Wastewater Operator Certification Training

Module 12: Laboratory Overview

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Unit 1 – Laboratory Equipment, Terms, and Techniques

Learning Objectives

- List the various types of glassware used in a laboratory and explain the use of each.
- List the various types of preparatory equipment and explain the use of each.
- List the various types of analytical equipment and explain the use of each.
- List and define the pertinent chemical, biological, and analytical terms.
- List six sample preparation techniques and explain the importance of each.
- List five common sample analysis techniques and explain the importance of each.

Glassware

One of the things that impresses most people the first time they enter an analytical laboratory is the many different types of glassware that are used. Each piece of glassware is constructed to be used for a particular purpose. The following are some common pieces of glassware found in an analytical laboratory:

Beaker

- A beaker is the most common of all laboratory glassware.
- Beakers come in many different volumes and are used primarily to mix chemicals.
- Beakers should not be used to measure accurate volumes.

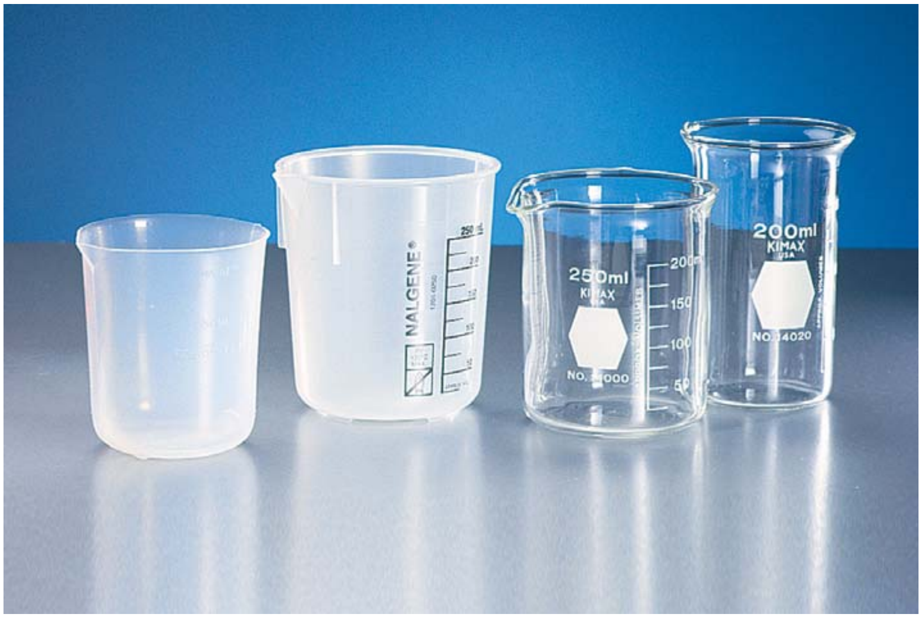

Figure 1.1 Beakers[1]

Graduated Cylinder

- Graduated cylinders come in a variety of sizes and are used primarily to measure accurate volumes of chemicals or solutions.
- Some graduated cylinders are calibrated as “To Contain” and some are calibrated as “To Deliver.”
    - “To Contain” cylinders are marked TC and are used to accurately measure how much of a liquid is in a container.
    - “To Deliver” cylinders are marked TD and are used to measure the amount of liquid that needs to be poured from the cylinder into another container.

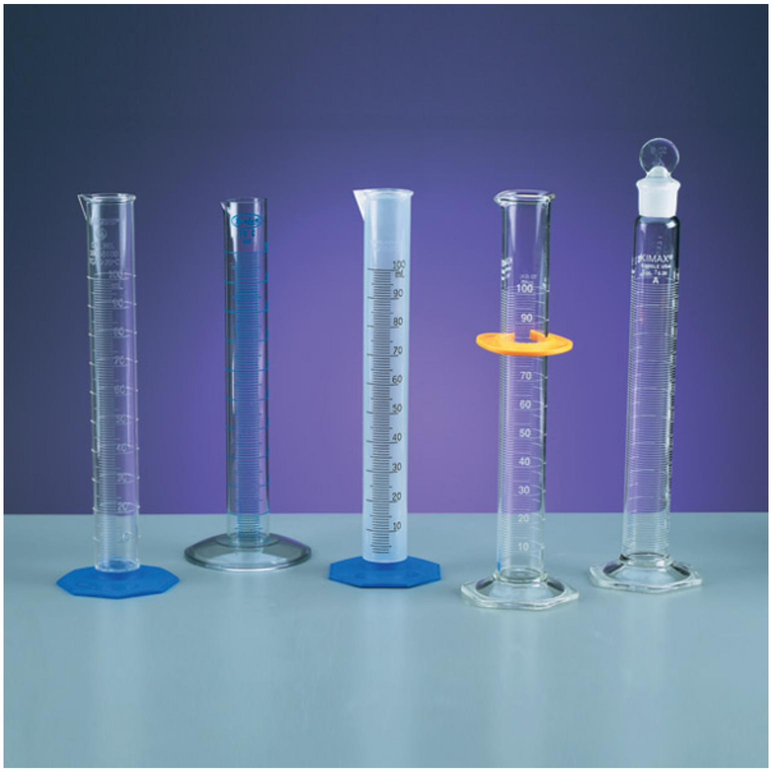

Figure 1.2 Graduated Cylinders[2]

Pipet

- Pipets come in a variety of volumes and are used to accurately measure and transfer volumes of chemicals or solutions.
- Pipets are typically used to measure smaller volumes than graduated cylinders.
- There are three main types of pipets:
  - Volumetric pipets, which are made to contain and deliver one specific volume.
  - Graduated pipets can be used to transfer fractions of their total volume. A graduated pipet can be filled and drained to any level marked on the side of the pipet to deliver the desired volume.
  - Serological pipets can also be used to transfer fractions of their total volume. It is somewhat different from a graduated pipet. A serologic pipet is filled only up to the level of the desired amount of liquid and the pipet is allowed to drain completely to deliver the total volume.
- Pipets, like graduated cylinders, are also made in TC and TD versions.

Buret

- Burets are available in a variety of volumes and are used to accurately deliver volumes of solutions.
- Burets are similar to pipets, but the difference is that burets have a valve at the bottom of the cylinder that can be used to add very minute and precise volumes of a solution. These valves are referred to as stop-cocks.
- Burets are typically used to conduct an analytical procedure known as titration.

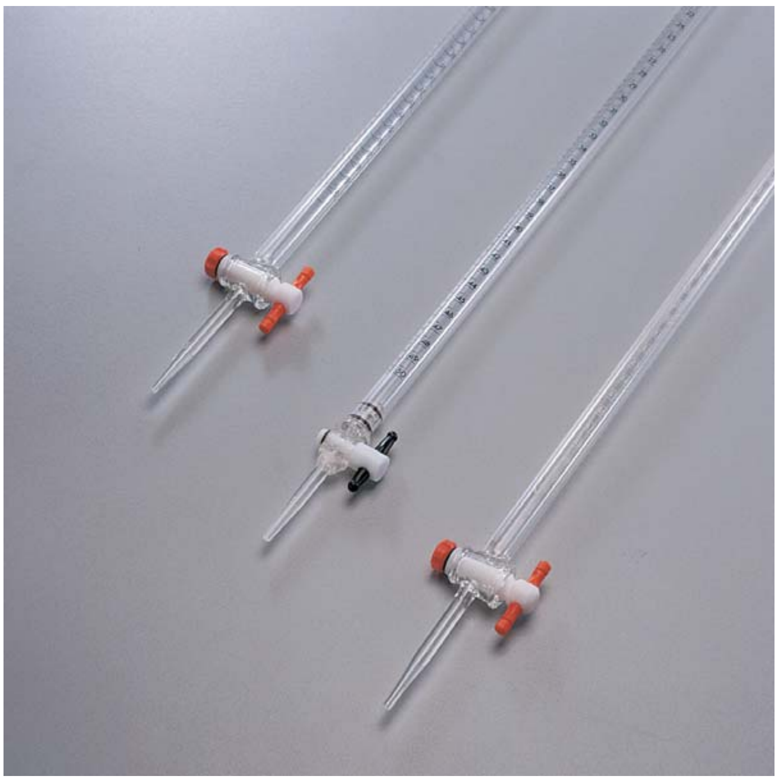

Figure 1.3 Burets[3]

Flask

- Many different types of flasks are used in an analytical laboratory.
- They come in a number of volumes and are typically used to store or mix chemicals or to conduct chemical reactions such as digestion.
- The most common type of flask is known as an Erlenmeyer flask.
- Another common type of flask is a volumetric flask, which is made to contain a very precise amount of chemical. Volumetric flasks are usually used to prepare standard solutions.

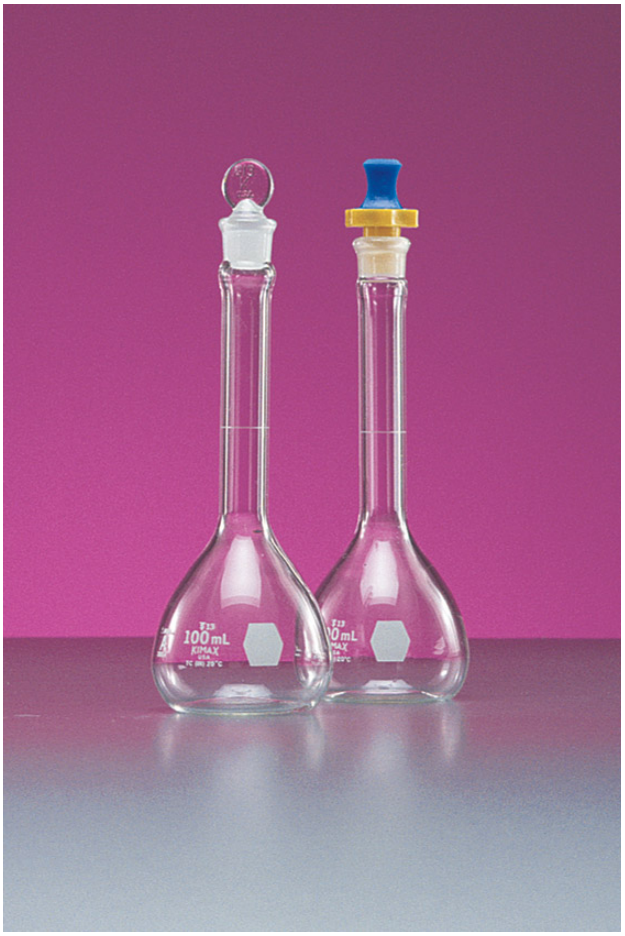

Figure 1.4 Volumetric Flasks[4]

Bottle

- Bottles have three primary uses:
  - To store chemicals or solutions.
  - To collect samples.
  - To conduct analyses.
- Reagent bottles are typically used to store chemicals.
- A Biological Oxygen Demand (BOD) bottle is used to conduct BOD analyses and has a “ground glass” stopper fitting. This stopper allows the bottle to be filled completely and forms an air tight seal so that no oxygen can enter the bottle during the 5 day BOD incubation.

Funnel

- Funnels are used to transfer liquid or solid chemicals from one container to another.
- Filter paper can be used with a funnel to separate solids from a liquid.
- There are two specialty types of funnels:
  - A Buchner funnel contains a perforated plate in the bottom and is used with a filter flask and a vacuum to separate solids from a mixture.
  - A separatory funnel is used to separate two chemical mixtures, of different densities, from one another. The chemical mixtures are added to the separatory funnel and the heavier mixture sinks to the bottom of the funnel. The funnel has a stop-cock which, after the mixtures have been separated, is opened, allowing the heavier mixture to drain off the bottom.

Test Tube

- Test tubes are used to contain or mix small quantities of chemicals.
- They are primarily used for bacterial testing.
- Nessler tubes are used for colorimetric analyses using a color comparator.

Imhoff Cone

- An Imhoff cone is used to conduct sludge volume analyses.
- A known volume of sludge is added to the cone and the solids are allowed to settle. Then a determination of volume of solids compared to total volume can be made.

Condenser

- A condenser is used as part of a distillation.
- Cold water is circulated through the condenser, which causes the vapor produced during the distillation to recondense to a liquid. The liquid is then collected and analyzed.

Petri Dish

- Petri dishes are used primarily for bacterial analyses. They are available in a variety of sizes and can have either a loose or tight fitting lid.

Exercise

You need to mix a standard solution and wish to add precise amounts of the components of the solution so that you know the exact concentration. Which combination of glassware would you use to mix the solution as precisely as possible?

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Preparatory Equipment, Incubators, Miscellaneous Equipment

Many laboratory analyses can not be conducted on samples as they are collected. The samples must be prepared prior to analysis. Preparation may be as simple as filtering the sample to remove solid material or as involved as adding acid to the sample and boiling it during a process known as digestion. The purpose of these preparatory steps is to convert the substances in the sample for which analysis is desired to a state that is detectable by the instrumentation you are using or to remove substances which may interfere with the detection of the target substance.

Burner

- Burners use natural gas to heat chemicals or solutions.
- Typically, this is done to evaporate undesirable substances in the solution and to change the target analyte in a sample from a liquid to a solid.
- There are many different styles of burners; however, the Bunsen burner is the most common type.

Crucible

- Crucibles are used to contain the sample while it is being heated on a burner.

Hot Plate

- A hot plate is similar in function to a burner, however it is electric.
- Hot plates deliver a more controlled amount of heat and can be used to warm solutions as opposed to heating them to boiling.
- Many hot plates are also capable of stirring a solution when used with a magnetic mixing bar.

Oven

- Ovens are used to bake chemical reagents or samples to either dry the reagents or to drive off undesirable constituents from a sample.

Desiccator

- A desiccator is a glass container with an airtight lid.
- The desiccator is filled with desiccant and is used to keep chemical reagents and samples dry. Typically, a sample is heated in an oven to dry it and then placed in the desiccator to cool prior to weighing or undergoing further preparation.

Incubator

- An incubator is a device that will hold a sample at a desired temperature. It is capable of holding the temperature in a very narrow range, usually fluctuating less than 0.5° C.
- Two common types of incubators are:
  - BOD incubators, which are used for holding BOD samples during the 5 day incubation period.
  - Bacteriological incubators, which are used to incubate samples undergoing bacteriological analysis.

Muffle Furnace

- A muffle furnace is capable of heating substances to extremely high temperatures. It is generally used for drying chemical reagents to drive off water or other volatile impurities.

Refrigerator

- A refrigerator can be used to store samples that may degrade if stored at room temperature prior to analysis.
- Examples include BOD, microbiological, organic and metal analyses.
- Chemical solutions and reagents should never be stored in the same refrigerator as samples.
- Food should never be stored in laboratory refrigerators.

Fume Hood

- A fume hood is a device that vents potentially dangerous or noxious fumes created by certain chemicals or chemical reactions from the laboratory to the outside atmosphere.

Vacuum Pump

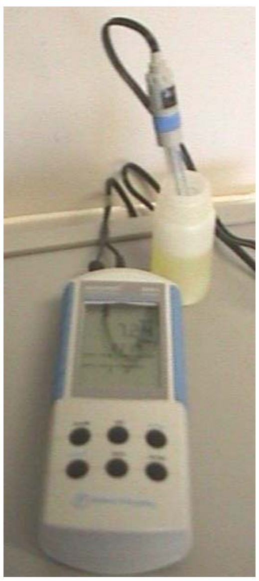
- Vacuum pumps are typically used during the filtration of samples prior to analysis.

Analytical Equipment

There are many different types of analytical equipment that could be present in a laboratory. The most common types you may encounter are listed below.

pH Meter

- A pH meter is one of the most common pieces of analytical equipment in any laboratory.
- A pH meter measures the pH of samples, which is a measure of the acidity or basicity of a sample.
- Measuring pH is essential since changes in pH can have a significant impact on the effectiveness of many treatment processes.



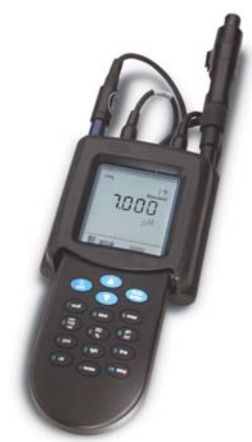


Figure 1.5 pH Meters[5]

Balance

- A balance is used to weigh items that are a part of solids analyses, such as dry chemical, filters or crucibles.

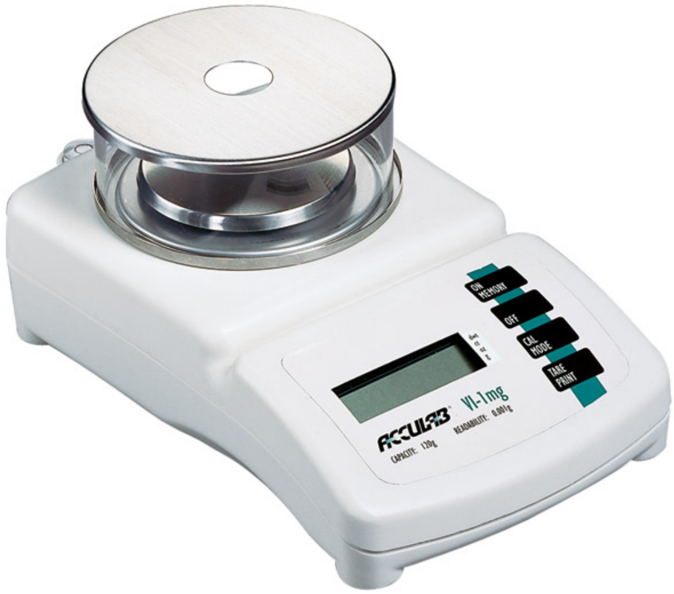


Figure 1.6 A Balance[6]

Spectrophotometer

- A spectrophotometer measures absorbance/transmittance of a sample.
- It uses chemical reagents to react with the substance to be quantified. The reaction usually produces a color change in the sample. The degree of color change is determined by the amount of the substance in the sample.
- Each spectrophotometer can do hundreds of different tests.

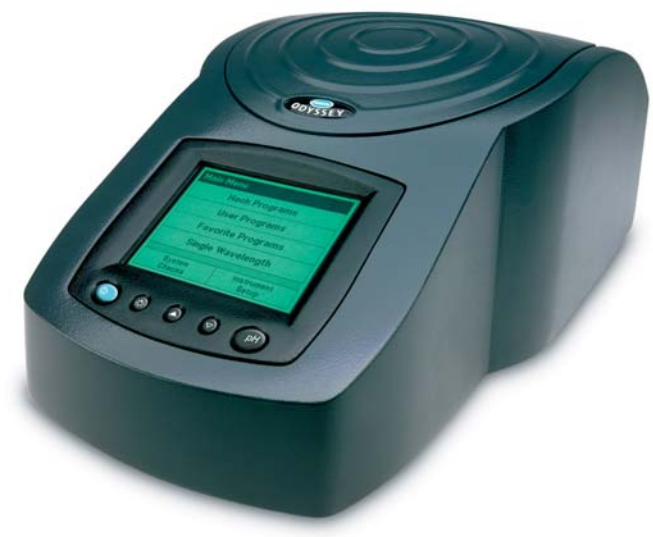


Figure 1.7 Spectrophotometer[7]

Thermometer

- A thermometer is used to conduct temperature determinations, which can have a significant effect on some treatment processes.

Amperometric Titrator

- An amperometric titrator is generally used to conduct chlorine residual testing.
- It utilizes a platinum electrode which senses when equilibrium has been reached. An indicator will let you know when equilibrium has been achieved.

Colorimeter

- A colorimeter is a type of spectrophotometer that uses chemical reagents to produce a color change in the sample.
- Colorimeters test for a variety of parameters such as chlorine or phosphorus; however, a specific colorimeter will only test for one parameter, not multiple parameters.
- Colorimeters compare the color of the sample (after reagent addition) to a graph of color vs. concentration that is entered into the memory of the instrument.
- A N,N-Diethyl-p-Phenylenediamine kit, commonly called a DPD kit, is a type of colorimeter.

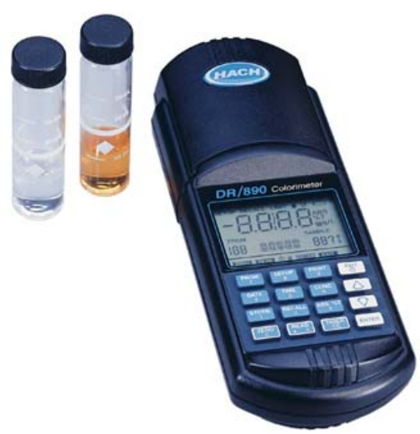


Figure 1.8 Colorimeter[8]

Many terms used in the laboratory are unique and not frequently used in normal conversation. Therefore, it is necessary to learn the meanings of these terms in order to function efficiently in the laboratory. These terms are divided into three categories: chemical, biological, and analytical.

Chemical

There are numerous chemical terms used in the laboratory. Many of the terms, such as element, compound, mole, molecular weight, oxidation, reduction and specific gravity are defined in Module 3 and will not be repeated in this module.

- A **Buffer** is a chemical or solution which can neutralize acids or bases with very little or no change to the pH of the solution.

- **Buffer Capacity** is the capacity of the solution or liquid to neutralize acids or bases OR the capacity of water or wastewater to resist a change in pH. The buffer capacity of a solution is determined by the alkalinity of the solution; a solution with high alkalinity has a large buffer capacity and a solution with a low alkalinity has very low or poor buffer capacity.

- **Percent Saturation** is the amount of a substance dissolved in a solution compared to the total amount of the substance that can be dissolved in a solution.

- **Precipitate** is a product of a chemical reaction which is insoluble and tends to separate from the solution.

- **Reagent** is a pure chemical substance that takes part in a reaction or is used in tests to detect or measure other substances.

- **Reflux** is a part of the distillation process. The substance condenses after heating or evaporation and flows back into the flask.

- **Solution** is a substance or mixture of substances dissolved in a solvent.

- **Surfactant** is a surface active agent. It is usually used to refer to detergents.

- **Volatile** is a term used to refer to a substance that evaporates at relatively low (ambient) temperatures.

Biological

The following are common biological terms you will encounter in a laboratory setting.

- **Aerobic** means with oxygen. It is a condition in which atmospheric oxygen is present in an aquatic environment.

- **Anaerobic** means without oxygen. It is a condition in which atmospheric oxygen is not present in an aquatic environment.

- **Aseptic** means sterile or an environment free of disease causing organisms. It is a technique which prevents the introduction of disease causing organisms.

- **Facultative** means capable of metabolizing in aerobic or anaerobic environments. It is typically used to describe certain types of bacteria.

- **Most Probable Number** (MPN) is an expression of the density of coliform bacteria in a sample.

Analytical

While conducting analyses, a Wastewater Treatment Plant Operator may encounter analytical terms that he or she is not familiar with. The following are some of those terms.

- **Aliquot** is a representative portion of a larger sample.

- **Ambient** is the temperature of the surroundings. It is typically used to signify room temperature.

- **Blank** is a sample containing only distilled or dilution water. Tests are often run on the sample and the blank and the results are compared.

- **Calibration** is the “setup” of the analytical instrument. A calibration is done by analyzing the response of an instrument to known concentrations of the analytes. These responses are recorded and compared to the results obtained when analyzing the unknown sample. A calibration usually results in the creation of a calibration curve which is used during the analysis of the unknown. These curves are often stored in the instrument’s memory. Many instruments are pre-calibrated, but it is important to verify the accuracy of this calibration regularly.

- **Distillate** is the condensed portion of the sample after distillation.

End Point is the completion of the chemical reaction. The term end point is often used to describe the color change that occurs during titration when the titrant has completely reacted with the sample. The end point is detected visually through a color change, formation of a precipitate, or with a pH meter.

An **Indicator** is a substance that gives a visual indication that the end point has been reached.

Meniscus is the curved surface of a liquid at the top of a column of liquid. Volume is read from the bottom of the curve.

Standard Solution is a solution in which the exact concentration of the compound or chemical is known.

Standardize means to use a standard to determine the exact concentration of a substance. Using a standard solution and recording the amount required to neutralize or react with a substance of unknown concentration, the unknown concentration can be determined.

Titrate is the process of adding a titrant drop-by-drop to a sample. The titrant is of known concentration (standard solution) and the amount of titrant necessary to reach the end point is used to calculate the sample's concentration.

Volumetric is a measurement based on the volume of substance used. A titration is a volumetric analysis.

Exercise

Observe the graduated cylinder presented by your instructor. What is the volume contained in the cylinder?

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Sample Preparation

Frequently, a sample is not suitable for direct analysis as collected and it must be prepared prior to analysis. This preparation can be physical or chemical in nature. There are some specific points you should be aware of during the collection, preservation, concentration, dilution, extraction and filtration of samples.

Collection

- Some analyses require that samples be collected in specialized containers. Some containers will add or absorb the analytes from the sample. For instance, residual chlorine can be absorbed by the plastic in plastic sample bottles and lead to erroneous analytical results.
- The acceptable sample containers by analyte will be presented in the Sampling Section.

Preservation

- If samples can not be analyzed immediately after collection they may need to be preserved. The preserving chemicals are analyte specific and will be presented in the Sampling Section.

Concentrate

- At times there is too little of the analyte to be detected using the analytical instrumentation. This limitation can be overcome by concentrating the analyte, which means increasing the concentration to a point that the analyte is detectable.
- Concentration also can be used to remove interfering or extraneous material from the sample. This is actually "purifying" the sample by removing the undesirable substances and is not really a concentration technique.
- When concentrating samples, the amount that the sample is concentrated must be known in order to calculate the amount of the analyte in the original sample. There are a number of concentrating techniques which may be used. The technique utilized is usually dictated by the analyte for which analysis is desired.

- Concentrating techniques include:
  - Centrifuge – This is a mechanical method that separates the analyte from the rest of the sample. This can be used when there is a difference in the specific gravity between substances in the sample but is more likely used to remove a solid material from a liquid sample. A centrifuge spins the sample at extremely high RPMs and causes the heavier material to be forced to the bottom of the tube. The separated material is carefully extracted from the tube and analyzed.

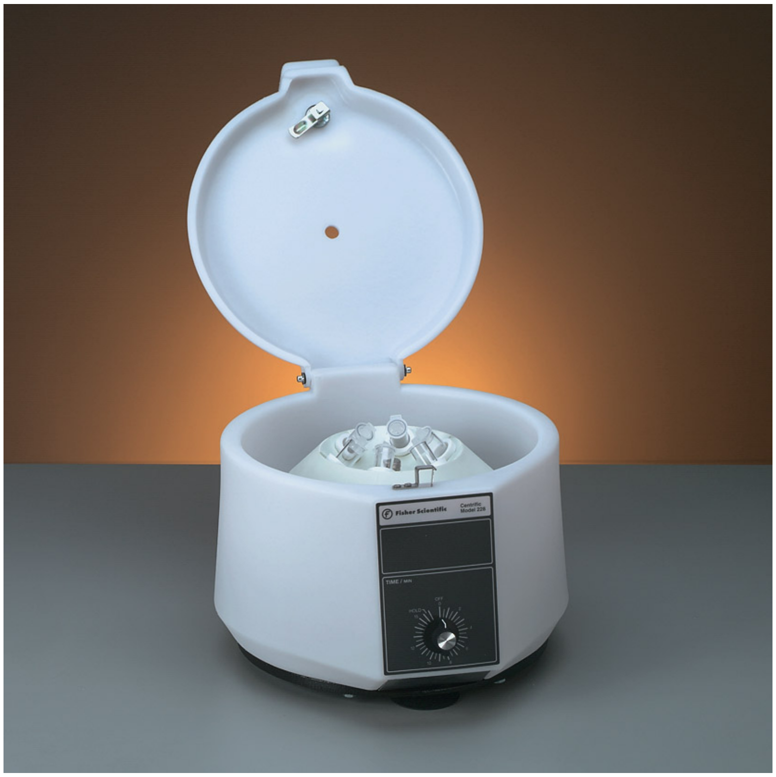

Figure 1.9 Centrifuge[9]

  - Evaporation – This is a technique that takes advantage of differences in the volatility of two compounds. The sample is allowed to evaporate and the remaining substance is the analyte.
  - Distillation – This is similar to evaporation, however, this technique uses the application of heat to speed the process. It is also used when the substance does not volatilize at room temperature. Distillation has the advantage of allowing the analyst to collect the distillate if that is the portion for which analysis is desired.
  - Digestion – This is a technique that involves “cooking down” the sample to a smaller volume. The analyte can not be volatile or it will be lost during the digestion. Digestion can also be used to chemically change the analyte to allow for analysis.

Dilution

- Dilution is used to lower the level of the analyte in the original sample. Some samples contain too much of the analyte and will be beyond the detection range of the instrument. The substance with which the dilution is done must be compatible with the sample and must not contain the analyte or interfere with the analysis. The amount that the sample is diluted must be carefully measured so that the original concentration can be calculated.

Extraction

- Extraction takes advantage of differences in the characteristics of the substances in a sample. A solvent is passed through the sample and removes the analyte and the solvent with the analyte in it is then analyzed.

Filtration

- Filtration is used to remove interfering material or determine the amount of solids in a sample.

Sample Analysis

There are many different types of analytical techniques which can be employed in the laboratory. Five of the most common techniques used in a Wastewater lab include ion specific analyses, gravimetric analyses, spectrophotometric analyses, titration analyses, and volumetric analyses.

Ion Specific

- An ion specific analysis typically involves the use of an electrode and a meter. The electrode is usually specific to the ion itself and detects only the ion of interest. The meter is really a millivolt meter that receives the signal from the electrode. The higher the concentration in the sample, the higher the millivolt reading on the meter.

- Typical equipment used to conduct an ion specific analysis includes a pH meter and D.O.

Gravimetric

- Gravimetric analyses are used to detect the mass or change in mass of a sample after some type of analytical technique has been applied to it.

- A balance is the tool used to do a gravimetric analysis.

Spectrophotometric

- A spectrophotometer takes advantage of different chemicals' abilities to absorb or transmit different wavelengths of light. The amount of a specific wavelength of light transmitted or absorbed is proportional to the amount of the analyte in the sample. Often an indicator and/or reagent is added to the sample to alter or maximize the light transmittance or absorbance. A colorimeter operates using similar techniques. A spectrophotometer typically can adjust the wavelength being used and can be used for many different analytes. A colorimeter typically uses just one wavelength and is suitable for only one analyte.

Titration

- A titration analysis is a technique where a known amount of a standard solution is added to a sample. The amount of the standard solution added is proportional to the concentration of the analyte in the sample.

- Equipment used to conduct titration analyses includes burets and amperometric titrators.

Volumetric

- A volumetric analysis is used to compare the total volume of the sample to the volume of the analyte in the sample. Some sludge analyses use this technique.

Exercise

1. An Imhoff cone would most likely be used for what type of analysis?

    a. Chlorine residual
    b. Sludge volume
    c. pH
    d. BOD

2. What is the purpose of a desiccator?

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3. An analytical balance would be used to do what type of analysis?

    a. Spectrophotometric
    b. Ion Specific
    c. Titration
    d. Gravimetric

4. List three sample concentration techniques.

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Key Points

- Beakers are commonly used to mix chemicals but should not be used to measure accurate amounts
- To Contain (TC) accurately measures how much liquid is in a container and To Deliver (TD) accurately measures how much liquid is delivered into another container
- Burets are used in titrations
- Volumetric glassware (flasks, pipettes, etc.) are extremely accurate (and costly) and are used when preparing standard solutions
- Common analytical equipment used in the laboratory analysis include:
    - pH meters
    - Spectrophotometers
    - Colorimeters
- Specific terminology is used in chemical, biological and analytical procedures. It is important to know what these terms mean in order to understand the procedures and the results.
- Beyond the direct analysis, sample preparation is extremely important in obtaining accurate test results. Sample preparation can include:
    - Collection
    - Preservation
    - Concentration
    - Dilution
    - Extraction
    - Filtration
- Analysis common in wastewater treatment include:
    - Ion Specific - ex: pH, Ammonia
    - Gravimetric – ex: Solids
    - Spectrophotometric – ex: Chlorine Residual
    - Titration – ex: Alkalinity

[1] Sean Brubaker, (Hach Co. USA, 2002)

[2] Sean Brubaker, (Hach Co. USA, 2002)

[3] Sean Brubaker, (Hach Co. USA, 2002)

[4] Sean Brubaker, (Hach Co. USA, 2002)

[5] Sean Brubaker, (Hach Co. USA, 2002)

[6] Sean Brubaker, (Hach Co. USA, 2002)

[7] Sean Brubaker, (Hach Co. USA, 2002)

[8] Sean Brubaker, (Hach Co. USA, 2002)

[9] Sean Brubaker, (Hach Co. USA, 2002)

Unit 2 – Chemical Hygiene and Lab Safety

Learning Objectives

- Explain the importance of laboratory hygiene.
- Explain the importance of a chemical hygiene plan and describe its critical components.
- List two common hazards a Treatment Plant Operator may be exposed to in a laboratory and explain how to avoid them.
- List five common rules of laboratory safety.
- List three articles of personal protective equipment and explain how each prevents injuries.
- In terms of personal hygiene, list three possible routes of infection and how to avoid them.
- List six common types of laboratory accidents and explain how to prevent them.

Laboratory Hygiene and Safety

There are many potential hazards both from an infectious and safety standpoint in a wastewater laboratory. Although it is the employer's responsibility to provide a safe working environment, ultimate responsibility for working safely falls on the individual. We will discuss the types of hazards which may be encountered in a wastewater laboratory and the ways wastewater treatment plant operator can best protect himself from infection or a laboratory accident.

Laboratory Hygiene refers to the process in which a plant operator employs safe practices when handling known or suspected hazardous material.

- The goal of the process is to minimize the opportunity for exposure to infectious or toxic substances. First and foremost the plant operator must know what he is working with and how to avoid exposure to the substance.

- Information on specific chemical hazards is included in the Material Safety Data Sheet (MSDS) for that chemical. An MSDS should be included with all chemicals (lab and treatment) received at your facility. Information regarding specific chemical hazards should be included in the plant's Chemical Hygiene Plan. The Chemical Hygiene Plan is part of a Hazard Communication Program which every wastewater plant is required to have.

Chemical Hygiene Plan Requirements

The goal of a Chemical Hygiene Plan is to limit the exposure to hazardous materials. All treatment plants that have a laboratory are required to have an acceptable Chemical Hygiene Plan in place. Some items which must be included are:

- Standard operating procedures to be used when handling hazardous substances.
- Criteria that are used to establish control measures to minimize employee exposure to hazardous substances. These measures include engineering controls, personal protective equipment use, and proper laboratory hygiene practices.
- A method for ensuring the proper operation of fume hoods and measures to be taken to ensure that all protective equipment will function properly.
- Employee training procedures including Hazard Communication procedures.
- Criteria for determining if specific laboratory procedures will require special approval prior to implementing.
- Criteria used to determine if medical consultation or examination is required.
- Designation of a Chemical Hygiene Officer.
- Criteria to determine if additional protective measures will be required for work with exceptionally hazardous substances such as carcinogens or extremely toxic material.

The Pa. DEP Bureau of Laboratories can provide you with more detailed instructions to be used in creating or updating your Chemical Hygiene Plan.

A plant operator may find himself exposed to two general types of hazards: infectious wastes and toxic chemicals.

Infectious Wastes

- Infectious wastes are usually found in the raw influent and can be contracted thorough breaks in the skin, ingestion or inhalation.
- To minimize or avoid infectious waste hazards:
  - DO NOT pipet by mouth.
  - Wash hands, arms, and face thoroughly when exposed to wastes. This will prevent infection through the skin.
  - Immunizations are the best defense against diseases contracted through inhalation and ingestion.

Toxic Chemicals

Many treatment chemicals and laboratory reagents are toxic. Know what you are working with by consulting the MSDS for all chemicals you are working with or exposed to. Keep a binder with all MSDS documents for your lab in a place where it can be accessed quickly.

Activity

Refer to the MSDS for aluminum sulfate liquid in Appendix A of your workbook and look for the following sections: PPE, First Aid, Toxicology and Health Data, Spill Procedures and Waste Disposal.

Lab safety is at least as much about common sense and orderliness as it is about hazardous chemicals and infectious wastes. A few common sense type rules and regulations are listed below.

- Always keep work areas clean and avoid clutter.
- Maintain access to safety showers and eyewashes and test them regularly.
- Keep a properly stocked first aid kit available at all times.
- Do not transfer chemicals from original containers to store in unmarked or poorly marked bottles. All chemical containers should be labeled with contents, date opened or prepared, and appropriate warning labels.
- Store chemicals safely. Store acids and bases separately. Store flammables and volatile chemicals in storage locker intended for that purpose. Keep oxidizing agents away from other chemicals.
- Use care when transporting chemicals. Use proper carrying equipment and personal protective equipment.
- Keep emergency numbers posted next to the phone.
- Always add acid to water. Never add water to acid.

Personal Protective Equipment

- The use of personal protective equipment (PPE) is the single most important item in preventing injuries in the laboratory. Examples of PPE include eye protection, gloves, lab coats and respirators.
- Eye protection should be worn at all times in the lab. It can protect you from broken glass, flying objects and spilled chemicals.
- Gloves should be worn whenever handling hazardous material. Gloves will prevent hazardous chemicals from entering your body through your hands.
- Some chemicals can be transmitted directly through your skin even without a cut to travel through. Lab coats not only save your own clothing or uniform they may prevent a chemical spill from damaging your clothes or reaching your skin.

Personal Hygiene

Personal hygiene involves some basic concepts: wash up after working with samples or chemicals, do not smoke or eat in the lab and do not store food in the sample or reagent refrigerator.

There are typically three possible routes of infection in a laboratory:

- Cutaneous

  Cutaneous infections occur through the skin. This is the typical route for bacterial infections. In order to avoid cutaneous infections, wash your hands thoroughly on a frequent basis. If necessary, wear gloves and/or cover breaks in the skin.

- Oral ingestion

  Viruses and some bacterial infections can enter the body through this route. These typically cause gastroenteritis (diarrhea, nausea or vomiting). Thorough hand washing and immunizations against viral pathogens are the best defense against these agents. Consider changing out of work clothes before returning home. Work and street clothes should be stored in separate lockers.

- Inhalation

  There is very little defense against airborne disease transmission. However, there are no documented cases of a sanitary worker being infected with Tuberculosis of other types of airborne contaminants. The best defense against these diseases is immunization and conscientious personal hygiene.

Accident Prevention

Most accidents occur due to carelessness; routine duties become mundane and a lapse in concentration leads to disastrous results. There are a number of accident possibilities in a laboratory. Common accidents are listed below.

- Electric Shock

  Be mindful of electrical outlets and frayed wires. Use grounded outlets and GFCIs. Follow Lock Out/Tag Out procedures when working on electrical equipment.

- Cuts

  Broken laboratory glassware is a common source of cuts. Promptly clean up any broken glass and place in a container designated for broken glass. Do not place broken glass into the waste paper basket as it will get covered and people may try to push the paper down further to make more room in the basket and then cut themselves on the hidden glass. Discard chipped or cracked glassware.

- Burns

  There are two possible types of burns: burns caused by heat and burns caused by chemical action.

  - **Heat** - You can not tell by looking at an item if it is hot, so treat all items as if they were. This will minimize the possibility of heat burns. Use gloves or tongs to transport glassware that may be hot. Do not allow an open flame to be unattended. If you must leave the immediate area where a Bunsen burner is in use—turn it off!

  - **Chemical -** Both acids and bases can cause chemical burns. Use PPE to minimize the exposure of skin and eyes. If exposure does occur, immediately flush with water or eyewash solution.

- Toxic Fumes

  Volatile chemicals should only be handled under a ventilated lab fume hood. The hood should provide adequate flow to carry the vapors away from the analyst. An air flow meter can be installed to verify the proper operation of the hood. Some acids and other chemicals create noxious fumes and should be handled only under the fume hood.

- Chemical Spills

  There are commercially available spill cleanup kits. These should be purchased for each type of hazardous chemical used at the laboratory. Typically, there should be a spill cleanup kit for acids, bases, and solvents or volatile chemicals. The proper spill kit should be used on the spill. Dispose of the cleanup materials in accordance with local regulations. Do not wipe up an acid spill and throw the towels into the waste basket. Do not dump volatile chemicals down the drain. It could damage the plumbing.

- Slip and Fall

  These types of accidents can be caused by clutter or careless storage or use of chemicals. Opened drawers, blocked exits and no access to safety showers or eyewash stations and fire extinguishers can cause a bad situation to become disastrous.

- Fire

  All laboratories should be equipped with a fire blanket and fire extinguisher. A fire blanket is to be used in case a person or his clothing catches fire. Fire extinguishers are rated for specific kinds of fires. Use the proper extinguisher for the fire you have. An ABC extinguisher can be used on most types of laboratory fires. Most small fires in beakers or dishes can be extinguished by covering it with a glass plate.

Exercise

1. List the two general types of hazards that a Wastewater Treatment Plant Operator may find himself exposed to.

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2. List the three most common routes that infectious agents can enter your body.

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3. List seven common types of laboratory accidents.

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Key Points

- Good Laboratory Hygiene protects the operator from infection and/or a laboratory accident.
- A chemical hygiene plan includes standard operating procedures (SOPs) and established control measures designed to protect operators by making good Laboratory Hygiene familiar and routine.
- Wastewater operators are exposed to infectious wastes and toxic chemicals. Exposure can be limited by use of protective equipment (gloves, goggles, lab coats, respirators) and by following standard laboratory safety rules.
- Standard laboratory safety rules include:
    - Access to first aid, safety showers and eyewash stations
    - Proper chemical storage areas
    - Clean work area
    - No food in the lab – EVER
- Routes of infection incude:
    - Cutaneous – through the skin
    - Oral – by mouth, no mouth pipetting EVER
    - Inhalation
- Common lab accidents include:
    - Burns – glassware doesn't appear hot, check first
    - Cuts – glassware breaks easily
    - Electrical shock – replace or discard equipment with frayed wiring, take care when working around water
    - Falls – clean-up spills promptly

Unit 3 – Sampling

Learning Objectives

- Describe the importance of sampling.
- List the common sampling techniques used in a laboratory.
- Explain the importance of sampling time.
- Name two common types of sampling and explain each.
- Explain the purpose of sludge sampling and explain how it is done.
- List four types of sampling devices and explain when to use each.
- Explain why sampling preservation is important and identify the types of preservatives used for different types of analyses.

In order to analyze a sample it must first be collected. While this may seem obvious, the importance of collecting a representative sample can not be overstated. If the sample is not representative, the analysis is worse than useless; it could be misleading and result in changes in treatment that are unnecessary and potentially damaging to the treatment process.

The most important part of the analytical process is the collection of representative samples. Many lab errors are the result of improper sampling. The goal of sample collection is to collect a sample that is truly representative of the conditions that exists at the time of collection.

There are many ways to collect samples. For example, you could use a dipper for grab samples or you could use a refrigerated composite sampler. The most important factor is to ensure the sample that is collected is representative of the treatment process.

During the collection of the sample itself, it is essential to ensure that the sampler you are using will not affect the sample. Some important considerations are listed below.

- Plastic can absorb chlorine from aqueous samples.
- Using an old chemical reagent bottle for a sampling jar may not be a good idea—it could still contain trace amounts of the chemical it originally contained.
- A non refrigerated composite sampler would be inappropriate for BOD analyses due to possible sample degradation over the composting period.
- Analyzing pH or chlorine residual from a composite sample is not appropriate due to possible sample degradation.

The time at which samples are collected is significant. Since it is not possible to sample the entire sample location at all times, it is important to collect samples when the sewage is “typical” for the plant. To collect a sample when the influent is not typical and adjust treatment based on the results of that test will create operational problems. Routine samples should be taken at a time when the sample is typical for the location. At times there may be unusual events and the operator may wish to sample at those times in order to identify the cause of the anomaly.

- Twenty-four hour composite sampling will give a more accurate picture of the facility’s average influent or effluent quality. However, if there are wide swings in the influent quality, a composite sample will mask these variations.

- If the plant can not obtain consistent treatment it may be due to widely fluctuating influent quality. It would then be necessary to analyze individual samples throughout the day to identify the nature of the influent at different times of the day.

- Once the nature of the influent at various times is known, the operator can anticipate which treatment changes need to be made and at what time they should be implemented.

Grab Samples

A **grab sample** is a single sample of wastewater taken from a particular location.

- Grab samples are neither flow nor time based. They can be collected at any time and at any flow. Obviously the results of the analysis will be greatly affected by the flow and time of collection but it will accurately reflect the quality of the stream sampled at that time.

- Grab samples can only characterize the waste at the time collected. Only grab samples can be used for dissolved oxygen (DO), coliforms, total chlorine residual, temperature, and pH since samples for these analyses can not be preserved and must be analyzed immediately after collection.

Composite Samples

A **composite sample** is a sample collected over a specified time period. A specific volume is collected at specific time intervals. A composite sample more accurately characterizes the average quality of the wastewater.

- The composite sample may be proportioned according to the flow entering the plant.

- In order to collect a time based composite, the sampler should be programmed to collect the same volume at each time interval. For instance, the sampler can be programmed to collect 500 ml of sample once per hour for 24 hours. This would be a 24-hour time based composite sample.

- It is possible to collect composite samples without using a composite sampler.
  - For a time based composite the operator would simply grab a specific volume from the same location once per hour (or any other consistent time interval). All of the samples would then be mixed together and analyzed. This is a time based composite sample.
  - For a flow based composite the operator would again collect a specific volume from the same location once per hour (or any other consistent time interval). But before mixing the individual samples together he would need to examine the hourly flow rates for the time period in question and calculate how much of each sample will be required for the composite sample. For instance, if the operator collected 500 ml of plant effluent every hour, the plant flow rate was 2.5 million gallons per day (MGD) and the flow was 250,000 gallons from 8 AM to 9 AM, 10% of his composite should be made up of the 8 AM sample.

- Composite samples should be refrigerated until the time of analysis to prevent bacterial degradation of the samples. Additionally, the samples must be well mixed prior to analysis to assure that the analytical results are accurate.

☑ Exercise

This is your first week of work in the lab at a large Wastewater Treatment Plant and the effluent composite sampler is broken. You need to run samples for NPDES compliance. The boss has told the operators to get grab samples, put them in the refrigerator and to read the effluent totalizer every hour. This morning he has told you to take the individual grab samples the operators collected and make the composite sample yourself. You are required to do a flow based composite and you will need about 1,000 ml of sample to conduct all of the required tests. The night shift operator threw a sheet at you as he ran out the door. It reads:

Time	Totalizer (1,000s)	Time	Totalizer (1,000s)
Midnight	002215	1 PM	010960
1 AM	002740	2 PM	010992
2 AM	003925	3 PM	011012
3 AM	005037	4 PM	011124
4 AM	006135	5 PM	011276
5 AM	007500	6 PM	011409
6 AM	008555	7 PM	011650
7 AM	009869	8 PM	011788
8 AM	010050	9 PM	011952
9 AM	010650	10 PM	012050
10 AM	010725	11 PM	012134
11 AM	010801	Midnight	012215
Noon	010859		

How much of the sample collected for the 8 AM to 9 AM time period should be used to make the 24 hour composite sample?

As with all other sample collection, the collection of a representative sample of sludge is extremely important to assure proper operation of the facility.

- Obtaining a truly representative sludge sample can be very difficult since solids concentration can change dramatically during pumping. Solids concentrations at the start of pumping may tend to be higher than average and solids concentrations at the end of the pumping cycle could be quite low. Using only a grab sample from either of these times may lead the operator to conclude that his sludge is stronger or weaker than actual.

- Sludge samples should be composited and taken at 30 second intervals during pumping. The analysis of the individual samples can indicate the proper pumping duration.

- It is critical to mix the composite sample well to ensure a representative sample is analyzed.

- Refrigeration of the composite is important to prevent the deterioration of the sample.

Types of Sampling Devices

There are many different types of sampling devices. The type of device that is used to collect a sample is determined by the type of sample to be collected and the analysis to be performed. Different types of sampling devices include:

- Bucket or Jar

  These can be used for grab or composite samples, but they only allow the surface of the basin to be sampled.

- Bottle

  This sampling device enables a sample to be collected slightly submerged below the surface of the basin. The bottle has a tube to allow sample to enter and a tube to allow the air to escape.

- Depth Sampler

  This device permits the collection of a sample from any desired level of a basin. The bottle sinks to the desired depths; the sampler is shut to trap the sample and is then withdrawn from the basin.

- Sludge Sampler

  A sludge sampler is used to sample a profile of sludge in a basin. The tube is inserted into the sludge blanket. The tube then fills with sludge. The top of the tube is sealed and withdrawn from the basin.

Nearly all substances for which analysis is desired must be preserved if the analysis can not be conducted immediately.

- Some analyses, like residual chlorine and pH, must be conducted immediately after collection and no type of preservation is permissible for these types of tests.
- The EPA has created a summary sheet listing many of the most common analyses, the type of bottle and preservative to be used. It also lists maximum holding time information.
- Typically, your certified laboratory will supply you with the proper types of sample bottles with the appropriate preservative added but it is possible that you may need to collect a sample.

Exercise

1. Explain the importance of collecting a representative sample.

2. What is the single biggest source of errors in laboratory results?

3. Explain how to manually prepare a flow based composite sample.

Key Points

- Obtaining a representative sample is the first step to obtaining accurate laboratory results.
- Samples can be grab or composite.
- Individual analyses have specific requirements for containers, holding time, preservation, etc, that maintains the integrity of the analyte.

Unit 4 – Laboratory Procedures

Learning Objectives

- List common laboratory analyses performed in wastewater treatment.
- Describe the purpose of Solids, pH, Alkalinity, Biochemical Oxygen Demand, Chemical Oxygen Demand, Coliform, Metals, Chlorine Residual, Nitrogen and Phosphate laboratory analyses.
- List the equipment needed to conduct common wastewater treatment analysis.
- Describe the general procedure that should be followed for the common wastewater treatment laboratory analysis.

Most wastewater treatment plant (WWTP) laboratories are not equipped to conduct all of the analyses required to maintain compliance with existing regulations. Many laboratories have only the equipment necessary to maintain process control of the facility. In spite of this, a plant operator should have an understanding of the procedures used even if he is contracting with an outside laboratory to do the work.

Solids determinations are used to quantify the amount of solid material in various types of samples. They are used most frequently on influent, effluent and sludge samples.

Dissolved Solids

- Significance

  Dissolved solids is a characterization of the quality of the wastewater. Solids analyses are important in the control of biological and physical wastewater treatment processes.

- Sampling Collection Locations

  The sample is collected from the influent and at the end of various treatment processes.

- Equipment to Conduct Analysis

  Equipment used includes an evaporating dish, drying oven desiccator, graduated cylinders, analytical balance, Gooch crucibles, glass fiber filters and a vacuum pump.

- References for Approved Analysis Procedure
  - Standard Methods 2540C.
  - Pa. DEP Wastewater Laboratory Procedures Manual Chapter 2, pp.11-13.

- Approved Analysis Procedure
  - Filter a well mixed sample through a glass fiber with a specific pore size.
  - Evaporate the filtered sample at 180^{o}C to a constant weight.
  - The increase in weight of the dish and solids compared to the dish is the total dissolved solids (TDS).

Settleable Solids

- Significance

  Settleable solids analysis indicates the volume of solids removed by sedimentation.

- Sampling Collection Locations

  The sample is collected from the following locations: the influent, primary effluent, secondary effluent, and mixed liquor.

- Equipment to Conduct Analysis

  The only equipment needed to conduct the analysis is an Imhoff cone.

- References for Approved Analysis Procedure
  - Standard Methods 2540F.
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 4, pp. 523 – 524.
  - Pa. DEP NPDES Laboratory Training Manual – Chapter 2 pp. 22-24.

- Approved Analysis Procedure
  - Collect a well mixed 1 liter sample from the above noted locations.
  - Allow them to settle for one hour.
  - Record results as mls of solids per liter of sample.

Total Suspended Solids

Significance

Total Suspended Solids (TSS) indicates influent wastewater quality and is used to gauge plant performance at various locations in the plant. It is also frequently used to verify discharge compliance.

Sampling Collection Locations

The sample is collected from the influent, primary effluent, secondary effluent, mixed liquor, return or waste sludge, digester supernatant and plant effluent.

Equipment to Conduct Analysis

The equipment used to conduct the analysis includes: glass fiber filters, membrane filter funnel or Gooch crucible, filter flask, vacuum source, drying oven, desiccator and an analytical balance.

References for Approved Analysis Procedure

- Standard Methods 2540D.
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 4, pp. 524- 529.
- Pa. DEP NPDES Laboratory Training Manual – Chapter 2 pp. 14-18.

Approved Analysis Procedure

- Draw a well mixed sample through a pre-weighed glass fiber filter.
- Dry the filter at 103-105 ^{o}C.
- Weigh the dried filter. The increase in weight of the filter and solids is the Total Suspended Solids (TSS).

Total Solids (Volatile and Fixed)

- Significance

  Total solids is the combined amounts of suspended and dissolved material in the sample. It is comprised of volatile and fixed solids. Volatile solids are composed of organic compounds which are either plant or animal origin (such as waste material that can be treated biologically). Fixed solids are inorganic compounds such as sand, gravel and minerals.

- Sampling Collection Locations

  The sample is collected from the raw sludge, raw sludge with waste activated sludge and recirculated sludge.

- Equipment to Conduct Analysis

  The equipment used to conduct the analyses includes: an evaporating dish, analytical balance, drying oven, graduated cylinder and a muffle furnace.

- References for Approved Analysis Procedure
  - Standard Methods 2540B and 2540E.
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 4, pp. 529 – 533.
  - Pa. DEP NPDES Laboratory Training Manual – Chapter 2 pp. 6-9 and 18-21.

- Approved Analysis Procedure
  - Evaporate a well mixed sample in a weighed dish.
  - Dry to a constant weight at 103-105 ^{o}C.
  - The increase in weight of the dish and solids represents the Total Solids (TS).
  - Ignite the solids remaining after the TS test at 550^{o}C to a constant weight.
  - The weight lost from the TS analysis is the volatile portion of the total solids and the remaining weight is the fixed solids.

Exercise

1. List the four types of solids analyses and explain the significance of each.

pH

Significance

The pH is a measure of the acidity or basicity of the wastewater. It is the activity of the hydrogen ions in the sample. The purpose of the test is to determine whether the pH at various points of the treatment process is favorable for the process. Each plant process has its own favorable pH range. A pH of 6-8 is usually considered acceptable for most treatment activities. It is also used to verify discharge compliance.

Sampling Collection Locations

The sample is collected from the influent, recirculated sludge, digester supernatant and plant effluent.

Equipment to Conduct Analysis

The equipment used includes a pH meter with pH and reference electrode or combination electrode and standard buffers for meter calibrations.

References for Approved Analysis Procedure

- Standard Methods 4500 – H^+.
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter16, Section 1, p. 556.
- Pa. DEP NPDES Laboratory Training Manual – Chapter 3.

Approved Analysis Procedure

- Place the electrode into the solution to be tested.
- Stir the solution slowly.
- Record results after the meter readout has stabilized.

Alkalinity

- Significance

  Alkalinity is a measure of the wastewater's ability to neutralize acids. It is an indirect measure of the concentration of carbonate, bicarbonate and hydroxide in the sample.

- Sampling Collection Locations

  The sample is collected from the influent and effluent.

- Equipment to Conduct Analysis

  Equipment needed includes: a pH meter, electrode, stirrer, buret and a standard solution of sulfuric acid. OR a buret, sulfuric acid, and pH 4.5 indicator solution if the Titration method is used.

- References for Approved Analysis Procedure

  - Standard Methods 2320 B (Titration method).
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter16, Section 2, p. 557.

- Approved Analysis Procedure

  - When using the pH meter method, add a standard sulfuric solution to the sample until a pH of 4.5 is reached.
  - When using the Titration method, a color indicator is used to denote when the pH 4.5 endpoint is reached.

Exercise

1. What is the significance of conducting pH and Alkalinity analyses?

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2. When conducting a pH analysis, the sample is collected from which locations?

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3. When conducting an alkalinity analysis, the sample is collected from which locations?

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Dissolved Oxygen

- ## Significance

  The test measures the amount of free oxygen in the water or wastewater. The breakdown of organic products present in wastewater is depended on aerobic or facultative bacteria. If insufficient DO exists in the treatment units, the breakdown will be incomplete and the waste will become aerobic and septic, causing objectionable odors and the death of aquatic organisms.

- ## Sampling Collection Locations

  The sample is collected from the influent, primary and secondary effluent, oxidation ponds and activated sludge effulent.

- ## Equipment to Conduct Analysis

  The equipment used includes a DO probe and meter, or reagents for the Electrometric Meter Method, or burette and glassware for the Modified Winkler Method.

- ## References for Approved Analysis Procedure

  - Standard Methods 4500 - O.
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 7, pp. 587 - 595.
  - Pa. DEP NPDES Laboratory Training Manual – Chapter 4.

- ## Approved Analysis Procedure

  - For the Electrometric Method: calibrate the DO meter and measure the DO by placing the DO probe into the sample and recording the results.
  - For the Modified Winkler Method: add a number of reagents and titrate with sodium thiosulfate or phenylarsene oxide. The amount of titrant used to reach the end point is proportional to the amount of DO in the sample.

Biochemical Oxygen Demand (BOD)

Significance

The BOD measures the amount of oxygen used by microorganisms as they consume the wastes delivered to the Wastewater Treatment Plant. BOD test results will indirectly indicate the concentration of the wastes at various points in the treatment process. BOD is also used to verify discharge compliance.

Sampling Collection Locations

The sample is collected from the influent, primary effluent, secondary effluent and the digester supernatant.

Equipment to Conduct Analysis

The equipment used includes 300 ml BOD bottles with ground glass stoppers, an incubator (20^{o}C +/- 1^{o}C), pipets and DO meter.

References for Approved Analysis Procedure

- Standard Methods 2540B and 2540E.
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter16, Section 7, pp. 587 – 595.
- Pa. DEP NPDES Laboratory Training Manual – Chapter 5.

Approved Analysis Procedure

- Pipet a specific amount of the test sample into a BOD bottle containing aerated dilution water.
- Measure and record the DO.
- Incubate the sample in the dark for five days at 20^{o}C.
- After incubation, measure the final DO and calculate the difference between the initial and final DO. Multiply the difference in DO by the sample dilution to calculate the BOD.
- Note: Guidelines indicate that in order for the BOD test to be valid, the sample should deplete the DO by at least 2 mg/l during the five day incubation and contain at least 1 mg/l DO at the end of the five days. For this reason, it is typical to do a series of different dilutions, assuming at least one of the dilutions will produce acceptable consumption and residual DO. If more than one dilution gives acceptable consumption and residual, then the results of the acceptable dilutions should be averaged together.
- Often a “seed” of microorganisms is required for chlorinated samples. These seeds can be from natural or commercial sources, however, it is important to take into account the BOD of the seed itself and subtract that from the BOD of the samples.

Chemical Oxygen Demand (COD)

- Significance

  COD measures the amount of oxygen used by a sample when treated with a strong chemical oxidant. There is a relationship between the BOD of a sample and the COD, but this relationship must be established for each sample location.

  COD generally can not be used for NPDES reporting purposes but offers the advantage of being a much quicker analysis than BOD. CODs can be used as a quick check of treatment efficiency and used to make process control adjustments.

- Sampling Collection Locations

  The sample is collected from the influent, primary effluent, secondary effluent and digester supernatant.

- Equipment to Conduct Analysis

  The equipment used includes: reflux set up using glassware and condenser, reagents and titrants for the titrimetric method or spectrophotometer for the colorimetric method.

- References for Approved Analysis Procedure
  - Standard Methods 5220.

- Approved Analysis Procedure
  - All COD procedures involve reflux of the sample. Add a strong oxidizing agent and various reagents to the sample. The reflux digests the sample and consumes all of the oxidizable organic material.
  - After reflux digestion, titrate the sample with a standard ferrous ammonium sulfate (FAS) solution. The amount of COD in the sample is proportional to the amount of FAS required to reach the end point of the titration.

Exercise

1. Explain the principal difference between BOD and COD analyses.

Total Coliform

Significance

Total coliform is widely used in water treatment as an indicator of the microbiological quality of raw and finished water. It is less widely used in wastewater treatment. Total coliform bacteria are indigenous to the digestive tracts of warm blooded animals and therefore can be used as a surrogate to indicate the presence of human or animal waste.

Sampling Collection Locations

The sample is collected from the primary effluent and secondary chlorinated effluents.

Equipment to Conduct Analysis

The equipment used includes a membrane filter apparatus or MPN test tubes, depending on the method used. Other equipment includes various bacterial media, sterile sample bottles, sterile buffered dilution/rinse water, a bacterial incubator and a refrigerator.

References for Approved Analysis Procedure

- Standard Methods 9221 B and 9222B.
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 6, pp. 568 - 585.

Approved Analysis Procedure

- Draw a sample through a membrane filter using a vacuum pump. The bacteria are trapped on the filter. Place the filter on bacterial growth media in a Petri dish then place the Petri dish in the incubator at 35^{o}C for 24 hours. The media and the incubation temperature will allow only coliform bacteria to grow.
- The multiple tube fermentation technique involves the use of test tubes filled with bacterial growth media. Add a number of different dilutions to a series of test tubes. Incubate the tubes 24 and 48 hours at 35^{o}C. Growth in the tubes, indicated by cloudiness of the media, and gas production, indicated by the presence of a gas bubble in the inverted tube placed inside the test tubes, indicates a positive test for total coliform bacteria. After the initial presumptive test, add a loop full of the media to a second set of tubes containing a different bacterial media. Incubate these tubes for 24 and 48 hours at 35^{o}C. Growth is indicated as described above. The number of tubes that display growth at each dilution is used to estimate the amount of bacteria in the sample. The results of the testing are compared to a table that lists the MPN (Most Probable Number) of bacteria present in the sample.

Fecal Coliform

Significance

Fecal Coliform is widely used in water and wastewater treatment as an indicator of the microbiological quality of raw and finished water. Fecal coliforms are not necessarily disease producing organisms but are present in large numbers in the waste of warm blooded animals. The disease producing organisms are present in much smaller numbers and therefore much more difficult to detect. The disease producing organisms are excreted from the body along with the fecal coliforms. For this reason, fecal coliform bacteria are used as a surrogate to indicate the presence of human or animal waste. The presence of fecal coliforms indicates that disease producing organisms may be present in the sample tested.

Nearly every Wastewater Treatment Plant has a limitation on the number of fecal coliforms that can be present in the effluent. This level is often adjusted seasonally with higher levels permitted in the winter months and lower levels allowed during the summer season.

Sampling Collection Locations

The sample is collected from the primary effluent and secondary chlorinated effluents.

Equipment to Conduct Analysis

The equipment used includes a membrane filter apparatus or MPN test tubes, depending on the method used. Additional equipment includes various bacterial media, sterile sample bottles, sterile buffered dilution/rinse water, a bacterial incubator and a refrigerator.

References for Approved Analysis Procedure

- Standard Methods 9221 E and 9222 D.
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 6, pp. 568 - 585.
- Pa. DEP NPDES Laboratory Training Manual – Chapter 7.

- Approved Analysis Procedure
  - For the membrane filtration method: Draw a sample through a membrane filter using a vacuum pump. The bacteria are trapped on the filter. Place the filter on the bacterial growth media in a Petri dish, then place the Petri dish in the incubator at 44.5ºC for 24 hours. The media and the incubation temperature will allow only coliform bacteria to grow.
  - For the multiple tube fermentation technique: Use test tubes filled with bacterial growth media. Add a number of different dilutions to a series of test tubes. Incubate the tubes for 24 and 48 hours at 44.5ºC. Growth in the tubes, indicated by cloudiness of the media, and gas production, indicated by the presence of a gas bubble in the inverted tube placed inside the test tubes, indicates a positive test for total coliform bacteria. After the initial presumptive test, add a loop full of the media to a second set of tubes containing a different bacterial media. Incubate these tubes are for 24 and 48 hours at 44.5ºC. Growth is indicated as described above. The number of tubes that display growth at each dilution is used to estimate the amount of bacteria in the sample. The results of the testing are compared to a table that lists the MPN (Most Probable Number) of bacteria present in the sample.

Exercise

1. Explain the purpose of testing a WWTP's effluent for total coliform.

2. Explain the purpose of testing a WWTP's effluent for fecal coliform.

Aluminum

- ## Significance

  Aluminum is the third most abundant element of the earth's crust and is prevalent in waters and wastewater. Large amounts of aluminum can be toxic to some forms of aquatic life and some studies have correlated elevated aluminum levels with the early onset of Alzheimer's disease. All metals can be of concern in wastewater treatment because the toxic effects of the metals can inhibit effective wastewater treatment. Depending on the loading of the receiving stream some Water Treatment Plants or Wastewater Treatment Plants may have NPDES limits for aluminum in their discharge.

- ## Sampling Collection Locations

  The sample is collected from the plant influent and effluent from various treatment units.

- ## Equipment to Conduct Analysis

  An atomic absorption spectrophotometer (AA) or inductively coupled plasma (ICP) analyzer are generally used for the quantification of aluminum when reporting to regulatory agencies. Laboratory colorimeters or spectrophotometers can be used to estimate the amount of aluminum in a sample for plant process control purposes.

- ## References for Approved Analysis Procedure

  - Standard Methods 3500-Al.

- ## Approved Analysis Procedure

  - The determination of aluminum in the discharge of a WWTP is usually done by a contract laboratory since the equipment required to conduct one of the certified methods is quite expensive.
  - A colorimeter or spectrophotometer can be used to estimate the amount of aluminum in a sample as a process control procedure, but these results can not be submitted for compliance with NPDES regulations.

Iron

- ## Significance

  All metals can be of concern in wastewater treatment since the toxic effects of the metals can inhibit effective wastewater treatment. Depending on the loading of the receiving stream, some water treatment plants or wastewater treatment plants may have a NPDES limit for iron in their discharge.

- ## Sampling Collection Locations

  The sample is collected from the plant influent and effluent from various treatment units.

- ## Equipment to Conduct Analysis

  An atomic absorption spectrophotometer (AA) or inductively coupled plasma (ICP) analyzer are generally used for the quantification of iron when reporting to regulatory agencies. Laboratory colorimeters or spectrophotometers can be used to estimate the amount of iron in a sample for plant process control purposes.

- ## References for Approved Analysis Procedure

  - Standard Methods 3500-Fe.

- ## Approved Analysis Procedure

  - The determination of iron in the discharge of a wastewater treatment plant is usually done by a contract laboratory since the equipment required to conduct one of the certified methods is quite expensive.
  - A colorimeter or spectrophotometer can be used to estimate the amount of iron in a sample as a process control procedure, but these results can not be submitted for compliance with NPDES regulations.

Copper

Significance

All metals can be of concern in wastewater treatment since the toxic effects of the metals can inhibit effective wastewater treatment. Depending on the loading of the receiving stream, some water treatment plants or wastewater treatment plants may have a NPDES limit for copper in their discharge.

Sampling Collection Locations

The sample is collected from the plant influent and effluent from various treatment units.

Equipment to Conduct Analysis

An atomic absorption spectrophotometer (AA) or inductively coupled plasma (ICP) analyzer are generally used for the quantification of copper when reporting to regulatory agencies. Laboratory colorimeters or spectrophotometers can be used to estimate the amount of copper in a sample for plant process control purposes.

References for Approved Analysis Procedure

- Standard Methods 3500-Cu.

Approved Analysis Procedure

- The determination of copper in the discharge of a wastewater treatment plant is usually done by a contract laboratory since the equipment required to conduct one of the certified methods is quite expensive.
- A colorimeter or spectrophotometer can be used to estimate the amount of copper in a sample as a process control procedure, but these results can not be submitted for compliance with NPDES regulations.

Exercise

1. Why are there limits placed on the amount of certain metals that can be discharged from a WWTP?

____

____

____

____

Total Residual Chlorine

- **Significance**

  Chlorine serves many purposes in wastewater treatment. Chlorine is used to control odor, reduce BOD, aiding coagulation, scum and grease removal, and to control sludge bulking. The most important use of chlorine, by far, is for disinfection of the effluent. Virtually every wastewater discharge has a limitation on the levels of fecal coliforms that can be present in the effluent. Chlorine disinfects the effluent and allows the WWTP to limit the amount of fecal coliform in the effluent.

  Chlorine is toxic to aquatic life. The presence of chlorine in the discharge can cause fish and plant kills in the receiving stream. For this reason almost all WWTP's have a limitation on the level of total residual chlorine that can be present in the effluent. Some plants have to remove the residual chlorine from the effluent prior to discharge. This is typically done with reducing agents such as sodium thiosulfate or sulfur dioxide.

- **Sampling Collection Locations**

  The sample is collected primarily at the effluent, but chlorine residuals should be run at the beginning and end of any treatment unit that utilizes chlorine.

- **Equipment to Conduct Analysis**

  There are a variety of methods that can be used for chlorine determinations in wastewater. The iodometric method is a titration that uses a standard iodine solution as the titrant. The DPD titrimetric method is a titration that uses DPD indicator solution and standard Ferrous Ammonium Sulfate as the titrant. The amperometric titration method uses standard phenylarsine oxide as the titrant. The end point is indicated by the amperometric titrator.

- **References for Approved Analysis Procedure**

  - Standard Methods 4500-Cl.
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 5, pp. 562- 565.

- Approved Analysis Procedure
  - All three procedures listed above require a titration with a standard solution to neutralize the chlorine in the sample.
  - The iodometric and DPD titrations use a visual endpoint, while the amperometric titration uses an electrometric endpoint that is indicated for the analyst.
  - The amount of titrant used is proportional to the amount of chlorine in the sample. Chlorine is volatile and will be lost from the sample as it sits, therefore it is important to analyze the sample immediately after collection.
  - Water treatment plants frequently use chlorine colorimeters for chlorine determinations. This method utilizes DPD and can be used for free or total chlorine determinations. This method can be used for wastewater testing but care should be used due to a number of interferences that may affect the test. Organic chloramines, oxidized manganese and combined chlorine residuals will interfere with the free DPD test.

Exercise

1. What is the significance of conducting a chlorine analysis?

Nitrate/Nitrite

- Significance

  The presence of nitrate in the effluent of a WWTP is significant because it is an essential nutrient for algae growth. Excessive amounts of nitrate can cause algae blooms. When the algae dies and decays it can exhibit a large oxygen demand on the stream which in turn can cause the fish and other aquatic life to be killed.

- Sampling Collection Locations

  The sample is collected from the secondary/plant effluent.

- Equipment to Conduct Analysis

  Equipment necessary to conduct the analysis includes a reduction column, spectrophotometer, various reagents and glassware. Electrode methods are also available for this analyte.

- References for Approved Analysis Procedure

  - Standard Methods 4500- NO_3 and 4500-NO_2.
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 10, pp. 607 - 612.
  - Pa. DEP NPDES Laboratory Training Manual – Chapter 9.

- Approved Analysis Procedure

  - The nitrate in the sample is reduced to nitrite and analyzed using a spectrophotometer.
  - This method is susceptible to a wide variety of interferences including turbidity, oil and grease. Turbidity can be removed by filtration. Oil and grease is removed by acidifying the sample and removing the oil and grease with a chloroform extraction.

Ammonia

- Significance

  Ammonia in the effluent of a wastewater treatment plant can create a significant oxygen demand in the receiving stream. This demand will lower the amount of DO available for aquatic life and lead to fish and aquatic life kills.

- Sampling Collection Locations

  The sample is collected from the secondary/plant effluent.

- Equipment to Conduct Analysis

  Equipment necessary to conduct the analysis include a distillation apparatus and various reagents. If the titration method is used, then titration equipment, titrant and indicator solution are needed. For the electrode method, an ammonia selective electrode is needed and for the colorimetric method, a spectrophotometer is needed.

- References for Approved Analysis Procedure

  - Standard Methods 4500- NH_3.
  - *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 10, pp. 597 - 603.
  - Pa. DEP NPDES Laboratory Training Manual – Chapter 9.

- Approved Analysis Procedure

  - All the procedures consist of the distillation of the ammonia from the sample and collection of the distillate.
  - The titrimetric procedure uses and indicator and titrant to determine the amount of ammonia in the sample. The amount of titrant used is proportional to the amount of ammonia in the sample.
  - The colorimetric method uses a reagent to produce a color change in the distillate. This color change is measured using a spectrophotometer which has been calibrated using ammonia standards of various concentrations. The intensity of the color in the sample is proportional to the amount of ammonia in the sample.
  - The electrode method uses an electrode and millivolt meter that has been calibrated with various ammonia standards. The amount of electric current measured by the electrode and displayed on the meter is proportional to the amount of ammonia in the sample.

Total Kjeldahl Nitrogen (TKN)

Significance

Total Kjeldahl Nitrogen (TKN) is the sum of organic nitrogen and the ammonia nitrogen in a sample. The term TKN takes its name from the analytical procedure used to analyze the sample. Ammonia nitrogen's effect on the receiving stream's DO has been discussed. Organic nitrogen also exhibits a DO demand on the receiving stream leading to possible effects on aquatic life.

Sampling Collection Locations

The sample is collected from the secondary/plant effluent.

Equipment to Conduct Analysis

Equipment necessary to conduct the analysis include a Kjeldahl digestion apparatus, heating unit, fume hood, distillation apparatus and various reagents. For the colorimetric procedure, a spectrophotometer is needed and for the titrimetic procedure, titration equipment is needed.

References for Approved Analysis Procedure

- Standard Methods 4500- $N_{org.}$
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 10, pp. 603 – 607.
- Pa. DEP NPDES Laboratory Training Manual – Chapter 9.

Approved Analysis Procedure

- Both procedures begin with the digestion of the sample.
- The digestion converts the organic nitrogen to ammonia and then the sample is distilled as described in the ammonia procedure above.
- The TKN is then determined using the ammonia titration method or ammonia colorimetric procedures described above.

Exercise

1. List the three types of nitrogen/ammonia analyses and explain the significance of each.

Phosphate

Significance

Phosphorus containing compounds are common since it is an essential nutrient for plant growth. Wastewater is usually quite rich in phosphorus compounds and its removal is extremely important because their presence can stimulate the growth of algae. These growths can be a great nuisance and the die-off of algae will create a large DO demand in the receiving stream. Typical phosphorus containing compounds found in wastewater are orthophosphate, condensed phosphate or organically bound phosphate.

Sampling Collection Locations

The sample is collected from the influent and effluent.

Equipment to Conduct Analysis

For orthophosphate, a spectrophotometer and various reagents are needed. For total phosphorus determinations, a digestion apparatus is required.

References for Approved Analysis Procedure

- Standard Methods 4500- P.
- *Operation of Wastewater Treatment Plants* 5th Ed., Volume II, Chapter 16, Section 10, pp. 614 – 615.

Approved Analysis Procedure

- Orthohosphate is determined colorimetrically using reagents to develop the color and a spectrophotometer to measure the absorbance of the sample. The intensity of the color of the sample after treatment is proportional to the amount of orthophosphate in the sample.
- To determine total phosphorus, the sample must be digested using a persulfate digestion method. The digestion converts the condensed phosphate and organically bound phosphate to orthophosphate. The sample is then analyzed as described above in the orthophosphate procedure.

Exercise

1. What is the significance of conducting a phosphate analysis?

Key Points

- Common laboratory analysis in wastewater treatment includes:
    - Solids
    - pH
    - Alkalinity
    - BOD
    - COD
    - Metals
    - Coliform
    - Nitrogen
    - Phosphate
- Equipment used includes:
    - Ion specific electrodes
    - Titration set-up
    - Spectrophotometer
    - AA
    - ICP
    - Microbiological equipment – Petri dishes, membrane filtration units, MPN tubes
    - BOD bottles and incubator
    - Analytical balance, drying oven, evaporating dishes
- Procedures for approved analytical analyses are found in Standard Methods

Unit 5 – Laboratory Quality Assurance and Quality Control

Learning Objectives

- Explain why a quality assurance plan is important and list the important components of a quality assurance plan.
- Explain the importance of a QA manual, training, chain of custody, bench sheets and reporting to a quality assurance plan.
- Explain why quality control is important.
- Explain the importance of each of the flowing and give a brief description of how each analysis is conducted:
    - Duplicates
    - Spikes
    - Blanks
    - External Standards
    - Blinds

The goal of any analytical laboratory is to produce accurate data. Since this data may be thoroughly scrutinized by customers, regulators, or even attorneys, the laboratory must ensure the data it reports is accurate and they must ensure they can prove its accuracy. To guarantee that the generated data is defensible, the laboratory must develop a Quality Assurance (QA) plan and adhere to its requirements.

A thorough QA plan should contain the following elements:

- A cover sheet with plan approval signatures.
- A laboratory organization chart naming individuals responsible for analyses and supervision of laboratory activities.
- Sample control and documentation procedures.
- Standard Operating Procedures (SOPs) for each analytical method.
- Analyst training procedures.
- Equipment preventative maintenance procedures.
- Calibration procedures.
- Quality control procedures.
- Data reduction, validation and reporting procedures.

QA Manual

- The heart of a QA plan is QA manual. It contains the written instructions for carrying out all of the above described elements of a QA plan.
- Specifically, the QA manual contains the written SOPs for each analytical procedure and the QC procedures to be followed during sample collection, handling and analysis.
- In many laboratories, different analysts conduct the same analyses on different days. To ensure that the results generated by different analysts are comparable, each analyst must follow the exact same procedure. Likewise, these written procedures assure that the analysts use the exact same methodology from day to day.

Training

- The best way to assure that the laboratory is producing accurate data is to thoroughly train all of the analysts in the proper operating procedures. As just mentioned, the QA plan should contain these operating procedures. Therefore, a well written QA manual can be used as a training manual for new analysts.

Chain of Custody

A **chain of custody** is the procedures and the form that must accompany the sample from the time of collection to the reporting of results.

- The goal of the chain of custody procedure is to assure that no tampering of the sample has occurred.

- The chain of custody contains the sampling information and includes signature spaces for all of the people who have handled the sample. If the results of an analysis are ever called into question, one of the first questions to be asked is who had access to the sample during collection and analysis.

Bench Sheets

A laboratory **bench sheet** is where the analyst records the results of testing conducted. Although sample results are often transferred from the bench sheet to a more "official" report, the bench sheet is actually the official record of the result of the analysis. As such, these records must be retained according to the standards outlined in Unit 6 of this module.

- Since these results are the official record of the analysis, a standard laboratory bench sheet should be created. At a minimum the bench sheet should include:
  - The date.
  - The time.
  - The analyst's initials.
  - The sample results for the test.
- These bench sheets can take on a number of forms. Usually a sheet is either created for a particular instrument or analysis and is posted by the instrument or work station or one sheet is used to record the results for all of the analyses performed on a particular day. The former method works well when multiple analysts use the lab at the same time, the latter method may be more convenient if there is only one analyst on duty at any one time.
- Since the bench sheet is the official record of the analytical result, the analyst should not record results on scraps of paper and later transfer them on to a report form. If there is a question as to the validity of an analytical result or there is a laboratory inspection, the analyst should not have to search through a drawer looking at various scraps of paper to find the "official" record of the analysis in question.

Reporting

- Reporting involves much more than writing the results of the analysis down on a piece of paper and handing it to the boss. There may well be data reduction and validation procedures required before the results can be reported.

Data reduction is the process of applying correction factors to the raw results due to things such as sample extraction efficiency and instrument performance.

Data validation is, in part, the process of examining the analytical results to determine if they are statistically acceptable.

- Upon completion of these procedures, a report can be created. The report should include the pertinent sampling information listed below.
  - Date
  - Time
  - Sampler
  - Analysis date
  - Analyst's name
  - Date of report
  - Lab address
  - Lab phone number
- Results should be reported in standard units—usually milligram per liter for common analytes in wastewater.

Duplicates

A **duplicate analysis** is the process of analyzing a sample a second time to compare the results to the results of the first analysis. This is a way to quantify the laboratory's precision.

- The allowable difference between the two results depends on the analyte itself and the level of the analyte in the sample.
  - Generally, for metals like iron present at relatively low levels, a difference in the results of +/- 25% is considered acceptable.
- Duplicate analyses should be run on at least 5% of samples. That means at least one of every 20 samples analyzed for a particular parameter should be analyzed in duplicate. For example, if you had 20 samples to analyze for BOD, at least one of the samples should be analyzed in duplicate. Most small wastewater labs do not run samples 20 at a time; in that case one duplicate should be run with each sample set.

Spikes

Spike samples are used to calculate the ability of the laboratory to produce accurate results.

- Spike sample analysis, also called known additions, consist of adding a known amount of the target analyte to the sample after an initial analysis. By calculating the difference between the two analyses the amount of the spike that was quantified during the second analysis can be determined. Since the amount that was added is known and the amount recovered is calculated the percent recovery for the analysis can be determined. The acceptable percent recover range for metals is 80 – 120%. Spikes should be done on 10% of the samples analyzed.

Blanks

A reagent **blank** is an analysis of the reagents and procedures used in the laboratory.

- A blank is typically made by taking deionized water or another source of sample that is known to be free of the contaminant being tested for and preparing it as if it were a regular sample. The blank sample is then analyzed and the results examined. If the blank contains a measurable amount of the contaminant then the "real" sample results may not be accurate and lab procedures must be examined to identify the cause of the error. Five percent of all samples analyzed should be reagent blanks.

External Standards

External standards are standards obtained from an outside agency. They are also known as QC standards.

- The concentration of the analyte in the external standard is known and the results of the analysis are compared to this known concentration. If the results of the analysis do not agree with the known concentration, corrective action must be taken in the laboratory to identify the cause of the error. The acceptable amount of difference between the lab result and the known concentration is usually +/- 10%.

Blinds

Blinds analyses is an analytical procedure in which an outside agency, usually the State's lab certification agency, supplies a sample to the laboratory for analysis.

- The sample provided contains a known amount of the analyte. The laboratory, however, is "blind" to this information and does not know how much of the analyte is present in the sample. The lab runs the sample and reports the results to the agency that supplied the sample. The agency then determines if the laboratory's results are acceptable. Blind samples are also known as Performance Evaluation (PE) samples.

Exercise

1. List 5 elements of a good QA plan.

2. Duplicates are used to demonstrate the ____________________ of a laboratory method.

3. Spikes are used to demonstrate the ____________________ of a laboratory method.

4. A well written QA manual can be used for what other purpose?

   a. As a door stop
   b. As a training manual for new analysts
   c. As a plant operations manual
   d. As a substitute for a lab QA Officer

Key Points

- Quality Assurance Plans help to maintain the integrity of laboratory data by establishing protocols for sample control, analytical methods, training, equipment maintenance and calibration, quality control procedures (including temperature data, reagent standardization information, dates, use of spikes, blanks, external standards, and blinds).

Unit 6 – Data Handling, Records and Reporting

Learning Objectives

- Define Method Detection Limit.
- List two types of laboratory records, explain the significance of each and explain how results should be recorded and stored.
- Identify the data required to complete a Discharge Monitoring Report (DMR) and explain why each piece of data is important.
- Explain the purpose of the Frequency of Analysis and Sample Type sections of the DMR.
- List the three main sections of a DMR and give a brief explanation of what is included in each section.
- Specify the deadline for submission of the DMR.
- Explain the requirements for non-compliance reporting.
- Explain the requirements of the records retention policy.

Laboratory Math

There are many instances in which mathematics will be required in the laboratory. The math operations that will be required were discussed in previous modules.

Molecular Weights and Solution Strengths

- As discussed in Module 3, it is necessary to be able to calculate molecular weights of compounds in order to determine how much of the compound to add when preparing solutions. Please refer to Module 3 for more detailed instructions on calculating molecular weights and solution strengths.

Analytical Results

- At times, the results from an analysis cannot be reported directly from the instrumentation.
- The results of two analyses, BOD and fecal coliform, must be calculated from measurements taken during the analyses. The methods to conduct both of these calculations have been covered elsewhere and will not be discussed here.
  - Generally, the BOD calculation involves measuring the depletion of dissolved oxygen after a five day period and multiplying the depletion by the amount that the sample was diluted prior to analysis.
  - The fecal coliform result is generated by calculating the geometric mean of all of the results gathered during the monitoring period. This formula is presented in the Basic Math Module.

Method Detection Limits

- Every analytical equipment method has a limit of resolution.

The **limit of resolution** is a limit below which accurate measurements can not be made.

- This limit differs for every analyte and for every piece of analytical equipment. This level is reported on analytical reports as the method detection limit.
- When a lab report is received with a result of <0.5 mg/l, it is considered a non-detect or a result of zero for the analyte.
- In reality, if it is not a result of zero, it means that there was not enough of the analyte in the sample to accurately quantify it. This could mean that there was none of the analyte in the sample, however, we cannot say this for sure. Therefore, we say that the analyte was not present in detectable quantities or it was less than the method detection limit.

Analytical Results

- Analytical results are the records that document the operational procedures and their effectiveness at your plant.
- Analytical records can be an invaluable tool when attempting to identify and correct operational problems at your facility.
- Analytical records can be recorded and stored in a number of ways.
  - The most common method is still by hand-recording data on lab bench sheets. Bench sheets are typically daily or weekly sheets on to which the results of lab analyses are recorded. It usually contains spaces to record the result of a single analysis for multiple days or all the analyses conducted on a particular day.
  - Laboratory notebooks are another method to record data. A laboratory notebook is typically a sewn bound book into which analytical results are entered. Lab notebooks frequently have numbered pages and a bound spine so that pages can not be removed without being evident.
- The following guidelines should be followed when recording information on the bench sheet or in the laboratory notebook:
  - All data should be entered in ink.
  - The date and time of collection and analysis performed should be evident.
  - The name of the analyst or at least their initials should be recorded.
  - Any corrections made to a bench sheet or notebook should not be made by erasing the previous result. Corrections should be crossed out with a single line and initialed by the analyst.

QC Results

- QC results are the other common type of laboratory record. QC results are the verification that the analytical results that have been recorded are accurate.
- QC results should be recorded and stored in the same manner as analytical records.

Required Data

Most wastewater treatment plants are limited in the amount of flow and material permitted to be in their discharge. These amounts are determined by the type and size of plant being operated and the loading of each contaminant the receiving stream can tolerate.

- All wastewater treatment plants have a flow limitation which can not be exceeded and this information must be recorded on the DMR.
- There are also typically limits placed on the amount of organic and inorganic substances that can be discharged.
- The plant's ability to achieve removals of various contaminants is reported on the DMR.
- Adverse operating occurrences such as combined sewer overflows are to be reported on the monthly DMR.
- Typically, average monthly, average weekly, maximum daily and instantaneous maximum concentration data is requested on the DMR.
- Often average monthly, average weekly and maximum daily loading data is also required. This is calculated by multiplying the analytical results by the appropriate flow data and converting the results to an amount in pounds.

Flow

- The amount of flow permitted to be discharged is determined by the type and size of the plant being regulated. The data for the DMR report should be obtained from the daily discharge flow meter totalized readings.

Analytes

- There are numerous potential contaminants for which monitoring could be required. Monitoring is required for those contaminants known to be used by industries or commercial establishments in the collection system and by examining the loading of particular contaminants on the receiving stream.
- There are a number of analytes which are regulated in nearly all wastewater treatment plants discharges. These contaminants include CBOD, suspended solids, fecal coliform and pH. These analytes are included not only due to concerns of their impact on stream water quality but also because they indicate how well the plant is functioning.

Removals

- Another check on the effectiveness of the treatment process is to examine the percent removals through the treatment plant. Many NPDES permits require that the treatment plant achieve at least an 85% removal of CBOD and suspended solids. If this removal is not achieved on average every month, it must be reported to the regulatory agency.

Operations

- Unusual operational occurrences like activation of combined sewer overflows during wet weather events must also be reported to the regulatory agency on a supplement to the DMR. The plant must report cause, frequency, duration, and quantity of flow for each wet weather CSO event. Dry weather overflows are a permit violation and must be immediately reported to the regulatory agency.

Data Collection

On the right side of the DMR is a section labeled "Monitoring Requirements," which contains two sections: Frequency of Analysis and Sample Type. The purpose of these two fields is discussed below.

Frequency of Analysis

- This refers to how often you must collect and analyze samples for a particular parameter. The frequency varies by parameter but is usually designated as either daily, weekly (or twice per week), or monthly.

Sample Type

- The last column on the DMR is labeled sample type, which indicates whether the sample is to be a composite or a grab sample.

- Composite samples were discussed in Unit 3 of this module. They are typically gathered over an 8-hour or 24-hour time frame.

- Grab samples were also described in Unit 3 and are a single sample taken at a particular location. Grab samples are typically used for parameters that may degrade if not analyzed immediately after collection and therefore are not suitable for compositing. Parameters such as pH, total chlorine residual and fecal coliforms must be analyzed from grab samples.

Data Manipulation

Once the required DMR samples have been collected and analyzed it may be necessary to manipulate the data to satisfy reporting requirements. If multiple samples are required, the DMR usually asks for the average of the results, the minimum and the maximum results from the samples collected.

- Some analyses may require further manipulation. The DMR may require the fecal coliform result to be expressed as the geometric mean of all of the sample results.

The **geometric mean** is a method that lessens the influence of the extreme values obtained from some of the analyses.

- We will not attempt to describe the procedure to calculate the geometric mean in this module, since many computer spreadsheets will do it automatically. Some electronic calculators are capable of performing this calculation as well.

Reporting

Proper reporting of analytical results is as important as proper analysis of the samples themselves. Just as a facility can be cited by the regulatory agency for operational abnormalities at the plant they can also be cited reporting errors. Therefore, it is very important to understand the proper method for completing a DMR.

Report Completion

- Detailed instructions for the completion of the DMR are included with the NPDES Permit. A summary of the method to complete the DMR is presented below.
- The DMR is divided into three sections: Facility Identification and Monitoring period, Testing Results Reporting and Identification of the Responsible Party.

Facility Identification and Monitoring Period

- This is the top section of the DMR and consists of:
    - Name and address of the regulated entity (i.e., Sanitary Authority, Borough or Company).
    - The facility itself (i.e., WWTP or industrial treatment plant etc).
    - The physical location of the facility.
- Often this information is already entered on the DMR that is received from the regulatory agency.
- There are also spaces for the facility's permit number and the discharge number.
- The monitoring period is the time frame over which the testing is required; typically monthly reporting is required.

Testing Results Reporting

- This section of the DMR is where the results for plant flow and effluent quality testing are recorded. The parameters are identified in the left-hand column.

- The next three columns are titled “Quantity or Loading” and provide space for the sample measurement results and the permit requirements for quantity or loading.
  - The quantity or loading is calculated by multiplying the concentration of an analyte that was obtained during the testing by the flow that was measured during the sampling period.
  - The permit requirements are typically already entered into the appropriate columns and do not need to be entered by the report preparer.
  - The last column in this group is titled “Units” and is typically either MGD (Million Gallons per Day) or LB/DY (Pounds per Day). This column is usually already filled in and does not need to be completed by the report preparer.

- The next three columns are headed “Quality or Concentration.” This is where the results of the analyses are entered and the permit requirements are listed. The permit requirements usually are already entered onto the DMR.
  - The “Quality or Concentration” columns are followed by a “Units” column this is similar to the “Units” column in the “Quantity or Loading” section. Units in this area are usually MG/L or Std Units (for pH).

- Just to the right of the “Quality or Concentration” section is a column labeled “No. Ex.” This stands for number of exceedences. In this field, the report preparer would enter the number of samples analyzed during the monitoring period that did not comply with the permit requirements for that parameter. If there are no exceedences for that parameter a zero should be entered in the appropriate space.

- The last two columns contain the sampling frequency and sample type information. Typically the required frequency and sample type are already entered on the DMR. In the fields above the permit requirements the report preparer should enter the sampling frequencies and sampling methods that were actually used.

Identification of Responsible Party

- The final section to be completed on the DMR is the Identification of the Responsible Party. The responsible party is typically the principal executive officer of the organization. This person must be identified and he must sign and date the DMR prior to submission.

Report Submission

- The completed DMR must be received within 28 days after the end of each monthly report period.

Non Compliance Reporting

- Any non-compliance with NPDES permit requirements that may endanger health or the environment must be reported orally to the appropriate regulatory authority, and if reasonably possible, known downstream users immediately from the time that the permittee becomes aware of the circumstances.

- A written submission must be provided within 5 days of the time the permittee becomes aware of the circumstances. The written submission must contain a description of the non-compliance, its cause and the period of non-compliance.

- If the non-compliance is ongoing, the permittee must provide the anticipated time the non-compliance is expected to continue and actions taken to reduce, eliminate, or prevent reoccurrence of the non-compliance.

- These non-compliance events include, but are not limited to: unanticipated bypasses that exceed permit limits, catastrophic events that cause the discharge to exceed permit limits and exceedence of maximum daily discharge limits listed by the regulatory agency to be reported within 24 hours.

- Any instances of non-compliance not listed above must be reported at the time of DMR submission.

Record Retention

- Storage of construction prints and operating records from at least the last five years is extremely important.

- Laboratory records, results of sample analysis and QA/QC results should be maintained for a minimum of five years. Seven to ten years is recommended for storage.

- Current regulations require that completed DMRs and the sources of the data used to complete them must be maintained for at least three years from the date of the sample measurement, report or application. Monitoring information related to sludge disposal must be maintained for a minimum of five years.

Exercise

1. What are the two general types of laboratory records?

2. Which of the following information does not need to be reported on a DMR?

   a. Flow
   b. BOD
   c. Chemical Deliveries
   d. Sampling Frequency

3. DMRs must be submitted within ________ days of the end of the monitoring period.

4. Completed DMRs and the data used to complete them must be maintained for at least ________ years after the date of submission, sample measurement, report or application.

Key Points

- The Method Detection Limit is the limit of resolution for a particular instrument, meaning, the lowest concentration the instrument is capable of measuring.
- Laboratories normally maintain records of laboratory results and Quality Control records.
- The DMR is a report that records the data required by a plant's NPDES permit.

Appendix A – Sample MSDS for Aluminum Sulfate, Liquid

Delta Chemical Corporation

Aluminum Sulfate, Liquid **MSDS No. 011**

Date of Preparation: 3/15/02 Revision: 2.0

Material Safety Data Sheet

Section 1 - Chemical Product and Company Identification

Product/Chemical Name:	Aluminum Sulfate, Liquid	**Manufacturer:**		**HMIS**
Chemical Formula:	$Al_2(SO_4)_3 \bullet 14(H_2O)$	Delta Chemical Corporation,		**H** 1
CAS Number:	10043-01-3	2601 Cannery Avenue,		**F** 0
General Use:	Water Treatment Chemical	Baltimore, MD 21226-1595,		**R** 0
Emergency Contact:	**800-424-9300**	Phone	410-354-0100, (7:00am 5:00pm)	**PPE**†
	Chemtrec	FAX	410-354-1021	†Sec. 8

Section 2 - Composition / Information on Ingredients

Ingredient Name	CAS Number	% wt
Aluminum Sulfate	10043-01-3	27.8
Water	7732-18-5	72.2

	OSHA PEL		ACGIH TLV		NIOSH REL		NIOSH
Ingredient	**TWA**	**STEL**	**TWA**	**STEL**	**TWA**	**STEL**	**IDLH**
Aluminum Sulfate	2 mg/m^3 *as aluminum*	none estab.	none estab.	none estab.	none estab.	none estab.	none estab.

Toxicity Data:

Section 3 - Physical and Chemical Properties

Physical State:	liquid	**Water Solubility:**	Complete
Appearance and Odor:	colorless, clear amber or light green	**Other Solubilities:**	
Odor Threshold:	negligible odor	**Boiling Point:**	109° C/228° F
Vapor Pressure:	NA	**Freezing/Melting Point:**	-13° C/9° F
Vapor Density (Air=1):	NA	**Viscosity:**	
Density:		**Surface Tension:**	
Specific Gravity (H_2O=1, at 4 °C):	1.32	**% Volatile:**	NA
pH:	2.1 ± 0.5		

Section 4 - Fire-Fighting Measures

Flash Point:	NA
Burning Rate:	NA
Autoignition Temperature:	NA
LEL:	NA
UEL:	NA
Flammability Classification:	
Extinguishing Media:	NA
Unusual Fire or Explosion Hazards:	If evaporated to dryness and exposed to temperatures greater than 1400°F aluminum sulfate will decompose generating toxic and corrosive gas.
Hazardous Combustion Products:	See Section V
Fire-Fighting Instructions:	Do not release runoff from fire control methods to sewers or waterways.

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Section 5 - Stability and Reactivity

Stability:	Aluminum Sulfate, Liquid is stable at room temperature in closed containers under normal storage and handling conditions.
Polymerization:	Hazardous polymerization cannot occur.
Chemical Incompatibilities:	Alkalies and water-reactive materials.
Conditions to Avoid:	N/A
Hazardous Decomposition Products:	Thermal oxidative decomposition of Aluminum Sulfate occurs at temperatures greater than 1400°F and can produce sulfur oxides.

Section 6 - Health Hazard Information

Potential Health Effects

Primary Entry Routes:	Ingestion
Target Organs:	N/A
Acute Effects	No unusual
Eye:	May cause a burning feeling.
Skin:	May cause a skin rash or burning feeling.
Ingestion:	
Carcinogenicity:	IARC, NTP, and OSHA do not list Aluminum Sulfate, Liquid as a carcinogen.
Medical Conditions Aggravated by Long-Term Exposure:	None reported.
Chronic Effects:	There is no evidence that aluminum sulfate causes cancer or affects reproduction.

Emergency and First Aid Procedures

Inhalation:	(mist or spray) Remove from exposure, seek medical treatment if any symptoms occur.
Eye Contact:	Immediately flush with large amounts of water for at least 15 minutes, occasionally lifting upper and lower lids. Seek medical attention.
Skin Contact:	Remove contaminated clothing and wash contaminated skin with water.
Ingestion:	Do not induce vomiting, drink milk or water and immediately seek medical attention.

After first aid, get appropriate in-plant, paramedic, or community medical support.

Section 7 - Spill, Leak, and Disposal Procedures

Spill /Leak Procedures:	Spill procedures are dictated by site wastewater flow controls and will vary from site to site. General procedures are provided in this document, but authorization for any wastewater discharge must be obtained prior to the discharge.
Small Spills:	If directed to an industrial sewer, wash down with large volumes of water. Spills can be neutralized and absorbed with soda ash or lime, but neutralization will release carbon dioxide, which can generate a breathing hazard.
Large Spills	For large spills, dike far ahead of liquid spill for later disposal. Do not release into sewers or waterways. Pump residue into storage containers or neutralize with lime or soda ash. Neutralization will release carbon dioxide, which can generate a breathing hazard.
Containment:	
Cleanup:	Wash or neutralize impacted areas after liquid removal to remove residues.
Regulatory Requirements:	Follow applicable OSHA regulations (29 CFR 1910.120).
Disposal:	Contact your supplier or a licensed contractor for detailed recommendations. Follow applicable Federal, state, and local regulations.
Container Cleaning and Disposal:	

Ecological Information:

EPA Regulations:

RCRA Hazardous Waste Number:	Not listed (40 CFR 261.33)
RCRA Hazardous Waste Classification	(40 CFR 261.??): Not classified
CERCLA Hazardous Substance (40 CFR 302.4)	listed CWA, Sec. 311 (b)(4)
CERCLA Reportable Quantity (RQ)	5,000 lbs (2,270 kg) as $Al_2(SO_4)_3$ 17,900 lbs (8,120 kg) as a 27.8% solution
SARA 311/312 Codes:	immediate (acute) health hazard
SARA Toxic Chemical (40 CFR 372.65):	Not listed
SARA EHS (Extremely Hazardous Substance) (40 CFR 355):	Not listed

OSHA Regulations:

Air Contaminant (29 CFR 1910.1000, Table Z-1, Z-1-A):	Not listed
OSHA Specifically Regulated Substance (29CFR 1910.????)	Not listed

State Regulations:

Section 8 - Exposure Controls / Personal Protection

Engineering Controls:

Ventilation: Under normal conditions, liquid alum will not generate mists or vapors. No special ventilation is recommended.

Administrative Controls:

Respiratory Protection: Seek professional advice prior to respirator selection and use. Follow OSHA respirator regulations (29 CFR 1910.134) and, if necessary, wear a MSHA/NIOSH-approved respirator. Select respirator based on its suitability to provide adequate worker protection for given working conditions, level of airborne contamination, and presence of sufficient oxygen. For emergency or non-routine operations (cleaning spills, reactor vessels, or storage tanks), wear an SCBA. *Warning! Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.* If respirators are used, OSHA requires a written respiratory protection program that includes at least: medical certification, training, fit-testing, periodic environmental monitoring, maintenance, inspection, cleaning, and convenient, sanitary storage areas.

Protective Clothing/Equipment: Wear chemically protective gloves, boots, aprons, and gauntlets to prevent prolonged or repeated skin contact. Wear protective chemical safety goggles, per OSHA eye- and face-protection regulations (29 CFR 1910.133). Contact lenses are not eye protective devices. Appropriate eye protection must be worn instead of, or in conjunction with contact lenses.

Safety Stations: Make emergency eyewash stations, safety/quick-drench showers, and washing facilities available in work area.

Contaminated Equipment: Separate contaminated work clothes from street clothes. Launder before reuse. Remove this material from your shoes and clean personal protective equipment.

Comments: Never eat, drink, or smoke in work areas. Practice good personal hygiene after using this material, especially before eating, drinking, smoking, using the toilet, or applying cosmetics.

Section 9 - Special Precautions and Comments

Handling Precautions:

Storage Requirements:

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DOT Transportation Data (49 CFR 172.101):

Shipping Name:	Aluminum Sulfate	**Packaging Authorizations**	
Shipping Symbols:	G	**a) Exceptions:**	173.155
Hazard Class:	9	**b) Non-bulk Packaging:**	173.203
DOT No.:	UN3082	**c) Bulk Packaging:**	173.241
Packing Group:	III	**Quantity Limitations**	
Label:	Class 9	**a) Passenger, Aircraft, or Railcar:**	no limit
Special Provisions (172.102):	8, T1	**b) Cargo Aircraft Only:**	no limit
		Vessel Stowage Requirements	
		a) Vessel Stowage:	A
		b) Other:	

Prepared By:
Revision Notes:

Disclaimer: The information presented herein is believed to be accurate and reliable, but is given without guaranty or warranty, expressed or implied. The user should not assume that all safety measures are indicated so that other measures may not be required. The user is responsible for assuring that the product and equipment are used in a safe manner that complies with all appropriate legal standards and regulations.

Appendix B – Discharge Monitoring Report (DMR)

PERMITTEE NAME/ADDRESS
(Include Facility Name/Location if different)
NAME ____________________
ADDRESS ____________________

FACILITY ____________________
LOCATION ____________________

NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES)
DISCHARGE MONITORING REPORT (DMR)

(2-16)	*(17-19)*
PERMIT NUMBER	DISCHARGE NUMBER

	MONITORING PERIOD						
	YEAR	MO	DAY		YEAR	MO	DAY
FROM				TO			
	(20-21)	*(22-23)*	*(24-25)*		*(26-27)*	*(28-29)*	*(30-31)*

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NOTE: Read instructions before comple

PARAMETER *(32-37)*		*(3-Card Only)* *(46-53)* AVERAGE	QUANTITY OR LOADING *(54-61)* MAXIMUM	UNITS	*(4-Card Only)* *(38-45)* MINIMUM	QUALITY OR CONCENTRATION *(46-53)* AVERAGE	*(54-61)* MAXIMUM	UNITS
C-Biochemical Oxygen Demand (5-Day)	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Chemical Oxygen Demend	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Oil and Grease	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
pH	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			Std. Unit
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Water Priority Chemical	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
(Name: ____________________)	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Total Suspended Solids (TSS)	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Total Phosphorus	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Total Kjeldahl Nitrogen (TKN)	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	
Iron (Dissolved)	SAMPLE MEASUREMENT	XXXXX	XXXXX	XXX	XXXXX			MG/L
	PERMIT REQUIREMENT	XXXXX	XXXXX		XXXXX	XXXXX	REPORT Daily Max.	

NAME/TITLE PRINCIPAL EXECUTIVE OFFICER	I CERTIFY UNDER PENALTY OF LAW THAT I HAVE PERSONALLY EXAMINED AND AM FAMILIAR WITH THE INFORMATION SUBMITTED HEREIN: AND BASED ON MY INQUIRY OF THOSE INDIVIDUALS IMMEDIATELY RESPONSIBLE FOR OBTAINING THE INFORMATION, I BELIEVE THE SUBMITTED INFORMATION IS TRUE, ACCURATE AND COMPLETE. I AM AWARE THAT THERE ARE SIGNIFICANT PENALTIES FOR SUBMITTING FALSE INFORMATION INCLUDING THE POSSIBILITY OF FINE AND IMPRISONMENT SEE 18 USC 1001 AND 33 USC 1319 *(Penalties under these statutes may include fines up to $10,000 and or maximum imprisonment of between 6 months and 5 years.)*		TELEPHONE	
TYPED OR PRINTED		SIGNATURE OF PRINCIPAL EXECUTIVE OFFICER OR AUTHORIZED AGENT	AREA CODE	NUMB

COMMENTS AND EXPLANATION OF ANY VIOLATIONS *(Reference all attachments here)*

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