL METHODS OF WATER ANALYSIS

Chromatographic Analysis of Water

These methods mainly iclude:

1) GC: Gas chromatography
2) GC/MS: Gas chromatography with mass spectrometric detection
3) HPLC: High performance liquid chromatography.
4) IC :Ion chromatography .

INSTRUMENTAL METHODS OF WATER ANALYSIS

Ion Chromatography

- It use conductivity detection techniques.
- It is used for common anions determination including:

arsenate,arsenite, borate, carbonate, chlorate, chlorite, cyanide, the halides, hypochlorite, hypophosphite, nitrate, nitrite, phosphate, phosphite, pyrophosphate, selenate, selenite, sulfate, sulfite, sulfide, trimetaphosphate, and tripolyphosphate.

- It can also be used for analysis of cations including the common metal ions, although they are relatively easy to determine by other means.

Chemical Parameters Commonly Determined in Water

Chemical species	Significance in water	Methods of analysis
Acidity	Indicative of industrial pollution or acid mine drainage	Titration
Alkalinity	Water treatment, buffering, algal productivity	Titration
Aluminum	Water treatment, buffering	AA,[1] ICP[2]
Ammonia	Algal productivity, pollutant	Spectrophotometry
Arsenic	Toxic pollutant	Spectrophotometry, AA, ICP
Barium	Toxic pollutant	AA, ICP
Beryllium	Toxic pollutant	AA, ICP, fluorimetry
Boron	Toxic to plants	Spectrophotometry, ICP
Bromide	Seawater intrusion, industrial waste	Spectrophotometry, potentiometry, ion chromatography
Cadmium	Toxic pollutant	AA, ICP
Calcium	Hardness, productivity, treatment	AA, ICP, titration
Carbon dioxide	Bacterial action, corrosion	Titration, calculation
Chloride	Saline water contamination	Titration, electrochemical, ion chromatography
Chlorine	Water treatment	Spectrophotometry
Chromium	Toxic pollutant (hexavalent Cr)	AA, ICP, colorimetry
Copper	Plant growth	AA, ICP
Cyanide	Toxic pollutant	Spectrophotometry, potentiometry, ion chromatography
Fluoride	Water treatment, toxic at high levels	Spectrophotometry, potentiometry, ion chromatography
Hardness	Water quality, water treatment	AA, titration
Iodide	Seawater intrusion, industrial waste	Catalytic effect, potentiometry, ion chromatography
Iron	Water quality, water treatment	AA, ICP, colorimetry
Lead	Toxic pollutant	AA, ICP, voltammetry

Table 26.4 (Cont.)

Lithium	May indicate some pollution	AA, ICP, flame photometry
Magnesium	Hardness	AA, ICP
Manganese	Water quality (staining)	AA, ICP
Mercury	Toxic pollutant	Flameless atomic absorption
Methane	Anaerobic bacterial action	Combustible-gas indicator
Nitrate	Algal productivity, toxicity	Spectrophotometry, ion chromatography
Nitrite	Toxic pollutant	Spectrophotometry, ion chromatography
Nitrogen (albuminoid)	Proteinaceous material	Spectrophotometry
(organic)	Organic pollution indicator	Spectrophotometry
Oil and grease	Industrial pollution	Gravimetry
Organic carbon	Organic pollution indicator	Oxidation-CO_2 measurement
Organic contaminants	Organic pollution indicator	Activated carbon adsorption
Oxygen	Water quality	Titration, electrochemical
Oxygen demand (biochemical)	Water quality and pollution	Microbiological-titration
(chemical)	Water quality and pollution	Chemical oxidation-titration
Ozone	Water treatment	Titration
Pesticides	Water pollution	Gas chromatography
pH	Water quality and pollution	Potentiometry
Phenols	Water pollution	Distillation-colorimetry
Phosphate	Productivity, pollution	Spectrophotometry
Phosphorus (hydrolyzable)	Water quality and pollution	Spectrophotometry
Potassium	Productivity, pollution	AA, ICP, flame photometry
Selenium	Toxic pollutant	Spectrophotometry, ICP, neutron activation
Silica	Water quality	Spectrophotometry, ICP
Silver	Water pollution	AA, ICP

Chemical Parameters Commonly Determined in Water

Table 26.4 (Cont.)

Sodium	Water quality, saltwater intrusion	AA, ICP, flame photometry
Strontium	Water quality	AA, ICP, flame photometry
Sulfate	Water quality, water pollution	Ion chromatography
Sulfide	Water quality, water pollution	Spectrophotometry, titra-ion, chromatography
Sulfite	Water pollution, oxygen scavenger	Titration, ion chromatography
Surfactants	Water pollution	Spectrophotometry
Tannin, Lignin	Water quality, water pollution	Spectrophotometry
Vanadium	Water quality, water pollution	ICP
Zinc	Water quality, water pollution	AA, ICP

[1] AA denotes atomic absorption
[2] ICP stands for inductively coupled plasma techniques, including atomic emission and detection of plasma-atomized atoms by mass spectrometry.