CIVE 450: Water and Wastewater Treatment and Laboratory

LAB SESSION 3: SOLIDS - TOTAL, SUSPENDED, DISSOLVED, FIXED, VOLATILE, & SETTLEABLE (Dr. L. Semerjian)

I. General Discussion

All matter except the water contained in liquid and semi-liquid materials is classified as solid matter. However, analytically, the usual definition of solids refers to the matter that remains as *residue upon evaporation and drying at 103 to 105 °C*. Typically, gravimetric methods are used for the determination of most types of solids. Exceptions are the volumetric measurement of settleable solids, and the estimation of dissolved solids by conductance measurements.

II. Types of Solids

Total solids (TS) is the term applied to the material residue left in a vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature of 103-105 °C. Total solids include *total suspended solids* and *total dissolved solids*.

Total suspended solids (TSS) are the portion of total solids retained by a filter of 2.0 μm (or smaller) nominal pore size. The type of filter holder, pore size, porosity, area, and thickness of the filter, and the physical nature, particle size, and amount of material deposited on the filter are the principal factors effecting separation of suspended solids. Total suspended solids may be also termed as non-filterable solids.

Total dissolved solids (TDS) is the portion of total solids that passes through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. Dissolved solids may be determined either by gravimetry or conductance measurements. Gravimetrically, dissolved solids are the material residues left in a vessel after evaporation of the filtrate and its subsequent drying in an oven at a defined temperature of 180 °C. Total dissolved solids may be also termed as filterable solids.

Fixed solids (FS) is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature (550°C). The weight loss on ignition is called *volatile solids (VS)*. Determinations of fixed and volatile solids do not distinguish precisely between organic and inorganic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts.

Settleable solids is the term applied to the material settling out of suspension by gravity under quiescent conditions within a defined period. It may include floating material, depending on the technique.

III. Environmental Significance of Solids Determinations

- *Water supplies:* Determination of TDS concentrations is mostly significant since they determine the suitability of water for domestic and potable use. In general, waters with a TDS content of less than 500 mg/L are most desirable for such purposes. Waters with higher solid contents often cause digestive problems. In cases in which turbidity

measurements are not deemed adequate to provide the necessary information, TSS measurements on water supplies may be required.

- *Polluted waters and domestic wastewaters:* Settleable and suspended solids determinations are of greatest value in assessing the strength of domestic wastes and lightly polluted waters. They are exremely valuable in determining the efficiency of wastewater treatment units and identifying changes in the density of wastewaters.

- *Industrial wastewaters*: The settleable solids test is particularly inportant in determining whether primary sedimentation facilities are required for treatment. Determination of inorganic dissolved salts are significant in determining the susceptibility of wastes to anaerobic treatment.

- *Sludges:* The total and volatile solids determinations are important in the analysis of raw and digested sludges. They are indispensable in the design and operation of sludge digestion, dewatering and incineration units.

IV. Laboratory Demonstration: Gravimetric Determination of Total, Dissolved, Suspended, Fixed, Volatile, and Settleable Solids

Scope and application

These methods are applicable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20,000 mg/L.

Objectives of experiment

- Gravimetric determination of total solids dried at 103–105°C.
- Gravimetric determination of dissolved solids dried at 180°C.
- Gravimetric determination of total suspended solids dried at 103–105°C.
- Gravimetric determination of fixed and volatile solids ignited at 550°C.
- Gravimetric and volumetric determination of settleable solids.

Sample handling and preservation requirements

- ❑ Collect samples in resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls.
- ❑ Analyze samples as soon as possible, otherwise refrigerate samples up to the time of analysis to minimize microbiological decomposition of solids.
- ❑ Preferably do not hold samples more than 24 hours. In no case hold samples more than 7 days.
- ❑ Bring samples to room temperature before analysis.

A. Determination of Total Solids (Gravimetric)

Summary of method

A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103-105°C. The increase in weight over that of the empty dish represents the total solids.

Calculation and data reporting

$$\textbf{Total solids, mg/L} = [(A - B) \times 1000] / C$$

Where,
A = weight of dried residue + dish, mg
B = weight of dish, mg
C = sample volume, ml

B. DETERMINATION OF TOTAL DISSOLVED SOLIDS (GRAVIMETRIC)

Summary of method

A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a wighed dish and dried to constant weight at 180°C to lose almost all mechanically occluded water. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

Calculation and data reporting

$$\textbf{Total dissolved solids, mg/L} = [(A - B) \times 1000] / C$$

Where,
A = weight of dried residue + dish, mg
B = weight of dish, mg
C = sample volume, ml

C. DETERMINATION OF TOTAL SUSPENDED SOLIDS (GRAVIMETRIC)

Summary of method

A well-mixed sample is filtered through a weighed standard glass fiber filter, and the residue retrained on the filter is dried to constant weight at 103-105°C. The increase in weight of filter represents the total suspended solids. The difference between the total solids and total dissolved solids may also provide an estimate of the total suspended solids.

Calculation and data reporting

$$\textbf{Total suspended solids, mg/L} = [(A - B) \times 1000] / C$$

Where,
A = weight of dried residue + filter + aluminum dish, mg
B = weight of filter + aluminum dish, mg
C = sample volume, ml

D. DETERMINATION OF FIXED AND VOLATILE SOLIDS

Summary of method

The residue from Methods A, B, or C is ignited to constant weight at 550°C. The remaining solids represents the fixed total, dissolved, or suspended solids, while the weight lost on ignition is the volatile solids.

Calculation and data reporting

Volatile solids, mg/L = [(A – B) × 1000] / D

Fixed solids, mg/L = [(B – C) × 1000] / D

Where,
A = weight of dried residue + dish or filter before ignition, mg
B = weight of dried residue + dish or filter after ignition, mg
C = weight of dish or filter, mg
D = sample volume, ml

E. DETERMINATION OF SETTLEABLE SOLIDS

Summary of method

Settleable solids may be determined either volumetrically or gravimetrically. Volumetric determination is applied to the material settling out of suspension by gravity under quiescent conditions within a defined period. Gravimetric determination utilizes the procedure of TSS.

Apparatus and glassware needed

- Volumetric test: Imhoff cone
- Gravimetric test: All *"Apparatus and glassware needed"* in section IVC.

Procedure

Volumetric determination:

- ❑ Fill an imhoff cone to the 1-L mark with well-mixed sample.
- ❑ Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle for an additional 15 min.
- ❑ Record volume of settleable solids in the cone as milliliters per liter.
- ❑ If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids.
- ❑ Do not estimate floating matter as settleable solids.

Gravimetric determination:

- ❑ Determine total suspended solids as described in section IVC.
- ❑ Pour a well-mixed sample into a glass vessel of not less than 9 cm diameter, and using not less than 1 liter and sufficeint sample to give a depth of 20 cm.
- ❑ Let stand quiescent for 1 hour, and without disturbing the settled or floating matter, siphon 250 ml from center of container at a point halfway between the surface of the settled material and the liquid surface.
- ❑ Determine TSS of this supernatant liquor. These are the non-settleable solids.
- ❑ Calculate settleable solids as follows:

Settleable solids, mg/L = total suspended solids, mg/L – non-settleable solids, mg/L

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LAB SESSION 3A: NITROGENOUS COMPOUNDS/NITRATE (Dr. L. Semerjian)

I. General Discussion

Nitrogenous compounds are of great interest to environmental engineers because of their importance in the life processes of all plants and animals. The chemistry of nitrogen is complex because of the several oxidation states that nitrogen can assume; however, the most dominating nitrogen species of environmental concern are organic nitrogen (proteins), ammonia (NH_3) and ammonium (NH_4^+), nitrogen (N_2), nitrates (NO_3^-), and nitrites (NO_2^-).

II. Environmental Significance of Nitrogen Data

- Prior to the development of bacteriological tests for determining the quality of waters and specifying the time of contamination, water supplies were analyzed for nitrogen compounds. Originally most of the nitrogen is present in the form of organic (protein) nitrogen and ammonia. As time progresses, more ammonia will be present, and later on, if aerobic conditions prevail, nitrites and nitrates will dominate. Therefore, waters that contained mostly organic and ammonia nitrogen were considered to have been recently polluted and thus pose health threat. Whereas waters with high levels of nitrate nitrogen were considered to have been polluted a long time ago and thus offered little threat to public health. However, high levels of nitrates often cause methemoglobinemia in infants; thus their concentration has been limited by the US Environmental Protection Agency to 10 mg/L as NO_3-N (44 mg/L $NO3^-$) in potable waters.
  Recent bacteriological test are more reliable, thus they have eliminated the need for extended nitrogen analysis to determine sanitary quality of waters.
- Nitrogen analysis is important in all biological wastewater treatment processes, since they serve as essential nutrients for the growth and reproduction of employed microorganisms. Also, nitrogen analysis is important in circumstances where algae growth is problematic in wastewater receiving water bodies.
- Ammonia nitrogen discharge into rivers and estuaries may seriously reduce dissolved oxygen levels, and thus pose a threat to aquatic life. The problem even aggravates when effluents rich in nitrifying bacteria from highly efficient biological treatment plants are discharged. One way to control such bacteria is by disinfection. Therefore, nitrogen analyses are important in assessing the possible significance of the problem, and in the operation of treatment processes designed to reduce ammonia discharge.
- Determinations of nitrogen are also significant in designing treatment schemes and controlling the degree of purification produced in biological treatment. For instance, unionized ammonia is toxic to fish life but ammonium is not, so different limits have been imposed for different nitrogenous compounds in treated wastewater effluents prior to discharge into receiving water bodies.

III. Application of Nitrogen Data

- In connection with disinfection practice to determine the amount of chlorine needed to obtain free chlorine residuals in breakpoint chlorination and to determine to some extent the ratio of monochloramines to dichloramines.
- Nitrate determinations are important in determining whether water supplies meet set guidelines for the control of methemoglobinemia in infants.

- For optimizing, controlling, and monitoring of biological wastewater treatment schemes.
- For assessing the fertilizing value of sludge before their application to soils.
- For stream pollution control where adequate dissolved oxygen levels are to be maintained and algae growth is to be inhibited.

IV. Laboratory Demonstration: Colorimetric Method for the Determination of Nitrate-N (using HACH reagent powder pillows)

CADMIUM RDUCTION METHOD FOR NITRATE-NITROGEN

Scope and application

This method is applicable to water and wastewater samples. Seawater samples can be analyzed; however, manual calibration is required. The measuring range is 0 to 30.0 mg/L NO_3^--N.

Objectives of experiment

Determination of nitrate-nitrogen in water, wastewater, and seawater samples.

Summary of method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. This salt couples to gentisic acid to form an amber-colored product whose intensity is determined colorimetrically at 500 nm.

Apparatus and glassware needed

- ❑ HACH DR 2010 Spectrophotometer
- ❑ Sample cells, 25-ml, matched-pairs
- ❑ Stoppers, rubber, size #2

Reagents and standards needed

- ❑ NitraVer 5 Nitrate Reagent powder pillows.
- ❑ Nitrate-nitrogen standard solution (optional)
- ❑ Concentrated sulfuric acid
- ❑ Sodium hydroxide, 5.0N
- ❑ Distilled or de-ionized water

Sample handling and preservation requirements

- ❑ Collect samples in clean plastic or glass bottles.
- ❑ Analyze samples as soon as possible. Alternatively, refrigerate samples to be analyzed within 24 to 48 hours.
- ❑ For maximum recommended storage periods up to 28 days, acidify samples to pH <2 with sulfuric acid and refrigerate. Before testing the stored samples, neutralize the sample with 5.0N sodium hydroxide.
- ❑ Warm samples to room temperature before analysis.

Procedure

1. Pour 25 ml sample into a 25-ml sample cell (SAMPLE)
2. Add the contents of one NitraVer 5 nitrate reagent powder pillow to the cell, stopper.
3. Shake the cell vigorously for 1 minute.
4. Allow a 5-minute reaction time, an amber color will develop if nitrate nitrogen is present.
5. Fill another 25-ml sample cell with 25-ml *sample* (BLANK). Place the BLANK into the cell holder, close the light shield, and ZERO the spectrophotometer.
6. READ the reacted sample at 500 nm, and record results as nitrate or nitrate-nitrogen in mg/L.

Interferences

Strong oxidizing and reducing substances, ferric iron, and chloride concentrations >100 mg/L may cause interferences. Nitrite interference may be compensated by adding bromine water and phenol solution, and results reported as total nitrate and nitrite.

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LAB SESSION 3B: PHOSPHATE (Dr. L. Semerjian)

I. General Discussion

The inorganic compounds of phosphorus most significant in environmental engineering practice are the phosphates or their molecularly dehydrated forms. Organically bound phosphorus is usually of minor consideration.
In public water supplies, polyphosphates are used to control corrosion, and to stabilize calcium carbonate in softened waters. In surface waters, polyphosphates are significant in the control of algal blooms. In domestic wastewaters, phosphorus and polyphosphates mainly originate from synthetic detergents. In fact, certain amounts of phosphorus are necessary in biological wastewater treatment schemes to ensure the reproduction and synthesis of new bacterial cell tissues. Phosphorus may also end up in the sludge generated from aerobic and anaerobic treatment processes and add to its fertilizing value.
On the other hand, phosphate compounds are widely used in steam power plants to control scaling in boilers.

II. Application of Phosphorus Data

- For corrosion prevention in water systems and control of scale in boilers.
- For assessing the potential biological productivity of surface waters.
- For assessing the operation of wastewater treatment plants.

III. Laboratory Demonstration:
Colorimetric Method for the Determination of Ortho-phosphates
(using HACH PhosVer 3 powder pillows of ascorbic acid method)

Scope and application

This method is applicable to water, wastewater, and seawater samples. The measuring range is 0.0 to 2.5 mg/L PO_4^{3-}.

Objectives of experiment

Determination of ortho-phosphates in water, wastewater, and seawater samples.

Summary of method

Orthophosphates react with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. The developed color is measured colorimetrically at 890 nm.

Apparatus and glassware needed

- ❑ HACH DR 2010 Spectrophotometer
- ❑ Sample cells, 10-ml, matched-pairs
- ❑ Cell riser, 10-ml

Reagents and standards needed

- ❑ PhosVer 3 phosphate reagent powder pillows
- ❑ Distilled or de-ionized water

Sample handling and preservation requirements

- ❑ Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 hydrochloric acid solution and rinsed with distilled water.
- ❑ Analyze samples as soon as possible for best results. Alternatively, filter and refrigerate samples
- ❑ Samples preserved in this manner are stable for a maximum recommended storage period of 48 hours

Procedure

1. Pour 10 ml sample into a 10-ml clean sample cell (SAMPLE)
2. Add the contents of one PhosVer3 phosphate reagent powder pillow to the cell. Swirl immediately to dissolve.
3. Allow a 2-minute reaction time
4. Pour 10 ml of de-ionized water into a second 10-ml sample cell (BLANK)
5. Place the BLANK into the cell holder, close the light shield, and ZERO the spectrophotometer at 890 nm.
6. Read the reacted SAMPLE at 890 nm, and record results in terms of phosphorus (P), phosphates ($PO4^{3-}$), or phosphorus pentoxide (P_2O_5) in mg/L.

Interferences

Large amounts of turbidity may cause inconsistent results in the phosphate test. Arsenate and hydrogen sulfide may also interfere. Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
The following ions may interfere when exceeding the listed below concentrations:

Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Zinc	80 mg/L

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LAB SESSION 4A: BIOCHEMICAL OXYGEN DEMAND (Dr. L. Semerjian)

I. General Considerations

Biochemical oxygen demand is usually defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions and at normal temperature (20°C). 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.

The BOD test may be considered as a wet oxidation procedure in which the living organisms serve as the medium for oxidation of the organic matter to carbon dioxide and water by consuming a quantitative amount of oxygen. Thus, it is possible to interpret BOD data in terms of organic matter on the basis of the following relationship:

$$C_nH_aO_bN_c + (n + a/4 - b/2 - 3c/4)\ O_2 \rightarrow nCO_2 + (a/2 - 3c/2)\ H_2O + cNH_3$$

Theoretically, an infinite time is required for complete biological oxidation of organic matter, but for all practical purposes, the reaction may be considered complete in 20 days at a temperature of 20°C. However, a 20-day period will render the test very long; thus the test has been developed on the basis of a 5-day incubation period since it has been found by experience that 70-80 percent of the total BOD is exerted in 5 days. Moreover, the 5-day incubation period was selected to minimize interference form oxidation of ammonia.

In the BOD test, the major requirements are (1) freedom from toxic materials, (2) favorable pH and osmotic conditions, (3) presence of nutrient elements, (4) standard temperature, and (5) presence of a significant population of mixed organisms of soil origin.

II. Application of BOD Data

- Determination of pollutional strengths of domestic and industrial wastes.
- Measurement of amount of biologically oxidized organic matter.
- Regulatory purposes, especially for controlled discharge of industrial wastewaters into receiving water bodies or sewers, to maintain desired dissolved-oxygen levels.
- Evaluation of purification capacities of receiving water bodies.
- Design, monitoring, and efficiency evaluation of wastewater treatment plants.

III. Methods of Determination

BOD test is based on the determination of dissolved oxygen levels. BOD may be measured directly in a few samples, but in general, a dilution procedure is required.

Direct method: This method is typical for samples whose BOD_5 does not exceed 7 mg/L, thus no dilution is needed. Mostly river samples fall in this category. In this method, the sample is adjusted to 20°C and aerated to nearly saturation. Then, the dissolved oxygen levels are measured at day 0 and after 5 days of incubation. BOD_5 is calculated by subtraction of the 5-day results from those obtained on day 0.

Dilution method: This method of measuring BOD_5 is based upon the concept that the rate of biochemical degradation of organic matter is directly proportional to the amount of

unoxidized material existing at the time. Therefore, 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. Similar to the direct method, dissolved oxygen levels are measured on day 0 and day 5 of incubation and BOD_5 values are calculated from the difference, considering the observed dilution factor.

IV. Laboratory Demonstration: Membrane Electrode Method for Determination of DO/BOD

Scope and application

The Biochemical Oxygen Demand test (BOD_5) is used for determining the oxygen uptake of surface waters, domestic and industrial wastes. This method is approved for compliance monitoring. The method can be used to determine BOD_5 concentration up to 70,000 mg/L. The reporting limit for this method is 2 mg/L.

Objectives of experiment

- Determination of BOD_5 values for water samples
- Determination of BOD_5 values for wastewater samples

Summary of method

The BOD test is an empirical bioassay procedure, which measures the dissolved oxygen (DO) consumed by microbial life while assimilating and oxidizing the organic matter present in a sample.

Apparatus and glassware needed

- ❑ Dissolved oxygen meter (bench-top WTW Oxi538)
- ❑ Dissolved oxygen membrane electrode (WTW StirrOx G)
- ❑ 300-ml BOD incubation bottles with plastic caps to maintain water seals.
- ❑ Thermostatically controlled incubator at 20± 1°C.
- ❑ Assorted pipettes - Eppendorf and volumetric pipettes.
- ❑ Graduated Cylinders, 10 mL, 25 mL, 50 mL, and 100 mL.

Reagents and standards needed

- ❑ Chlorine-free distilled water or de-ionized water
- ❑ Dilution water:
  - Potassium dihydrogen phosphate (KH2 PO4 .7H2 O) - ACS grade reagent.
  - Di-potassium hydrogen phosphate (K_2HPO_4)
  - Di-sodium hydrogen phosphate ($Na_2HPO_4.7H_2O$)
  - Ammonium chloride (NH_4Cl) - ACS grade reagent.
  - Magnesium sulfate ($MgSO_4.7H_2O$) ACS grade reagent.
  - Calcium chloride ($CaCl_2$) anhydrous - ACS grade reagent.
  - Ferric chloride ($FeCl_3.6H_2O$) - ACS grade reagent
- ❑ Hydrochloric acid (HCl), 1N
- ❑ Sodium hydroxide (NaOH), 1N
- ❑ Sodium sulfite (Na_2SO_3) anhydrous - ACS grade reagent

- ❑ Commercial seed of microbial population or fresh domestic wastewater
- ❑ 2-chloro-6-trichloro methyl pyridine (TCMP) for nitrification inhibition.

Sample handling and preservation requirements

- ❑ Collect samples in clean glass or plastic bottles.
- ❑ Analyze samples as soon as possible; otherwise refrigerate. Refrigerated samples are stable for a maximum recommended period of 6 hours.
- ❑ Warm chilled samples to 20°C before analysis.

Procedure

Preparation of dilution water: Place desired volume of chlorine-free distilled water in a suitable bottle and add necessary chemicals mentioned above. Test the BOD_5 of dilution water (preferably not exceeding 0.1 mg/L, maximum 0.2 mg/L), and store in cotton-plugged bottles to permit aeration.

Seeding: For samples that do not contain a sufficient microbial population, the dilution water must be seeded by adding a population of microorganisms. The seed source may be the effluent of biological treatment, or supernatant of domestic wastewater settled at room temperature for at least 1 hour but no longer than 36 hours. Optionally use a soil suspension or activated sludge, or a commercial seed preparation. Determine the BOD_5 of the seeding material as for any other sample to serve as the seed control. The dissolved oxygen uptake of seeded dilution water should be between 0.6 and 1.0 mg/L.

Sample pretreatment:

- ❑ Neutralize acidic or alkaline samples to pH 6.5 to 7.5.
- ❑ If possible, avoid samples containing residual chlorine; otherwise de-chlorinate samples with sodium sulfite and seed dilution water.
- ❑ Samples supersaturated with dissolved oxygen should be brought to nearly saturation dissolved oxygen levels.
- ❑ Cold samples should be brought to a temperature of 20°C before dilution and analysis.
- ❑ If nitrification inhibition is desired, 2-chloro-6-trichloro methyl pyridine (TCMP) should be added to each bottle or dilution water.

Dilution techniques: Dilutions that result in a residual dissolved oxygen of at least 0.1 mg/L and a dissolved oxygen uptake of at least 2 mg/L after 5 days of incubation produce the most reliable results. Make several dilutions of a prepared sample to obtain uptakes in this range. In the absence of prior knowledge, use the following dilutions as a guide: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25 % for biologically treated effluents, and 25 to 100 % for polluted river waters. Dilution can be performed directly in BOD incubation bottles by adding desired sample volume to individual BOD bottles, seeding if necessary, and filling the bottle with enough dilution water so that the insertion of stopper will displace all air, leaving no air bubbles.

Determination of initial dissolved oxygen (See DO lab session)*:* Determine initial dissolved oxygen preferably immediately after filling BOD bottle with diluted sample. Also, determine initial oxygen levels of dilution water blanks and, where appropriate, seed controls.

Incubation: Water seal and incubate at 20±1°C BOD bottles containing diluted samples, seed controls, and dilution water blanks.

Determination of final dissolved oxygen (See DO lab session)*:* After 5 days of incubation, determine dissolved oxygen levels by immediately inserting the probe into the opened BOD bottles.

Interferences

- All toxic substances that inhibit the activity of microbial life will decrease BOD values e.g. Cr, Cu, Cl_2
- Residual chlorine and hydrogen sulfide desensitize the dissolved oxygen probe.
- Samples, such as a supernatant from activated sludge, may be supersaturated with dissolved oxygen and should be agitated to reduce the oxygen levels below saturation at 20°C. If this is not done, dissolved oxygen will separate from the water, resulting in erroneous values.
- Refrigerated samples will have elevated dissolved oxygen values. Samples must be adjusted to room temperature before the analysis begins.
- High or low sample pH may cause low results.

Calculation and data reporting

When dilution water is not seeded:

$$\mathbf{BOD_5,\ mg/L = (D1-D2)/P}$$

When dilution water is seeded:

$$\mathbf{BOD_5,\ mg/L = [(D1-D2) - (B1-B2)}f\mathbf{\ ]/P}$$

Where,
D1 = Dissolved oxygen of diluted sample immediately after preparation, mg/L
D2 = Dissolved oxygen of diluted sample after 5 day incubation at 20°C, mg/L
P = Decimal volumetric fraction of sample used
B1 = DO of seed control before incubation, mg/L
B2 = DO of seed control after incubation, mg/L
f = Ratio of seed in diluted sample to seed in seed control = (% seed in diluted sample)(% seed in seed control)

- Average results for replicate samples in the acceptable range.
- Do not make corrections for dissolved oxygen uptake by the dilution water blank if the water meets the blank criteria ($BOD_5 \leq 0.2$ mg/L). If water does not meet these criteria, results are questionable and proper corrections are difficult.

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LAB SESSION 4B: CHEMICAL OXYGEN DEMAND (Dr. L. Semerjian)

I. General Considerations

The chemical oxygen demand (COD) test is widely used to measure the organic strength of domestic and industrial wastes. The organic strength is measured in terms of the total quantity of oxygen required for oxidation of organics into carbon dioxide and water. The principle of the test is based upon the fact that all organic compounds, with a few exceptions, can be oxidized by the action of strong oxidizing agents under acid conditions.
Limitations of test: Inability of COD test to differentiate between biologically oxidizable and biologically inert organic matter since organic matter is converted to carbon dioxide and water regardless of the biological degradability of the substances. This is the reason why COD values are greater than BOD values, and may be much greater when significant amounts of biologically resistant organic matter is present.
Another limitation of the COD test is that it does not provide any evidence of the rate at which the biologically active material would be degraded under normal conditions.
Advantages of test: COD test can be completed within 3 hours versus 5 days for BOD_5 test

II. Application of COD Data

- Regulatory purposes, especially for controlled discharge of industrial wastewaters into receiving water bodies or sewers.
- Monitoring the operation of wastewater treatment plants
- Indicating toxic conditions and the presence of biologically resistant organic substances.

III. Methods of Determination

COD can be measured in one of three ways as described in "Standard Methods for the Examination of Water and Wastewater", namely

A. Open reflux, titrimetric method
B. Closed reflux, titrimetric method
C. Closed reflux, colorimetric method

The test principles are essentially the same for the three methods as described in section IV. Method A is suitable for a wide range of wastes where a large sample size is preferred. Methods B and C are more economical in the use of metallic salt reagents, but require homogenization of samples containing suspended solids to obtain reproducible results.

IV. Laboratory Demonstration: Closed Reflux Colorimetric Determination of COD

Scope and application

This method covers the determination of COD in potable and groundwaters, surface waters, as well as domestic and industrial wastewaters. The working range of the analysis is 0-15,000 mg/l.

Objectives of experiment

- Determination of COD values for water samples
- Determination of COD values for wastewater samples

Summary of method

Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. In this procedure, the sample is refluxed in strongly acid solution with an excess strong oxidizing agent of potassium dichromate ($K_2Cr_2O_7$) in capped culture tubes. The sample is heated for two hours at 150°C. Oxidizable organic compounds react, reducing dichromate ion ($Cr_2O_7^{2-}$) to green chromic acid (Cr^{3+}). When the 0-150 mg/L colorimetric method is used, the amount of Cr^{6+} remaining is determined. When the 0-1,500 or 0-15,000 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.
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.

Apparatus and glassware needed

- ❑ Blender or homogenizer
- ❑ HACH DR 2010 or 4000U Spectrophotometer
- ❑ HACH COD reactor adjustable to 150°C
- ❑ Pipet, volumetric, 2.00 ml
- ❑ Pipet, Eppendorf, 0.1-1.0 ml
- ❑ Test tube rack

Reagents and standards needed

- ❑ COD reagent vials, Low range (0-150 mg/L)
- ❑ COD reagent vials, High range (0-1500 mg/L)
- ❑ COD reagent vials, Ultra high range (0-15000 mg/L)
- ❑ Potassium hydrogen phthalate standard (425 mg in 1000 ml distilled water) having a theoretical COD of 500 mg/L.
- ❑ Distilled or de-ionized water
- ❑ Mercuric sulfate, crystals

Sample handling and preservation requirements

- ❑ Preferably collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination.
- ❑ Test unstable samples without delay. If delay before analysis is unavoidable, preserve all samples by acidification to pH ≤ 2 using concentrated sulfuric acid and refrigerate.
- ❑ Preserved samples are stable for a maximum recommended period of 7 days.
- ❑ Blend samples containing settleable solids with a homogenizer to permit representative sampling.

Procedure

1. Turn on the COD reactor to preheat to 150°C (about 30 min).
2. Mix the sample and homogenize 100 ml of sample for 30 seconds in a blender (for samples containing large amounts of solids).
3. Remove the cap of a COD digestion vial of the appropriate range; hold the vial at 45-degree angle and pipet 2.0 ml of the sample or de-ionized water (blank) into the vial. (0.2 ml for the ultra high range).
4. Replace the vial caps tightly. Rinse the outside of the COD vials with de-ionized water and wipe the vials clean with a paper towel.
5. Invert the capped vials several times gently to mix the contents. Place the vials into the preheated COD reactor and heat for 2 hours.
6. Turn the reactor off. Wait about 20 minutes for the vials to cool to 120°C or less.
7. Invert vials several times while still warm, place them into a rack, and wait until the vials have cooled to room temperature.
8. Follow manufacturer's instructions for measurement of COD on HACH DR 2010 spectrophotometer.

Interferences

- Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent since such organics are present in the vapor space and do not come in contact with the oxidizing liquid. Such compounds oxidize more effectively when silver sulfate is added as a catalyst.
- Certain reduced inorganic ions, such as chlorides, bromide, and iodide, can be oxidized under the conditions of the COD test and thus can cause erroneous high results. Fortunately, this interference can be eliminated by the addition of mercuric sulfate prior to the addition of other reagents.
- Nitrites are oxidized to nitrites and this interference can be overcome by the addition of sulfamic acid to the dichromate solution. However, significant amounts of nitrites seldom occur in natural waters. This also holds true for other possible interferences such as ferrous iron and sulfides.

Exercise B

1. Calculate TS, TDS, TSS, VSS, VS, FS, and FSS in mg/L from the following information:

A = Weight of empty crucible (heated at 105°C/180°C) = 110 mg

B = Weight of aluminum dish + filter (heated at 105°C) = 50 mg

C = Weight of crucible + solids (heated at 105°C) = 190 mg

D = Weight of aluminum dish + filter + solids (heated at 105°C) = 80 mg

E = Weight of crucible + solids (ignited at 550°C) = 125 mg

F = Weight of aluminum dish + filter + solids (ignited at 550°C) = 55 mg

G = Volume of sample = 100 ml

2. Is it advisable to use a biological or a chemical treatment for a wastewater having a BOD_5 = 200 mg/L and a COD = 200 mg/L? Explain why?