Drinking Water Operator Certification Training

Module 31
Pa. Laboratory Supervisor Highlights for Drinking Water & Wastewater Laboratories

Workbook

This course module was developed by the Pennsylvania Department of Environmental Protection. Content sources are referenced at the end of every module unit.

Updated July 3, 2014

Note: This DRAFT version does not include the Appendices, which contain non-essential extra information.

DISCLAIMER: Why the word "Highlights" is in the title

This module does not include all the information a laboratory supervisor needs to know.

Instead, this module consists only of highlights of the "Need to Know" Laboratory Supervisor Criteria that were developed by the Pa. Water and Wastewater Laboratory Supervisor team. This team consisted of 8 individuals, including Pa. DEP Bureau of Laboratory personnel, Pennsylvania environmental laboratory managers, a member of the Pa. Laboratory Accreditation Advisory Committee, Pa. water and wastewater operator certification board members, and Pa. DEP BWSFR staff member.

Some of the information in this module is taken right from Pa.'s Chapter 252 for Laboratory Accreditation, as well as the documents listed below. However, many other sources of reference information are listed in the reference section at the end of each unit.

The highlights of this module contain excerpts from the following important documents (listed below) that environmental laboratory supervisors should have available to help meet the QA/QC, reporting and accreditation requirements.

- Chapter 252: Environmental Laboratory Accreditation. This can be found at http://www.pacode.com/secure/data/025/chapter252/chap252toc.html
- Pa. DEP's Bureau of Laboratory Accreditation Program at http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095
- EPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories (1979.) This handbook can be found at: http://www.epa.gov/region6/qa/qadevtools/mod4references/analytical_references/qc_handbook.pdf
- NELAC Environmental Laboratory Sector Volume 1 Management and Technical Requirements for Laboratories Performing Environmental Analysis (2009.) This can be found at: http://www.nelac-institute.org/docs/standards/2009/EL_Volume1_2011.pdf
- Drinking Water Laboratories should have the following documents:
    - EPA's Manual for the Certification of Laboratories Analyzing Drinking Water – Fifth Edition (2005.) This can be found at http://www.epa.gov/ogwdw/methods/pdfs/manual_labcertification.pdf
    - "Drinking Water Laboratory Training: Reporting Data to DEP" (2007.) (Contact Pa. DEP at 717-705-6348 or welloyd@pa.gov for a copy)
- Wastewater Laboratories should have the following documents:
    - The Pa. DEP NPDES Lab Manual (1998), which can be found at http://www.dep.state.pa.us/dep/deputate/waterops/redesign/pages/Npdeslab.htm
    - Information about submitting Discharge Monitoring Reports (DMRs) can be found at http://www.portal.state.pa.us/portal/server.pt/community/discharge_monitoring_report_information/21375
    - Pa. DEP Wastewater Module 12 "Laboratory Overview" can be found at http://www.portal.state.pa.us/portal/server.pt/community/training/21408/dep_training_modules/1522737 (scroll down the page to the table of wastewater modules.)

Topical Outline

Disclaimer: Why the word "Highlights" is in the title

Unit 1 – Laboratory Basics Review (1 hr)

I. Laboratory Equipment Review

II. Drinking Water & Wastewater Compliance Testing

III. Sample Collection Tips

IV. Laboratory Personnel Basics

Unit 2 –Basic Math Review (2.5 hrs)

I. Basic Math Calculations

II. Calculating Averages

III. Algebra Problems

IV. Calculating Percentages

V. Units of Measurement

VI. Laboratory Unit Conversion and Unit Cancellation

VII. Temperature Conversion

Unit 3 – pH and Solution Concepts (1 hr)

I. pH Concepts

II. Solution Concepts

Unit 4 – Solution Calculations (1 hr)

I. Solution Dilution Calculations

II. Solution Concentration Calculations

Unit 5 – Laboratory Operation and Maintenance (1 hr)

I. Sample Acceptance

II. Equipment and Instrument Calibration

III. Equipment Monitoring

IV. Laboratory Safety

Unit 6 – Laboratory Quality Assurance and Quality Control (1 hr)

I. Quality Assurance

II. Quality Control Samples

III. General Laboratory QC

IV. Analyst Performance

Unit 7 – Laboratory Accreditation Basics (30 min)

I. Laboratory Accreditation Definitions

II. Adding a Field of Accreditation

Unit 8 – Quality Control Calculations & Analysis (1.5 hr)

I. EPA Rounding Rules

II. Quality Control Calculations

III. Data Analysis

Unit 9 – Laboratory Reporting (30 min)

I. Required Lab Test Report Information

II. Pennsylvania Compliance Reporting Systems

Unit 10 – Laboratory Recordkeeping (1 hr)

I. General Supply Records

II. Record Editing and Maintenance

III. Equipment Records

IV. Training Records

V. Pa. Quality Manual Records Retention

VI. Records available for an Audit

Module Answer Key (For Units 1-10)

Appendices (Note: The Appendices are a separate document: Appendices information is not on the exam)

- Appendix A: Common Analytical Methods
- Appendix B: Background on Chapter 252 & Laboratory Supervisor Information and Resources
- Appendix C: Characteristics of Good Chemists and Supervisors
- Appendix D: Laboratory Safety
- Appendix E: Pa. Accredited Laboratory Quality Manual Details
- Appendix F: Laboratory Audit Checklist Highlights

Unit 1 – Laboratory Basics Review

Learning Objectives

At the end of this unit, you should be able to:

- Correctly match terms and definitions for a few of the types of glassware and lab apparatus that are used in a drinking water and wastewater laboratory.
- Be familiar with the most frequently used equipment in the laboratory.
- Be familiar with certain standard drinking water tests.
- Be familiar with certain standard wastewater tests.
- Review important sample collection tips.
- List the required training for laboratory personnel.

I. Laboratory Equipment Review

Let's do a quick review of some of the glassware used in a laboratory; pictures of the glassware are on the next page.

*(**Note:** If you feel you are knowledgeable about glassware and do not need a glassware review, feel free to go directly to the "Unit 1, Exercise #1 - Laboratory Glassware" questions a few pages from here and answer the questions.)*

Beakers are glass containers used in a laboratory setting for stirring, mixing and heating liquids. Beakers are often "graduated" on the sides (i.e. marked with the volume contained) but are not meant for obtaining a precise measurement or volume.

Erlenmeyer Flasks (also known as conical flasks) are "graduated" on the sides (i.e. marked with the volume contained). They also have a spot of ground glass or enamel where they can be labeled with a pencil.

Graduated Cylinders are glass or plastic tubes that are calibrated for measuring large volumes of liquids. Although not nearly as accurate as pipettes, graduated cylinders have an advantage in that they require much less technique to use and can generally be used for larger volumes.

Volumetric Flasks are a type of flask used for making up solutions to a known volume. They are glass or plastic and consist of a flat bottom bulb with a long neck and usually a stopper on top.

Pipets are long tubes that are open at both ends that are used for delivering a precise amount of liquid.

Test tubes are finger-like lengths of glass with a u-shaped bottom that are used to hold, mix, or heat small quantities of solids or liquids.

Petri dishes are shallow glass or plastic cylindrical lidded dishes. They are often filled with a growth medium (usually agar plus nutrients) in order to culture microorganisms.

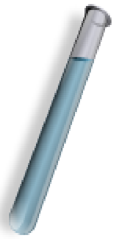
Burettes consist of a glass tube with etched graduations and a stopcock at the bottom. They are used for titrations (dispensing exact amounts of one chemical solution into another.)

(Note: Pa. DEP Wastewater Module 12 reviews laboratory basics in further detail; chapter 1 reviews various types of equipment and has more pictures of beakers, graduated cylinders, burets, and volumetric flasks.)

Beaker:

Beaker Photo from Microsoft Clip Art

Test Tube:



Test tube from Microsoft Clip Art

Burette:

Picture of burette by Mysid from http://en.wikipedia.org/wiki/File:Burette.svg

Erlenmeyer Flask:

Erlenmeyer Flask Photo by Juha Siitonen at http://commons.wikimedia.org/wiki/File:Erlat.jpg

Petri Dishes:

Petri Dishes from Microsoft Clip Art

Volumetric Flask:

Volumetric Flask from Pa. DEP WW Module 12

Graduated Cylinders:

Graduated Cylinders from Pa. DEP WW Module 12

Pipet:

Pipet Photo by Squidonius at http://en.wikipedia.org/wiki/File:Serological_pippette.jpg

Laboratory Glassware Considerations

Much of the glassware in today's analytical laboratories is a highly resistant borosilicate glass, such as that manufactured under the name "Pyrex" or under the name "Kimax." This glassware is satisfactory for many analyses. Other specific brands (such as Corning, Vycor, Ray-Sorb or Corex) may be used when special properties are needed such as resistance to heat, shock, and alkalis. Teflon and Polypropylene are other materials with special properties.

In choosing the glassware or plastic ware to use in a given situation, some factors to consider are:

- The stress the container will be put under,
- Whether the analysis container materials will react with the sample or any chemicals being added
- Whether the container can be properly cleaned following the analysis.

Hot glass also looks exactly like cold glass, so care must be taken to avoid grabbing hot glassware.

Note that after cleaning, laboratory glassware must have a final rinse with distilled or deionized water.

Volumetric Analyses

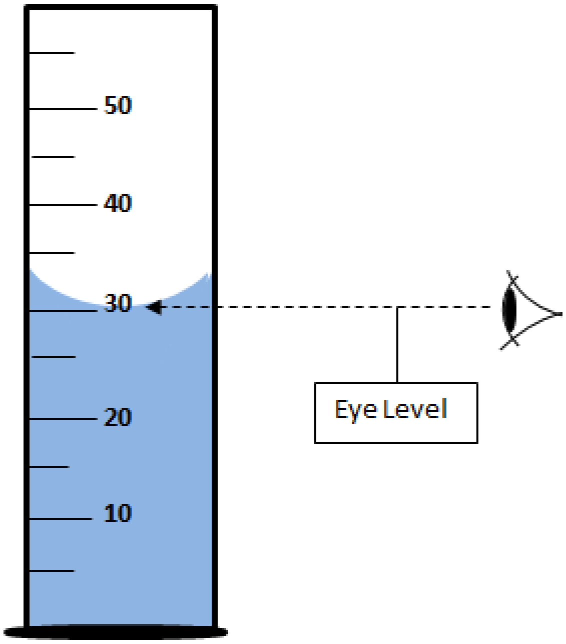
Volumetric glassware is calibrated glassware that is used for precise measurements of volume (such as volumetric flasks, volumetric pipets, and calibrated burets.)

Volumetric equipment is calibrated to contain or to deliver a definite volume of liquid and will be marked with the letters "TC" or "TD", respectively.

- TC = "To Contain" and means that that the container is made to hold (aka "contain") exactly the volume printed on the container.
- TD = "To Deliver" and means that the apparatus is made to deliver that exact amount into another container.

When exact volumes are not required, items such as graduated cylinders, serological pipets and measuring pipets may be used. Note that certain sources of error must be considered. Be sure to do the following:

- Read the meniscus of a liquid in a volumetric apparatus correctly. Volume is read from the bottom of the curve. (Note: see diagram of how to read a meniscus on the next page.)



Read a liquid meniscus at eye level; in the diagram above, the bottom of the meniscus has a reading of 30.

Class A glassware is more accurate and has smaller tolerances than Class B glassware as per the production and calibration required by the ASTM standards.

Class B glassware (or lower grade glassware) does not meet the same quality standards as Class A glassware.

Unit 1, Exercise #1 - Laboratory Glassware

(Note: Answers to all module questions are in the answer key which follows unit 10.)

Directions for questions 1-4 - Match the letter of the labels below with the number of the correct laboratory glassware picture on the next page*:

(*Note: All glassware exercise photos from Wikipedia – see references at end for more information)

A - volumetric flask; B – beaker; C – Erlenmeyer Flask

Picture #1 ___________________

Wikipedia photo by Nuno Nogueira

Picture #2 ________________

Wikipedia photo by Hannes Grobe

Picture #3 ________________

Wikipedia photo by Jaeger5432

Picture #4 ________________
(Note: Select the letters of all the glassware present)

Wikipedia photo by Tweek

Question #5: What does “TD” on the side of a piece of apparatus mean?

a. To contain
b. To Deliver
c. Teflon Dish

Question #6: Which type of glassware would you use for making up a solution to a known volume?

a. Beaker
b. Erlenmeyer Flask
c. Class A Volumetric Flask

Question #7: After cleaning, laboratory glassware must have a final rinse with distilled or deionized water.

a. True
b. False

Laboratory Measuring Equipment

First, let’s look at 2 definitions of entities that are related to laboratory measuring equipment.

ASTM (abbreviation for the American Society for Testing and Materials) is an organization which develops standards for materials, products, systems, and services. These standards are used in research and development, product testing and quality systems.

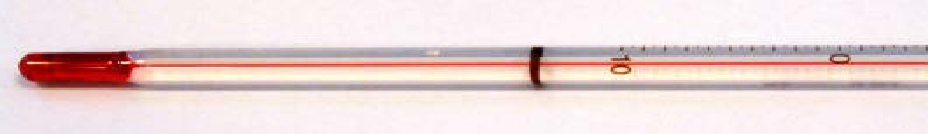
NIST (abbreviation for the National Institute of Standards and Technology) is a measurement standards laboratory. One of the assignments of this non-regulatory entity of the U.S. Department of Commerce is to provide weights and measures services. NIST publishes Handbook 44 that provides the specifications, tolerances, and other technical requirements for weighing and measuring devices.

Laboratory equipment that is used to measure various parameters includes the following pieces:

Thermometers:

Certified NIST-reference thermometer: A certified thermometer that has been tested against standards traceable to NIST. Environmental laboratories need to retain a certificate documenting traceability of the thermometer calibration to NIST standards.

- Glass, liquid filled thermometers are used for various laboratory applications. Note that in Chapter 5 we will discuss how glass, liquid-filled thermometers must be calibrated against the certified NIST reference thermometer every 12 months.



Picture of alcohol thermometer taken by chemical engineer from Wikipedia at http://en.wikipedia.org/wiki/File:SpiritTherm02.jpg

- Dial and electronic thermometers are used for general laboratory applications. Note that in Chapter 5 we will discuss how dial and electronic thermometers must be calibrated against the certified NIST reference thermometer every 3 months. Digital thermometers accompanied by a valid NIST traceable certificate of acceptance may be used for 12 months from the date of receipt before re-calibration.

Balances:

- Analytical or pan balances: Analytical and pan balances are designed to measure small mass in the sub-milligram range.

Picture of balance taken from
Pa. DEP WW Module 12

- Chapter 252 states that analytical or pan balances must provide sufficient accuracy and sensitivity for the weighing needs of the method.

- Note that in Chapter 5 we will discuss how balances must be calibrated with three ASTM reference weights that bracket the range of use on a daily basis.

- The balance calibration procedure must be written in the laboratory Standard Operating Procedures (SOP) with *acceptance criteria and corrective action if the calibration check does not meet acceptance criteria.

*(We will define and discuss more about the terms “acceptance criteria” and “corrective action” in later units.)

ASTM class 1, 2 or 3 (Class S or S-1) certified reference weights are used to calibrate an analytical balance or a pan balance.

Meters:

- pH meters are devices used to measure the pH of a liquid.
    - Note that they should be calibrated daily with at least 3 standard buffers.
    - These standard buffers should not be used for longer than 1 analysis day.

- Electrical conductivity meters measure the electrical conductivity in a solution. These meters should be calibrated daily.

Conductivity meter photo from Nuno Nogueira at
http://en.wikipedia.org/wiki/File:Electrical_conductivity_meter.jpg

Other Laboratory Equipment

- Water baths are used to incubate samples in water that is kept at a constant temperature.

- Laboratory ovens: Ovens for high-forced volume thermal convection applications. These ovens generally provide uniform temperatures throughout.

- Refrigeration equipment and freezers are used to keep samples cold. For samples with a storage temperature of 4°C, storage at a temperature of 0.5°C to 6°C is acceptable. Freezer temperatures must be less than 0°C.

Incubators are devices used to grow and maintain microbiological cultures at optimal conditions. Working thermometers must be present on the top and bottom of each working shelf in an incubator.

Incubator photo on right from Microrao at
http://en.wikipedia.org/wiki/File:Bacteriological_incubator.jpg

Heating blocks provide heating for a range of laboratory purposes such as digestion of samples, incubation of cultures, etc.

Test tube block heater photo from Lilly M at
http://commons.wikimedia.org/wiki/File:Laboratory_heating_block_Techne-03.jpg

Autoclave: A device used to sterilize equipment and supplies by subjecting them to high pressure saturated steam at 121 °C for around 10–30 minutes depending on the size of the load and the contents.

Autoclaves sterilize equipment and supplies by subjecting them to high pressure saturated steam at 121 °C.

Autoclave Photo from Wikipedia at
http://en.wikipedia.org/wiki/File:ExampleAutoclave.jpg

Analyte: The component, compound, element or isotope to be identified or quantified using a test or analysis.

Spectrophotometer: A device used to analyze samples of test material by passing light of a single wavelength through a sample and measuring the intensity, or amount, of the light absorbed by the sample. Different chemicals that may be in a sample absorb light at different specific wavelengths. The greater the amount of a particular chemical or analyte in a sample, the greater the amount of light that is absorbed by the sample. This property of an analyte to absorb light is used to determine the concentration of a chemical in a sample.

- Spectrophotometers must be calibrated to confirm the results are accurate. This procedure must be written is the laboratory SOP (Standard Operating Procedures) with acceptance criteria and corrective action if the calibration check does not meet acceptance criteria.
- Whenever the concentration of one or more analytes exceeds the Spectrophotometer calibration range, samples must be diluted and re-analyzed.

Spectrophotometer Photo from Wikipedia at
http://en.wikipedia.org/wiki/File:Spektrofotometri.jpg

The aforementioned lists of equipment are not all-inclusive, but each piece must be maintained through calibration.

Appendix A describes some common analytical methods.

In Unit 5, we will examine the calibration time frames for various pieces of laboratory equipment in more detail.

Unit 1, Exercise #2 - Laboratory Equipment:

Match the letters of the numbers that apply to the equipment. Selections may be used multiple times.

a. O° C b. 1 c. 3 d. 121 °C

1. ____________________ pH meter buffers should not be used more than this number of days

2. ____________________ Autoclaves must reach this temperature

3. ____________________ Balances must be calibrated with this number of weights

4. ____________________ Sample freezer temperatures must be under this amount

5. ____________________ pH meters should be calibrated with this many buffers.

II. Drinking Water and Wastewater Compliance Testing

Let's start this section by looking at two definitions.

Title 40 of the Code of Federal Regulations (abbreviated 40 CFR); Title 40 is a part of the U.S. Code of Regulations. Title 40 - aka 40 CFR - deals with the protection of the environment as administered by the Federal Environmental Protection Agency (aka EPA.) Acceptable laboratory testing methods for compliance monitoring are included in various sections of 40 CFR.

- CFR 141 addresses drinking water
- CFR 136 addresses wastewater

"Standard Methods for the Examination of Water and Wastewater" is a publication that includes hundreds of analytical techniques for water quality. The techniques are developed by the Standard Methods Committee which consists of over 500 individuals that review and approve the methods to be included each time the publication is edited.

Compliance Testing

Drinking water and wastewater facilities that meet the definitions of regulated facilities under 40 CFR (CFR 141 drinking water and CFR 136 for wastewater) need to perform compliance testing. Analytical methods that are approved for drinking water and wastewater compliance monitoring may be obtained from organizations such as ASTM International, Standard Methods, U.S. geological survey, or EPA. However, whatever the origin of the particular accepted laboratory test method for contaminant analysis, it must be listed in the applicable section of 40 CFR in order to be accepted as a compliance monitoring method for that particular contaminant.

Standard Drinking Water Tests

Let's review a few drinking water test definitions:

Coliform bacteria are a commonly used indicator of sanitary quality of foods and water. Coliforms themselves don't usually cause illness but are commonly present among other disease-causing organisms, which is why they are used as an indicator.

Disinfection Byproducts (abbreviated DBPs) are created when disinfectants react with natural organic matter in the water to form unintended organic byproducts which may pose health risks.

Inorganic Contaminants (abbreviated IOCs) are chemical compounds of mineral origin that do not contain carbon and hydrogen.

Most Radioactive Contaminants are naturally occurring, although contamination of drinking water sources from human-made nuclear materials can also occur.

Synthetic Organic Chemicals (abbreviated SOCs) are synthetically produced, meaning that they are man-made.

Volatile Organic Chemicals (abbreviated VOCs) come from animal or plant sources and contain carbon. Because they are volatile, they have enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere.

Drinking water testing requirements for a particular facility depend on the regulated facility characteristics, such as source type (surface water, ground water, or ground water under the influence of surface water [GUDI]), population served, disinfectant used, etc. Compliance testing requirements for drinking water systems are found in Chapter 109 (the Pa. Safe Drinking Water regulations).

Drinking water contaminants fit into the following categories:

A. Microbiological Contaminants
B. Surface Water Treatment Rule and related rule (IESWTR, LT1ESWTR, FBRR) contaminants
C. Inorganic Contaminants (IOCs)
D. Lead and Copper Rule Contaminants
E. Synthetic Organic Chemicals (SOCs)
F. Volatile Organic Chemicals (VOCs)
G. Radioactive Contaminants
H. Disinfection Byproducts (DBPs), Byproduct Precursors, and Disinfectant Residuals
I. Other Treatment Techniques

In a later unit we will talk more about proficiency testing. The Pa. DEP drinking water proficiency test tables can be found on the Pa. DEP Bureau of Laboratories Accreditation web site. The steps to finding this web site are:

- Type the following web address into the internet address search: www.depweb.state.pa.us
- Click on the left hand link labeled “DEP Programs A-Z”
- From the top line of alphabet linked letters that appear, click on the letter “L”
- Click on the first highlighted word on the list: “LABORATORY ACCREDITATION PROGRAM”
- Scroll down the page to the “Proficiency Testing” heading
- Look for the drinking water table

During much of 2014, you can also use the following quick link to locate the Lab Accreditation page: http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095 (look under the heading labeled ‘Proficiency Testing” for the drinking water table.)

Standard Wastewater Tests

Let's review a few wastewater test definitions:

Solids determinations are used to quantify the amount of solid material in various types of wastewater samples. These determinations help to determine the characteristics of influent, effluent, and sludge samples. Types of solids determinations are Dissolved Solids, Settleable Solids, Total Suspended Solids, and Total Solids.

Biochemical Oxygen Demand (abbreviated BOD): The amount of dissolved oxygen needed by aerobic biological organisms as they consume wastes. BOD test results indirectly indicate the concentration of wastes at various points in the treatment process. BOD is also used to verify discharge compliance.

Carbonaceous Biochemical Oxygen Demand (abbreviated CBOD): A measure of only the oxygen demand exerted by organic (carbonaceous) compounds, excluding the oxygen demand exerted by the nitrogenous compounds. To accomplish this, the nitrifying organisms are inhibited from using oxygen by the addition of a nitrification inhibitor to the samples.

Chemical Oxygen Demand (abbreviated COD): A test commonly used to indirectly measure the amount of organic compounds in water. CODs can be used as a quick check of treatment efficiency and used to make process control adjustments.

Total Kjeldahl Nitrogen (abbreviated TKN): A test that includes use of a Kjeldahl digestion apparatus to measure the sum of organic nitrogen and ammonia nitrogen in a wastewater effluent sample.

Some common laboratory analysis performed on treated wastewater are as follows:

- Solids
- pH
- Alkalinity
- Carbonaceous Biochemical Oxygen Demand (CBOD)
- Chemical Oxygen Demand (COD)
- Coliform
- Cyanide
- Metals
- Chlorine Residual
- Total Nitrogen, nitrate/nitrite
- Phosphate
- Sulfate
- Total Kjeldahl Nitrogen (TKN)

NPDES (abbreviation for **National Pollutant Discharge Elimination System**): A permit system for regulating point sources (i.e. single identifiable sources) of pollution. These sources include industrial facilities, municipal government and military facilities, and some agricultural (such as feedlot) facilities.

Wastewater Analyte Monitoring

- There are numerous potential wastewater contaminants for which monitoring could be required. Monitoring is required for those contaminants known to be used by industries or commercial establishments that discharge to the collection system. Monitoring is also required to examine the loading of particular contaminants on the receiving stream.

- There are a number of analytes which are regulated in nearly all wastewater treatment plant 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.

As mentioned previously, in a later unit we will talk more about proficiency testing. The Pa. DEP wastewater proficiency test tables can be found on the Pa. DEP Bureau of Laboratories Accreditation web site. The steps to finding this web site are:

- Type the following web address into the internet address search: www.depweb.state.pa.us
- Click on the left hand link labeled “DEP Programs A-Z”
- From the top line of alphabet linked letters that appear, click on the letter “L”
- Click on the first highlighted word on the list: “LABORATORY ACCREDITATION PROGRAM”
- Scroll down the page to the “Proficiency Testing” heading
- Look for the non-potable water table.

During much of 2014, you can also use the following quick link to locate the Lab Accreditation page: http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095 (look under the heading labeled ‘Proficiency Testing’ for the non-potable water table.)

III. Sample Collection Tips

General Sample Collection Tips

For **recordkeeping purposes**, be sure to record in a log book the following:

- client/project name,
- sample date & time
- location of sample collection
- sample collector name & field identification code
- a unique laboratory ID code

It's also a good idea to label the sample bottle. The sample bottle must contain a unique identifier.

For shipping/handling purposes, maintain a chain-of-custody record that documents each person that sent and received the samples.

To guarantee that holding times for the analytical parameters are not exceeded, ship or deliver samples to the laboratory on the day they are collected. All samples must be iced or refrigerated at 4°C from time of collection to analysis. Ice is not required in the field if the laboratory receives and refrigerates the sample within 15 minutes of collection.

Drinking Water Sample Collection Tips

Now let's look at a few tips for collecting drinking water samples.

(Note: Always use the specific method designated by the regulations for which you are performing compliance sampling.)

For **Lead & Copper sampling**, make sure you take a first-draw sample (i.e., water has remained in pipes, undisturbed, for 6 hours). Use a cold water kitchen or bathroom tap.

For **Volatile Organics (VOC) sampling** fill each of the two vials completely with the sample (creating a meniscus), but do not overflow/flush out the preservative. Cap and invert several times to mix. Check for air bubbles.

For **Total or Fecal Coliform Bacteria sampling**, if you use a sterilized 125 mL blue-capped bottle prefixed with Sodium Thiosulfate, remove the cap and hold it in your hand. Do not touch the inside of the cap or bottle. Fill sample bottle to neck (leave airspace) and do not overflow. Cap the bottle and invert several times to mix.

Wastewater Sample Collection Tips

Now let’s look at a few tips for collecting wastewater samples.

(Note: Always use the specific method designated by the regulations for which you are performing compliance sampling.)

For **Fecal Coliform Bacteria sampling**, if you are collecting samples of chlorinated effluents, the sample must be dechlorinated. If you are sampling using a sample container pre-treated with sodium thiosulfate solution and performing manual sampling, hold the bottle near the base during sampling. Submerge the sample bottle in the water to be sampled, sample against the current and keep the hand downstream from the neck of the bottle. Leave ample air space to allow the sample to be mixed by shaking prior to testing.

For T**otal Phosphorus sampling** make sure that all sampling containers that are being reused should be rinsed with diluted (1 + 1) hydrochloric acid. Then they should be rinsed 3 times with distilled water. (Note: Never use commercial detergents for cleansing any glassware used in the storage or analysis of samples for phosphorus determination.)

Wastewater Sample Collection Safety (from Ch. 1 of the 1998 Pa. NPDES Lab Manual)

- Whenever possible, rubber gloves should be worn when sample collection requires contact with wastewater (including final effluent) and sludge. Gloves should be washed thoroughly before being removed. After removing gloves, wash hands thoroughly using a disinfectant type soap.
- Do not climb over or go beyond guardrails or chains when collecting samples. Use sample poles or ropes as necessary to collect samples safely.
- The use of personal floatation devices around any body of water (especially moving water) can save your life!

Unit 1, Exercise #3 - Sample Collection Tips:

Directions: Choose the correct choice

1. For these types of drinking water samples, fill the vial completely with the sample (creating a meniscus) & check for air bubbles. Then, fill a second vial.

   a. Lead & Copper samples

   b. Total or Fecal Coliform Bacteria samples

   c. Volatile Organic Chemical samples

2. For these types of samples, if you are using a sterilized 125 mL blue-capped bottle prefixed with sodium thiosulfate, remove the bottle cap and hold it in your hand. Do not touch the inside of the cap or bottle. Fill sample bottle to neck (leave airspace) and do not overflow. Then cap the bottle and invert it several times to mix.

a. Lead & Copper samples

b. Total or Fecal Coliform Bacteria samples

c. Volatile Organic Chemical samples

d. Total Phosphorus samples

Directions: Select True or False

3. When collecting wastewater samples, the use of personal floatation devices (PFDs) around any body of water (especially moving water) can save your life.

a. True

b. False

4. It is good to use commercial detergents for cleansing any glassware used in the storage or analysis of samples for phosphorus determination.

a. True

b. False

IV. Laboratory Personnel Basics

Definitions:

Laboratory supervisor - A technical supervisor of an environmental laboratory who supervises laboratory procedures and reporting of analytical data.

Conflict of Interest: a personal interest or relationship, as defined by law or regulation, that conflicts with the faithful performance of your official duty.

Data Audit: A qualitative and quantitative evaluation of the documentation and procedures associated with measurements to verify that the resulting data are acceptable.

Note: For those interested, Appendix B has background information on how both Chapter 252 and the Operator Certification Laboratory supervisor category came into existence.

Required Training for Laboratory Personnel

Certain training is required for all laboratory personnel working for a Pa. accredited water and wastewater laboratory. The requirements for this ethics, legal, and technical training is as follows:

- Ethics Training: Laboratories are required to give their personnel ethics training within 2 months of being hired. Ethics training must then be provided for all laboratory personnel every 14 months.
    - Lab management may choose to develop their own ethics training course or may use a course developed by another organization as long as it meets the requirements of Chapter 252.
- Legal Responsibilities Training: Laboratories are required to give their personnel legal responsibility training within 2 months of being hired. Legal responsibility training must then be provided for all laboratory personnel every 14 months. This legal responsibility training is usually tied into the ethical training for lab personnel.

  The significance of ethics and legal responsibility training is to clearly outline the employee's ethical and legal responsibilities. It is important that employees understand the potential punishments and penalties for improper, unethical or illegal actions.

Importance of Laboratory Ethics

Falsification of Water Test Results

In 2013, a northeast U.S. laboratory was federally prosecuted and pled guilty to the falsification of thousands of laboratory test results on water samples from landfills and wastewater treatment plants. The company agreed to pay a criminal fine of $150,000 and restitution to victims, as determined by the court.

- Technical Training: Laboratory personnel need to participate in training courses or workshops on specific equipment, analytical techniques or laboratory procedures that relate to their job responsibilities.

More Information on Training Requirements

- More information on the ethics and legal responsibility training requirements for laboratory personnel can be found in the document “Writing a Quality Manual for PA State (Chapter 252) Accreditation” which is located on the Pa. DEP Bureau of Laboratories Accreditation web site. The steps to finding this web site and document are:
    - Type the following web address into the internet address search: www.depweb.state.pa.us
    - Click on the left hand link labeled “DEP Programs A-Z”
    - From the top line of alphabet linked letters that appear, click on the letter “L”
    - Click on the first highlighted word on the list: “LABORATORY ACCREDITATION PROGRAM”
    - Scroll down the page to the “Compliance Assistance” heading
    - Look for the linked heading about writing a Quality Manual for Pa State (Chapter 252) Accreditation; Item #4 in this document discusses the training procedure for ensuring laboratory personnel are trained about their ethics and legal responsibilities

- The regulatory statement about the technical and analytical training requirements for laboratory personnel can be found in Chapter 252 § 252.304 (b)(3)(iii) at http://www.pacode.com/secure/data/025/chapter252/chap252toc.html

General Supervisory Basics

Being a laboratory supervisor means that you have staff working for you. Being a good laboratory supervisor means that you are doing your best to balance the following simultaneous roles:

- A role as supervisor of a drinking water and/or wastewater environmental laboratory that needs to meet various regulatory requirements (e.g. Pa. Chapter 252 and Federal 40 CFR.)
- A role as a knowledgeable environmental chemist who can assist your employees when they need direction with their daily tasks.
- A role as a good leader.

Appendix C lists some of the qualities it takes to be a good chemist (so you can lead by example in this area) as well as being a good general supervisor. If you don’t naturally have a particular quality you can always work over time to develop it.

Unit 1 Review Exercise:

1. Coliform bacteria themselves don’t usually cause illness but are usually present among other disease-causing organisms, so they are used as an indicator of sanitary quality of foods and water.

   a. True

   b. False

2. Environmental laboratory temperatures are read in °C.

   a. True

   b. False

3. Under Chapter 252, every 14 months, laboratories are required to give their staff which types of training? (Directions: choose the best answer)

   a. Technical Training & Legal Training
   b. Legal Training & Ethics Training
   c. Technical Training & Ethics Training

Unit 1 Key Points:

- Volumetric glassware is calibrated glassware that is used for precise measurements of volume.
- TC means that that the container is made to hold (aka “contain”) exactly the volume printed on the container and TD means that the apparatus is made to deliver that exact amount into another container.
- Coliform bacteria themselves don’t usually cause illness but are usually present among other disease-causing organisms, so they are used as an indicator of sanitary quality of foods and water.
- A laboratory test method for contaminant analysis must be listed in the applicable section of 40 CFR in order to be accepted as a compliance monitoring method for that particular contaminant.
- Spectrophotometers must be calibrated to confirm the results are accurate.
  - Whenever the concentration of one or more analytes exceeds the Spectrophotometer calibration range, samples must be diluted and re-analyzed.
- Every 14 months, Pa. accredited laboratories are required to give their staff both legal training and ethics training.

Unit 1 References:

- Laboratory glassware consideration about grabbing hot glass from Wikipedia article on Laboratory Glassware at http://en.wikipedia.org/wiki/Laboratory_glassware

- Graduated cylinder definition was taken from Chapter 1, pg. 1-13 of the Pa. DEP NPDES Lab Manual (1998), at http://www.dep.state.pa.us/dep/deputate/waterops/redesign/Subpages/NPDESLabchap.htm

- Chapter Photos:
  - Beaker & Petri dishes taken from Microsoft Clip Art; Erlenmeyer Flask from Wikipedia as referenced under photo
  - Graduated Cylinders: Pa. DEP WW Module 12 (Pg. 1-3) from Sean Brubaker, (Hach Co. USA, 2002); Volumetric Flasks: Pa. DEP WW Module 12 (Pg. 1-6) from Sean Brubaker, (Hach Co. USA, 2002); Balance: Pa. DEP WW Module 12 (Pg. 1-12) from Sean Brubaker, (Hach Co. USA, 2002)Pipet from Wikipedia as referenced under photo
  - Test tube taken from Microsoft Clip Art

- Exercise Photos:
  - Photograph of beakers, taken by Jaeger5432 http://en.wikipedia.org/wiki/Beaker_(glassware)
  - Photograph of Volumetric Flasks by Nuno Nogueira http://en.wikipedia.org/wiki/Volumetric_flask
  - Photograph of Erlenmeyer Flask by Hannes Grobe http://en.wikipedia.org/wiki/File:Erlenmeyer_flask_hg.jpg
  - Photograph of group of glassware by Tweek: http://en.wikipedia.org/wiki/File:Lab_glassware.jpg

- Standard Conventional Pollutant Waste Water Tests Required Data information taken from DEP WW Operator Training Module #12 WB pp. 6-4 through 6-5

- TD and TC from http://www.ehow.com/facts_6063680_laboratory-glassware-identification.html

- Laboratory Glassware & Volumetric Analysis from EPA Handbook For Analytical Quality Control in Water And Wastewater Laboratories 1979 pp. 4-1 to 4-3

- Meniscus reading diagram created by Pa. DEP's W. Lloyd

- Equipment information was obtained from then following:
  - Autoclave: http://en.wikipedia.org/wiki/Autoclave
  - Laboratory Oven: http://en.wikipedia.org/wiki/Laboratory_oven
  - Heating block information from Thomas Scientific at http://scientific-supplies.thomassci.com/scientific-supplies/Dry%20Block%20Heater
  - Refrigerator and freezer information from Ch. 252 Section 252.306 (f)(7) (iv.-v.)
  - Water bath http://www.news-medical.net/Laboratory-Water-Baths
  - Certified NIST reference thermometer: http://www.nist.gov/pml/mercury_traceability.cfm and Ch. 252 Section 252.306 (f)(1)
  - Spectrophotometer: V. Hunsberger and Y. Creason from Pa. DEP BOL Accreditation Section, Wise Geek Spectrophotometer calibration at http://www.wisegeek.org/what-is-spectrophotometer-calibration.htm , and EPA's Calibration Curve Forum 10-2010 at http://www.epa.gov/fem/pdfs/calibration-guide-ref-final-oct2010.pdf
  - pH meter: http://en.wikipedia.org/wiki/Ph_meter

  - electrical conductivity meter: http://en.wikipedia.org/wiki/Conductivity_meter
  - burette: http://en.wikipedia.org/wiki/Burette

- Class A Glassware definition from http://www.titrations.info/pipette-burette and http://home.windstream.net/mikeric/Chap1to9/Chap4%20%20Measurements.htm
- Sample Collection Review Drinking Water procedures taken from the April 2002 "Pa. DEP Field Staff Sample Collection & Preservation Procedures" document

- Coliform bacteria definition taken from http://en.wikipedia.org/wiki/Coliform_bacteria

- Common Wastewater Treatment Analysis taken from Module 12, Ch. 2 (solids)

- BOD definition taken from Wikipedia at http://en.wikipedia.org/wiki/Biochemical_oxygen_demand + Pa. DEP Module 12 pg. 4-11

- COD definition taken from Wikipedia at http://en.wikipedia.org/wiki/Chemical_oxygen_demand + Pa. DEP Module 12 pg. 4-12

- Pa. DEP Module 12 pg. 4-24 used to create Total Kjeldahl Nitrogen definition.

- CBOD definition taken from Chapter 5, pg. 5-2 of the Pa. DEP NPDES Lab Manual (1998), at http://www.dep.state.pa.us/dep/deputate/waterops/redesign/pages/Npdeslab.htm

- Pa. DEP Module 12 pg. 4-24 was used to create the Total Kjeldahl Nitrogen (TKN) definition.

- NPDES definition taken from http://en.wikipedia.org/wiki/NPDES#NPDES_permits_for_point_sources and point source segment of definition taken from http://en.wikipedia.org/wiki/Point_source

- Title 40 definition taken from http://en.wikipedia.org/wiki/Title_40_of_the_Code_of_Federal_Regulations and http://en.wikipedia.org/wiki/Code_of_Federal_Regulations#List_of_regulation_titles

- ASTM definition taken from the ASTM International fact sheet at http://www.astm.org/ABOUT/factsheet.html

- NIST definition taken from http://en.wikipedia.org/wiki/Nist and from the NIST fact sheet at http://www.nist.gov/public_affairs/factsheet/nist_did_you_know.cfm

- Information in the table at http://water.epa.gov/scitech/drinkingwater/labcert/upload/AppendixAtoSubpartCofPart141.pdf was used to explain the 40 CFR definition as well as the resources used by EPA to create compliance monitoring requirements.

- Standard Methods for the Examination of Water and Wastewater taken from http://www.standardmethods.org/

- Required Training for Laboratory Personnel taken from Act 252 – Section 252.401(d)(2)

- New York July 17, 2013 Laboratory prosecution case taken from http://www.dcbureau.org/201311209337/natural-resources-news-service/tainted-water-testing-lab-flourished-under-lax-new-york-state-regulators.html#more-9337

Unit 2 – Basic Math Review

Learning Objectives

At the end of this unit, you should be able to perform the following:

- Basic math calculations
- Decimal calculations
- Calculation of averages
- Calculation of percentages
- Laboratory unit conversions
- Laboratory unit cancellations
- Converting between ppm and ppb
- Temperature conversions

(Note: If you feel you are able to perform all of the calculations listed above, you can always go directly to the Unit 2 Review Calculations at the end of the unit, which is a compilation of all of the unit example problems. Be sure to obtain the Operator Cert Testing Formula and Conversion Handout that is given to operators during the certification exam - since it contains a formula for temperature conversions. To obtain a copy of this handout, call 717-772-4018 and ask to speak to someone in the Training Section or e-mail DEPWSTechTrain@state.pa.us

I. Basic Math Calculations

Basic Rules for Performing Calculations

There are four general rules to remember when performing calculations:

- Rule 1: Perform calculations from left to right.
- Rule 2: Perform all arithmetic within parentheses prior to arithmetic outside the parentheses
- Rule 3: Perform all multiplication and division prior to performing all addition and subtraction.
- Rule 4: For complex division problems, follow the previous rules starting with parenthesis. Next perform all multiplication and division above the line (in the numerator) and below the line (in the denominator); then proceed with the addition and subtraction. Finally divide the numerator by the denominator.

Symbol Notes:

- A small “x” symbol denotes multiplication throughout this module.
- In the algebra segment and there-after, a capitol “X” symbol denotes an unknown number.
- When 2 numbers have a backslash in between denoted by a “/” it means they are being divided (e.g. 10/2 means 10 is divided by 2.)

Basic Math Calculations - Example 1:

18 + 73 – 45 + 32 = 78

Basic Math Calculations - Example 2:

(312 x 4) + (27 x 9) = 1248 + 243 = 1,491

Basic Math Calculations - Example 3:

$$\frac{385 + (21/7) - (5 \text{ x } 13 \text{ x } 4)}{17 + 11 - (6 \text{ x } 4)} = \frac{385 + 3 - 260}{28 - 24} = \frac{128}{4} = 32$$

Unit 2, Practice #1: Basic Math Calculations:

(Note: Answers to all module questions are in the answer key which follows unit 10.)

1. (85 x 17) + (22 x 12) =

2. $\frac{(145 \text{ x } 9 \text{ x } 2) - (14 \text{ x } 9 \text{ x } 2) + 162}{(7 \text{ x } 5) - (10/2) + 150} =$

Greater than and less than symbols

The **Less than** symbol is shown as <.

- When we look at quality control in a later chapter, if you see that your calculation must come out to be <20 mg/L, this means your quality control calculation must be less than 20 mg/L.
- ≤ is the symbol for less than or equal to; ≤20 mg/L means less than or equal to 20 mg/L.

The **Greater than** symbol is shown as >.

- For example, if your laboratory sample method said that you needed to bake a sample overnight at >100°C to eliminate contaminants, this means you need to bake the sample at a temperature that is greater than 100°C.
- ≥ is the symbol for greater than or equal to; ≥ 100 °C means the temperature must be greater than or equal to 100 °C.

Calculations with Decimals

Decimals have numbers that follow a decimal point. For example, the number 8 has no decimal point, but the number 8.12 is a decimal number that has two numbers which follow the decimal point. Adding and subtracting decimals is basically the same as adding and subtracting whole numbers.

When adding or subtracting decimals, it is critical to line up the terms so that all the decimal points are in a vertical line.

If a whole number is thrown into the calculation, make it into a decimal by adding a .0 to help line up the numbers.

Decimal Calculation Example:

What is the sum of 1.1 + 0.98 + 1.231 + 2?

Line up the decimals places to add the numbers:

1.1
0.98
1.231
2.0
5.311

Unit 2, Practice #2 - Decimal Calculation:

1. 11.85 + 1.5 + 14 =

II. Calculating Averages

Average: = Sum of Terms ÷ Number of Terms. In mathematics and statistics, the average is the sum of a collection of values divided by the number of values, or terms in the collection.

The term “Average” is also known as “Arithmetic Mean.”

The formula is often written as follows:

$$\text{Average} = \frac{\text{Sum of Terms}}{\text{Number of Terms}}$$

Since we are adding numbers with units (in the below example our units are °F), we keep the same unit for the answer. We will look more at units of measurement in a later section.

Calculating Averages Example:

Given the temperatures of 93 °F, 99 °F, 101 °F, and 91 °F, calculate the average.

$$\frac{93\ ^\circ\text{F} + 99\ ^\circ\text{F} + 101\ ^\circ\text{F} + 91\ ^\circ\text{F}}{4}$$

$$= 96\ ^\circ\text{F}$$

☞ Formula to Memorize: Calculating Averages

You are expected to know a formula for calculating averages, so if you can’t easily remember how to set up an equation to calculate an average, be sure to memorize a formula. The basic formula for calculating averages is as follows:

$$\text{Average} = \frac{\text{Sum of Terms}}{\text{Number of Terms}}$$

Unit 2, Practice #3 – Calculating Averages:

1. A drinking water system measured the pH of their system water at 4 different points in their distribution system. The pH levels were 7.5, 6.7, 7.7, and 6.5. Calculate the average of these pH readings and select the correct answer from the options below.

a. 6.9

b. 7.1

c. 7.0

d. 7.3

(Note: Next we have an average which involves using the decimal addition principals we discussed earlier in the chapter.)

2. A drinking water system with a filter plant measured the finished water turbidity at the entry point to their distribution system and found the following 5 readings: 0.21 NTU, 0.2 NTU, 0.113 NTU, 0.3 NTU and 1 NTU. Calculate the average of these finished water turbidity readings (keep all the decimal places in the answer.)

a. 0.3220 NTU

b. 0.262 NTU

c. 0.3646 NTU

d. 0.246 NTU

III. Algebra Problems

Algebra Problems – Solving for "X"

Algebra is a branch of mathematics that uses numbers and letters that represent numbers. Whereas arithmetic deals with specified numbers, algebra introduces quantities without fixed values, known as variables.

In this section we are reviewing basic algebra problems where we have to solve for an unknown which is X.

*Rules for Solving for an Unknown Variable (such as *X*)

1. X must be in the numerator.
2. X must be by itself (on one side of the equals sign).
3. Whatever you do to one side of the equation, you must do to the other side of the equation.

**Rules 1 and 2 are taken from pp. 11-12 of "Basic Math Concepts for Water and Wastewater Operators" by Joanne Kirkpatrick Price as cited in the references at the end of the Unit.*

Let's look at an example:

$7X = 42$

- X is in the numerator in this equation.

- However, X is not by itself, so we need to isolate X on one side. To get rid of the 7 (which is supposed to be multiplied by the X), we divide by 7.

$$\frac{7X}{7} = 42$$

- We must do the same thing to both sides of the equation, so we must divide both sides by 7. The 7's on one side of the equation than cancel out.

$$\frac{\cancel{7}X}{\cancel{7}} = \frac{42}{7} \longrightarrow X = \frac{42}{7} \longrightarrow X = 6$$

Calculating X - Example 1:

(Note: see Example #1 Question #1-#3 answers on the next page):

$6X = 18$

Example 1, Question #1: Is the ***X*** in the numerator? ______
Example 1, Question #2: Is the *X* alone on one side of the equation? _____

How do we get X alone on one side of the equation?

The answer is to divide both sides by "6" to get X alone and **treat both sides of the equation equally.**

$$\frac{\cancel{6}X}{\cancel{6}} = \frac{18}{6}$$

The 6"s on the one side of the equation cancel out, so you are left with the following: $X = \frac{18}{6}$

Example 1, Question #3: What does X equal?

Answers for Example #1:

Example 1, Question #1: Is the ***X*** in the numerator? ______ (Answer: Yes)

Example 1, Question #2: Is the *X* alone on one side of the equation? _____ (Answer: No)

Example 1, Question #3: X = 3

Calculating X - Example Calculation 2

(Note: see Example #2 Question #1-#3 answers on the next page):

$$2.5 = \frac{1{,}000}{X}$$

Rule 1, Example 2, Question #1: Is the *X* in the numerator? ______

How do we move the *X* into the numerator?

The answer is to multiply both sides of the equation by *X*.

$$X\,(2.5) = \frac{1{,}000\ \cancel{(X)}}{\cancel{X}} \longrightarrow X\,(2.5) = 1{,}000$$

Example 2, Question #2: Once we move the X into the numerator on the other side of the equation, is *X then alone* on one side of the equation? _____

How do get *X* alone on one side of the equation?

The answer is to divide by 2.5 on each side of the equation so that the *X* is alone, but the equation keeps the same value.

$$\frac{X\,\cancel{(2.5)}}{\cancel{2.5}} = \frac{1{,}000}{2.5}$$

The 2.5"s on the one side of the equation cancel out, so you are left with the following: $X = \frac{1{,}000}{2.5}$

Example 2, Question #3: What does X equal?

Answers for Example #2:

Example 2, Question #1: Is the *X* in the numerator? ______ (Answer: No)

Example 2, Question #2: Once we move the X into the numerator on the other side of the equation, is *X then alone* on one side of the equation? _____ (Answer: No; 2.5 is still there too.)

Example 2, Question #3: X = 400

Unit 2, Practice #4 – Solving for X:

Directions: Solve for x in the following problems.

1. $\frac{X}{200} = 2.4$ X = ______

2. $10 = \frac{3000}{X}$ X = ______

Solving Word Algebra Problems: Finding the Correct Formula

The term **"Word problem"** is often used to describe any mathematical exercise where significant information about the problem is given as text rather than in mathematical form.

When faced with a word problem where you have to solve for X, there is usually a formula that can assist you. As a result, you don't have to memorize standard equations, you just have to know where to locate them and how to switch them around to find what you are looking for.

Some recommendations for solving word problems (taken from Cuesta College in San Luis Obispo, CA) are as follows:

1- List the information you know and the information you don't.
2- Search for a formula that has the items you know as well as those you don't.
3- If you can change the formula around before plugging in the numbers for the item you need, do so. If not, plug in the numbers and then solve for the item you need.
4- Whatever is done to one side of the equation must be done to the other side of the equation. The unknown must end up on one side of the equation, by itself. If you have more than one unknown, then use the substitution or elimination method to solve the equations.
5- Put your answer back into the original equation to see if it is correct. If one side of the equation equals the other side of the equation, then you have the correct answer. If you do not have the correct answer, go back and try again.

IV. Calculating Percentages

A **percentage** is a number that is a ratio that is expressed as a fraction of 100.

A *formula that is used to determine % is:

$$\% = \frac{\text{Part}}{\text{Whole}} \times 100$$

Notes on this equation:

1. The “Part” and the “Whole” do not have units since the comparison is simply a ratio.
2. By multiplying the ratio by 100, the ratio becomes a percent (%).
3. If the unknown is the Part or Whole and you have to divide the % by 100, the % becomes a decimal number.

Calculating Percentages - Example 1: What percentage is 15 of 60?

Step 1: Determine what you know and what you do not.

% = unknown

Part = 15

Whole = 60

Step 2: Find your formula: We are using the following formula

$$\% = \frac{\text{Part}}{\text{Whole}} \times 100$$

Step 3: Plug your known and unknown information into the equation:

$$X = \frac{15}{60} \times 100$$

Step 4: Work to isolate your unknown on one side of the equation.

In this case, we are solving for % , which is already isolated on one side of the equation, so we just plug the numbers into the equation as is (using X as the unknown).

$$X = \frac{15}{60} \times 100$$

$$X = 0.25 \times 100$$

$$X = 25\%$$

(Note: Once the ratio was multiplied by 100, the number is converted to a percent.)

☞ Formula to Memorize: Calculating Percentages

You are expected to know a formula for calculating percentages, so if you can't easily calculate percentages in your head, be sure to memorize a formula. The easy one for percentage calculations is:

$$\% = \frac{\text{Part}}{\text{Whole}} \times 100$$

Now, let's look at a totally different question (that looks very similar):

Calculating Percentages - Example 2: What is 15% of 60?

Step 1: Determine what you know and what you do not.

% = 15

Part = Unknown (aka "X")

Whole = 60

Step 2: Find your formula; we are once again using the formula $\% = \frac{\text{Part}}{\text{Whole}} \times 100$

Step 3: Plug in your known numbers:

$$15\% = \frac{X}{60} \times 100$$

Step 4: Isolate X on one side of the equation

$$(60)\ 15\% = \frac{X}{\cancel{60}} \times 100 \times \cancel{(60)}$$ (We'll multiply both sides of the equation by 60)

$$\frac{(60)\ 15\%}{100} = \frac{(X\ \text{Part})\ \cancel{(100)}}{\cancel{100}}$$ (We'll divide both sides of the equation by 100)

X = 9

(Note: Once the left side was divided by 100, the % becomes a number.)

Answer: 15% of 60 = 9

Unit 2, Practice #5 – Solving Percentage Problems:

1. What percentage is 45 of 150?

2. What is 45% of 150?

V. Units of Measurement

Metric System Base Units

Metric System: A system of decimal measurement that originated in France and is now used internationally as the International System of Units (abbreviated SI). Over time, information has been incorporated to include more units. The U.S. is the only nation which does not use this system as the official system of measurement.

The metric system base units are considered the 7 units from which all others are derived; their physical quantities are as follows:

- meter for measuring length
- kilogram for measuring mass
- second for measuring time
- ampere for measuring electric current
- kelvin for measuring temperature (Note: used in conjunction with Celsius, which has the same magnitude)
- candela for measuring luminous intensity
- mole for measuring amount of substance.

Note: in this module we will use grams as our base mass unit and liters as our base volume unit.

Metric System Prefixes and Symbols

The Metric System is the most commonly used system of weights and measures around the world and used almost exclusively in the scientific community. It utilizes both prefixes and symbols to describe values in magnitudes of ten.

Prefixes and Symbols

The chart below can be used in determining how to move the decimal point for a conversion.

Prefix	Represents:	Symbol	Decimal Value
Micro-	One millionth	µ	0.000001
Milli-	One thousandth	m	0.001
Centi-	One hundredth	c	0.01
Deci-	One tenth	d	0.1
Unit	Base		1
Deka-	Ten Times	da	10
Hecto-	Hundred Times	h	100
Kilo-	Thousand Times	k	1,000
Mega-	Million Times	M	1,000,000

In the next section we will look at converting units of different increments.

VI. Laboratory Unit Conversion and Unit Cancellation

Converting within the Metric System

Sometimes laboratory activities require conversion between different magnitudes of a unit. First, let's look at 2 definitions we will be using in regard to these conversions.

Unit Relationship: Comparing the relationship of a base unit with different magnitudes of a unit that are much less than or much greater than 1.

- For example, the base unit of 1 liter (L) equals 1000 milliliters (mL).
- Another example is the base unit of a gram where 1,000 grams (g) equals 1 kilogram (Kg.)
- Unit relationships are especially significant in an environmental laboratory where very small amounts of contaminants are often searched for in the thousand or million range.

Vertical Format: Expressing the relationship of units as a fraction.

- For example, the base unit of 1 liter (L) equals 1000 milliliters (mL), so the vertical format expression of this would be as follows:

$$\frac{1\text{ L}}{1{,}000\text{ mL}}$$

The same relationship can be flipped:

$$\frac{1{,}000\text{ mL}}{1\text{ L}}$$

Expressed in the vertical format, these can also be thought of as "conversion factors." Other conversion factors:

Conversion:	Vertical Formats:	
1 m = 100 cm	$\frac{1\text{ m}}{100\text{ cm}}$	$\frac{100\text{ cm}}{1\text{ m}}$
1 g = 1,000 mg	$\frac{1\text{ g}}{1{,}000\text{ mg}}$	$\frac{1{,}000\text{ mg}}{1\text{ g}}$
1 mg = 1,000 ug	$\frac{1\text{ mg}}{1{,}000\text{ ug}}$	$\frac{1{,}000\text{ ug}}{1\text{ mg}}$
1 kg = 1,000 g	$\frac{1\text{ kg}}{1{,}000\text{ g}}$	$\frac{1{,}000\text{ g}}{1\text{ kg}}$

The next page contains some common conversion relationships you need to be able to use. The last column of the table shows the relationship between the base item and the item of greater or lesser magnitude. This relationship is what will be expressed in vertical format for performing a unit conversion.

☞ Unit Magnitude Relationships for Unit Conversion

For laboratory work, be sure to know how the different magnitudes of a unit relate to the base unit.

Prefix	Represents:	Symbol	Decimal Value	Relationship to base unit (using grams as an example)
Micro-	One millionth	µ	0.000 001	1 g = 1,000,000 ug
Milli-	One thousandth	m	0.001	1 g = 1,000 mg
Centi-	One hundredth	c	0.01	1 g = 100 cg
Deci-	One tenth	d	0.1	1 g = 10 dg
Unit	Base		1	Base unit
Deka-	Ten Times	da	10	10 g = 1 Dag
Hecto-	Hundred Times	h	100	100 g = 1 Hg
Kilo-	Thousand Times	k	1,000	1,000 g = 1 Kg
Mega-	Million Times	M	1,000,000	1,000,000 g = 1 Mg

(Note: Decimal Values are included in the 4th column above in case you prefer to convert by moving the decimal.)

Let's take a moment to look at the principals of unit cancellation and how they apply to laboratory conversions and calculations.

Basic Rules for Unit Cancellation

1. Any unit which appears in the numerator of one unit fraction and the denominator of another unit fraction is canceled.

   The following is an example of how units are canceled:

   $$\frac{100\ \text{cm}}{1\ \cancel{\text{m}}} \ \text{x} \ 2\ \cancel{\text{m}}$$

2. It may be necessary to invert data and the corresponding units.

   $$\frac{1\ \text{g}}{1{,}000\ \text{mg}} \quad \text{is the same as} \quad \frac{1{,}000\ \text{mg}}{1\ \text{g}}$$

Steps for using unit cancellation to convert laboratory units:

We'll use the following example problem: How many centimeters are in 2 meters?

Step 1: List unknown data including units followed by an equal sign (you can use "X" for the unknown number.

Example:

Unknown: X cm =

Step 2: Find data (known or conversion) that has the same numerator unit as the unknown number. Place it to the right of the equal sign and add a multiplication sign. This positions your numerator.

Example: $\text{X cm} = \frac{100\ \text{cm}}{1\ \text{m}} \ \text{x}$

Conversion

Step 3: To cancel unwanted denominator units, find data (known or conversion) that has the same numerator unit. Place it to the right of the data used in step 2. Continue to place data (known or conversion) into the equation to systematically cancel unwanted units until only the unknown denominator units remain.

Example: $\text{X cm} = \frac{100\ \text{cm}}{1\ \cancel{\text{m}}} \ \text{x} \ 2\ \cancel{\text{m}}$

Known

Step 4: Do the Math (multiply all numerator values, multiply all denominator values (if there are any), then divide the numerator by the denominator).

X cm = 100 cm x 2 = 200 cm

Let’s look at a unit conversion example which uses unit cancellation.

Unit Conversion Example 1:

How many grams are in 1,125 milligrams of sugar?

Step 1: List unknown data including units followed by an equal sign (you can use “X” for the unknown number).

$$X\ \text{g} =$$

Step 2: Find data (known or conversion) that has the same numerator unit as the unknown number. Place it to the right of the equal sign and add a multiplication sign. This positions your numerator.

$$X\ \text{g} = \frac{1\ \text{g}}{1{,}000\ \text{mg}} \times$$

Step 3: To cancel unwanted denominator units, find data (known or conversion) that has the same numerator unit. Place it to the right of the data used in step 2. Continue to place data (known or conversion) into the equation to systematically cancel unwanted units until only the unknown denominator units remain.

$$X\ \text{g} = \frac{1\ \text{g}}{1{,}000\ \cancel{\text{mg}}} \times 1{,}125\ \cancel{\text{mg}}$$

Step 4: Do the Math (multiply all numerator values, multiply all denominator values (if there are any), then divide the numerator by the denominator).

$$X\ \text{g} = \frac{1\ \text{g}}{1{,}000\ \cancel{\text{mg}}} \times 1{,}125\ \cancel{\text{mg}}$$

= 1.125 grams of sugar

Let’s look at another unit conversion example which uses unit cancellation.

Unit Conversion Example 2:

A 300 milliliter BOD bottle contains how many liters of sample?

Step 1: List unknown data including units followed by an equal sign (you can use “X” for the unknown number).

$$X \text{ L} =$$

Step 2: Find data (known or conversion) that has the same numerator unit as the unknown number. Place it to the right of the equal sign and add a multiplication sign. This positions your numerator.

$$X \text{ L} = \frac{1 \text{ L}}{1{,}000 \text{ mL}} \times$$

Step 3: To cancel unwanted denominator units, find data (known or conversion) that has the same numerator unit. Place it to the right of the data used in step 2. Continue to place data (known or conversion) into the equation to systematically cancel unwanted units until only the unknown denominator units remain.

$$X \text{ L} = \frac{1 \text{ L}}{1{,}000 \ \cancel{\text{mL}}} \times 300 \ \cancel{\text{mL}}$$

Step 4: Do the Math (multiply all numerator values, multiply all denominator values, then divide the numerator by the denominator).

$$X \text{ L} = \frac{1 \text{ L}}{1{,}000 \ \cancel{\text{mL}}} \times 300 \ \cancel{\text{mL}}$$

$$= 0.3 \text{ L}$$

Unit 2, Practice #6 - Unit Conversions

1. How many milliliters (mL) are in 30 liters?

2. How many grams are in 2,500 micrograms (ug)?

☞ Formula to Memorize: ppm to ppb

A common laboratory conversion, since you are working with very small amounts, is converting ppm to ppb.

1 ppm = 1,000 ppb

The difference between one million (1,000,000) and one billion (1,000,000,000) is a factor of a thousand (1,000).

The vertical format relationship is:

$$\frac{1\text{ ppm}}{1{,}000\text{ ppb}} \quad \text{or} \quad \frac{1{,}000\text{ ppb}}{1\text{ppm}}$$

Unit 2, Practice #7 - Converting between ppm and ppb

1. How many ppb are in 5.3 ppm?

2. How many ppm are in 1.5 ppb?

VII. Temperature Conversion

The metric unit of temperature is Celsius. Temperature can also be measured in Fahrenheit. Water boils at 100 °C or 212°F. The conversion formulas are as follows:

- To convert from Celsius to Fahrenheit, use the following formula:
  Fahrenheit = (°C x 1.8) + 32°

- To convert from Fahrenheit to Celsius, use the following formula:
  Celsius = (°F – 32°) x $\frac{5}{9}$

Note: To convert from Celsius to Fahrenheit or Fahrenheit to Celsius, use the math conversion information from the Pa. Operator Testing Formulas and Conversions Handout. To obtain a copy of the handout, call the Pa. DEP BSDW training section at 717-772-4018.

Temperature Conversion Example:

If the body temperature is 97°F, what is the equivalent Celsius temperature?

Step 1: Write what you know and what you don't.

Known = 97°F

Unknown = °C

Step 2: Find your formula. In this case, from the two available temperature conversion formulas, we are using the following formula:

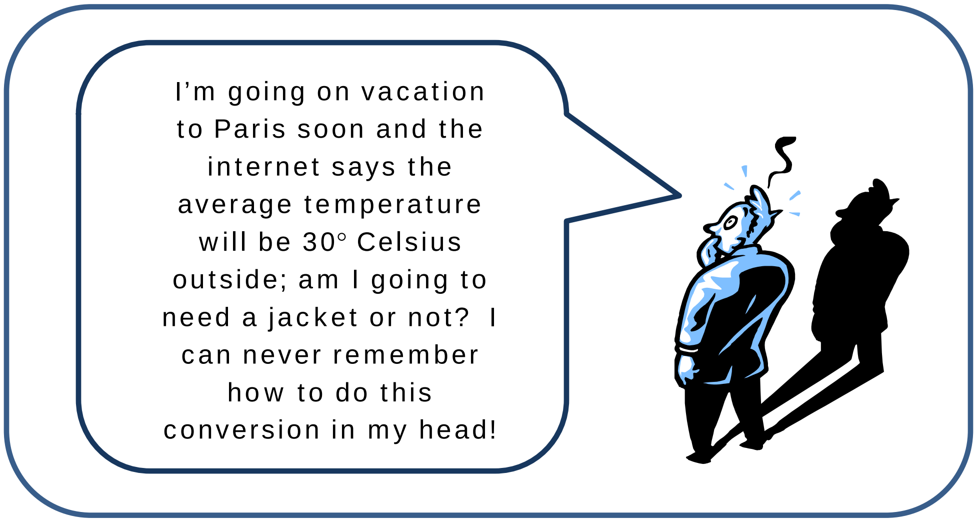
$$^{\circ}C = (^{\circ}F - 32^{\circ}) \times \frac{5}{9}$$

Step 3: Plug in your numbers:

$$\text{Celsius} = (97^{\circ}F - 32^{\circ}) \times \frac{5}{9}$$

$$\text{Celsius} = (65) \times \frac{5}{9}$$

$$= 36.1^{\circ}C$$



Unit 2, Practice #8 - Temperature Conversion:

1. What is the ° F value for 121° C (the temperature autoclaves must reach)?

2. If it is 30° C outside, will you need to wear a jacket?

Unit 2 Practice Quiz:

(Note: The questions below are extracted from all the example problems from each Unit 2 section; answers are included in the answer key located after Unit 10)

1. Solve the following equation: $\frac{385 + (21/7) - (5 \times 13 \times 4)}{17 + 11 - (6 \times 4)} =$

2. What is the sum of 1.1 + 0.98 + 1.231 + 2?

3. Given the temperatures of 93 °F, 99 °F, 101 °F, and 91 °F, calculate the average.

4. Solve for X in the following equation: $5X = 20$

5. Solve for X in the following equation: $2.5 = \frac{1,000}{X}$

6. What percentage is 15 of 60?

7. What is 15% of 60?

8. How many centimeters are in 2 meters?

9. A 300 milliliter BOD bottle contains how many liters of sample?

10. If the body temperature is 97°F, what is the equivalent Celsius temperature?

Unit 2 Key Points:

- Remember to perform all arithmetic within parentheses prior to arithmetic outside the parentheses and to perform all multiplication and division prior to performing all addition and subtraction.
- To convert from Celsius to Fahrenheit or Fahrenheit to Celsius, use the math conversion information from the Pa. Operator Testing Formulas and Conversions Handout.
- Units are important; if you have the correct math but the wrong units, the answer is wrong.
- If you have any problems calculating percentages, memorize the formula for calculating percent (P%/100)(“of’) = “is” and practice using it.
- Most algebraic formulas can be located – you just need to practice using the formulas you need in order to solve for X.

Unit 2 References:

- Greater than and less than symbols:
  - Definition taken from http://www.mathsisfun.com/equal-less-greater.html
  - W. Lloyd double-checked symbols by looking at the table in NELAC Vol. 1 (2011) on pg. 85
  - Examples taken from 2003 Pa. DEP Staff DBP Sample Collection Procedures document.

- "Basic Rules for Performing Calculations" was taken from the Pa. DEP "Overview of Basic Math" Module #28 workbook: pp. 1-8, 1-9

- Rules for solving for X taken from the following:

  - Price, Joanne Kirkpatrick. "Basic Math Concepts for Water and Wastewater Plant Operators" Lancaster: Technomic Publishing Company, Inc., 1991. Print. pp. 11-12

  - *Algebra Lab (Mainland HS Daytona Beach, FL) Solving One Step Equations" at http://www.algebralab.org/lessons/lesson.aspx?file=Algebra_OneVariableOneStep.xml*

- Laboratory Unit Conversion and Unit Cancellation Section:
  - Definitions:
    - Unit Conversion relationship concept taken from Brady, James E. and Humiston, Gerard E. "General Chemistry Principals and Structure - 3rd edition." New York: John Wiley & Sons Inc. 1982. Print. pp. 10-11 and Phoenix College Chemistry (Phoenix, AZ) web page at http://www.pc.maricopa.edu/data/GlobalFiles/file/chemistry/lee/Unit%20Equality.pdf
    - Vertical Format Concept taken from Pa. DEP 2013 Revised Hypochlorite Module 25 (edited by Pa. DEP's D. Rotz) pp. 3-8 and 3-9.
    - Metric System Definition and Base Unit information and table taken from Wikipedia
  - Vertical format conversion factor table created by Pa. DEP's B. McNamara
  - Steps for using unit cancellation to convert laboratory units taken from Pa. DEP 2013 Revised Hypochlorite Module 25 (edited by D. Rotz) pp. 3-8 and 3-9 and modified by B. McNamara to apply to laboratory calculations.
  - Unit conversion /unit cancellation examples and problems created by Pa. DEP's W. Lloyd. Steps for solving unit conversion /unit cancellation examples and problems taken from Pa. DEP 2013 Revised Hypochlorite Module 25 (edited by D. Rotz) pp. 3-8 and 3-9 and modified by B. McNamara to apply to laboratory calculations.

- Centimeter conversion example checked at http://www.asknumbers.com/MetersToCentimetersConversion.aspx

- Calculating Average practice calculations made up by W. Lloyd. Definition taken from http://en.wikipedia.org/wiki/Arithmetic_mean

- Decimal definition taken from Merriam-Webster Learner's Dictionary at http://www.learnersdictionary.com/search/decimal[1]

- Part of the "Decimal addition and subtraction" explanation taken from the Pa. DEP "Overview of Basic Math" Module #28 workbook: p. 1-5 & part created by W. Lloyd.

- Decimal examples and exercises created by W. Lloyd and checked using the Calculator Soup web site at http://www.calculatorsoup.com/calculators/math/math.php

- Percentage formula taken from the following:

    - Price, Joanne Kirkpatrick. "Basic Math Concepts for Water and Wastewater Plant Operators" Lancaster: Technomic Publishing Company, Inc., 1991. Print. p. 113
    - Nancy Molik, Augusta Technical College Mathematics Department,Augusta Technical College (Augusta, GA) web site at http://www.augustatech.edu/math/molik/solvingpercentprobs.pdf
    - Percentage Wheel at Wikispaces.com: http://percentagesactivity.wikispaces.com/Percentage+wheel+-+part,+whole,+percent

- Percent calculation explanation taken from Wikipedia at http://en.wikipedia.org/wiki/Percent

- Percent calculation problems made up by W. Lloyd and checked using the Online Conversion web site at http://www.onlineconversion.com/percentcalc.htm Temperature conversions checked at this same web site at http://www.onlineconversion.com/temperature.htm

- Word problem definition from http://en.wikipedia.org/wiki/Word_problem_(mathematics_education)

- Algebra word problem solving explanation rules #1 and #2, examples and exercise problems taken from Pa. DEP 2013 Revised Hypochlorite Module 25 (edited by D. Rotz) pp. 3-3 and 3-4. Rules #3 and #4 taken from Purple Math "Solving One Step Linear equations" at http://www.purplemath.com/modules/solvelin.htm

- Algebra definition taken from Merriam Webster at http://www.merriam-webster.com/dictionary/algebra and from Wikipedia at http://en.wikipedia.org/wiki/Elementary_algebra

- Recommendations for solving word problems taken from Cuesta College's "How to Solve Word Problems" web page at https://academic.cuesta.edu/acasupp/as/706.htm (Cuesta College in San Luis Obispo, CA)

Unit 3 – pH and Solution Concepts

Learning Objectives

At the end of this unit, you should be able to:

- Answer some basic questions about pH.
- Answer some basic questions about solution concepts and terms.

I. pH Concepts

An **Acid** is a substance that produces hydrogen ions in water. Acids can usually be recognized by the “H” at the beginning of the chemical formula (although some do not have this at the beginning.) For example, the chemical formula for hydrochloric acid is HCl.

In chemistry, **pH** is a measure of how acidic or basic an aqueous solution is. Solutions with a pH of less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline. (See diagram below definitions and explanation.)

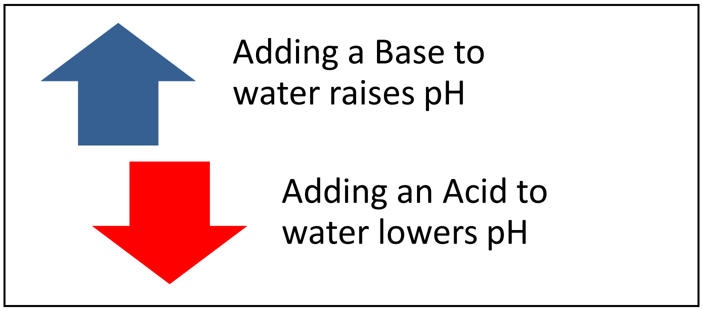
A **Base** is a substance that produces hydroxide ions in water. Bases can usually be recognized by the “OH” at the end of their chemical formula (although some do not have this ending.) For example, the chemical formula for sodium hydroxide is NaOH.

Adding an acid to pure water upsets the hydrogen-hydroxide ion balance. The water now has more hydrogen ions and the pH decreases.

If you add a base to pure water, there would be more hydroxide ions than hydrogen ions and the pH would increase.

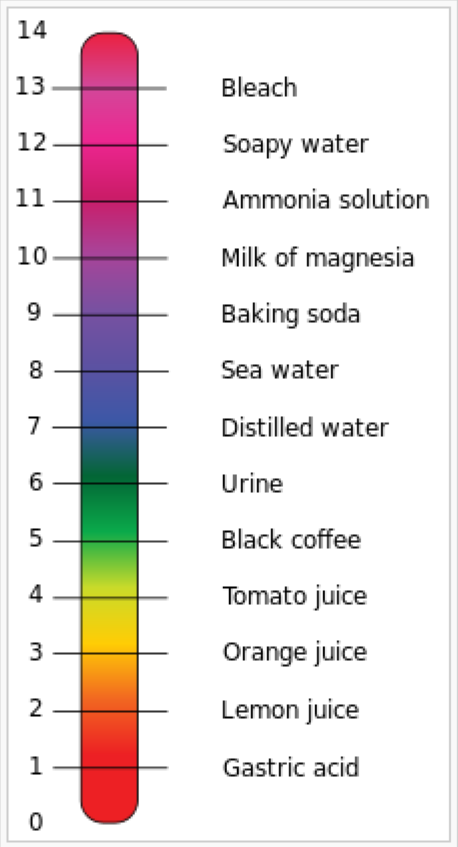
A pH of 0 is the most acidic that water can get. On the other end of the scale, a pH of 14 is the most basic.

- Adding a base to water **raises** the pH.
- Adding an acid to water **lowers** the pH.



Adding a Base to water raises pH

Adding an Acid to water lowers pH



pH values of some common substances

Above pH scale diagram taken from Wikipedia at http://en.wikipedia.org/wiki/PH

Common Bases:

Barium Hydroxide – $Ba(OH)_2$ – used to titrate weak acids

Calcium Hydroxide – $Ca(OH)_2$ – known as slaked lime

Potassium Hydroxide - KOH – a soap precursor

Sodium Carbonate – Na_2CO_3 – soda ash

Sodium Hydroxide - NaOH – used to make drain cleaner

Common Acids:

Acetic Acid – CH_3COOH - found in vinegar

Boric Acid – H_3BO_3 – used as an antiseptic or insecticide

Hydrochloric Acid - HCl – used in household cleaning

Nitric Acid – HNO_3 – used in the production of fertilizer and explosives

Sulfuric Acid – H_2SO_4 - found in car batteries

Unit 3, Exercise #1 - pH:

(Note: Exercise answers can be found in the answer key located after Unit 10.)

1. Choose whether the following are a. Acids or b. Bases

Chemical	Is it an acid or a base?
Sodium Hydroxide - NaOH	a. Acid b. Base
Sodium Carbonate - Na_2CO_3	a. Acid b. Base
Sulfuric Acid - H_2SO_4	a. Acid b. Base
Boric Acid - H_3BO_3	a. Acid b. Base
Barium Hydroxide - $Ba(OH)_2$	a. Acid b. Base

2. If Hydrochloric Acid – HCl - is added to water, will it raise or lower the pH?

a. Raise the pH

b. Lower the pH

3. If Calcium Hydroxide – $Ca(OH)_2$ – (known as slaked lime) is added to water, will it raise or lower the pH?

a. Raise the pH

b. Lower the pH

II. Solution Concepts

Solution Definitions

Let's start this section by looking at some definitions related to solutions.

A **Solution** is a mixture where a solute is dissolved in a solvent. For example, in a sugar-water solution, the sugar (the solute) is dissolved in the water (the solvent).

Solute: A substance dissolved in another substance.

Solvent: A substance that dissolves a solute.

The **Concentration** of a mixture is the measure of how much solute is dissolved in the solvent.

Dilution - Lowering the concentration of a solution by adding more solvent (usually distilled water).

The **Stock Solution** is a more concentrated solution that will be diluted to a lower concentration for actual use.

The **Standard Solution** is a solution in which the exact concentration of a chemical or compound is known. A standard solution is made by pipetting a stock solution into a volumetric flask and diluting to volume with solvent.

A **Mole** is a unit of measurement used in chemistry to express amounts of a chemical substance, defined as the amount of any substance that contains as many elementary entities (e.g., atoms, molecules, ions, electrons) as there are atoms in 12 grams of pure carbon-12. The mole is widely used in chemistry instead of units of mass or volume as a convenient way to express amounts of reactants or of products of chemical reactions.[1] The concentration of a substance is usually given in moles per liter (mol/L) which is also known as Molarity.

Molarity (expressed as a capital "M") is the number of moles of a substance per liter of solution. A 1.0 M solution contains one mole of solute per liter of solution.

Reagent water - Water with no detectable concentration of the component, compound, element or isotope to be analyzed and that is free of substances that interfere with the method. Reagent water may be prepared by distillation, deionization, adsorption, reverse osmosis or a combination thereof.

Working Solution – The name given to a chemical solution made for actual use in the lab, usually made from diluting or combining stock or standard solutions.

Diluting a Solution

An easy example of a dilution is when you take a container of frozen concentrated lemonade and dilute it with several cans of water to make a more diluted lemonade solution.

Let's look at a laboratory example of how these terms relate to a situation where we are diluting a solution.

We have determined that we will be using 0.5 liters of a 4.0 M sulfuric acid (H_2SO_4) solution to prepare 2 liters of a 1.0 M sulfuric acid solution. In this situation:

- Our stock solution concentration is measured in Molarity (M)
- Our stock solution and diluted solution volumes are in liters (L)
- We are diluting the stock solution to a 1.0 M sulfuric acid solution
- In most situations we are probably diluting our solution by adding reagent water.

Unit 3, Exercise 2 – Solution Dilution Concepts

(Note: This exercise involves no mathematical calculations.)

1. We have 1.11 L of an 18 M H_2SO_4 solution. We dilute the solution to 200 L to create a 0.1 M H_2SO_4 .solution.

Question 1-1: What is our stock solution concentration?

a. 1.11 L

b. 18 M

c. 200 L

d. 0.1 M

Question 1-2: What are the units of volume for both our stock solution and diluted solution?

a. milliliters (mL)

b. Molarity (M)

c. liters (L)

d. micrograms (ug)

Question 1-3: What is the concentration of our diluted solution?

a. 1.11 L

b. 18 M

c. 200 L

d. 0.1 M

2. Reagent water may be prepared by distillation, adsorption or reverse osmosis. Reagent water may **not** be prepared by deionization.

a. True

b. False

ppm

Molarity is used for solutions which contain relatively large concentrations of solute. In solutions with lower concentrations, the concentrations are listed in smaller concentration units of parts per million (ppm) and milligrams per liter (mg/L.) Note that mg/L = ppm.

Let's look at the dilution statement below.

You have 10 mL of a 45 ppm standard. You dilute the stock solution to 18 mL to make a working solution at 25 ppm.

In this statement, both the stock solution and diluted solution concentrations are measured in ppm.

More Solution Terms

Let's start this section by looking at a few more lab-related definitions you might use in creating solutions.

Aliquot: A portion of a total amount of a solution.

The **Analyte** is the component, compound, element or isotope to be identified or quantified using a test or analysis. (Note: We defined this back in Unit 1, but repeated it here again since it is used in adjacent definitions.)

The **Matrix** is the non-analyte components of a sample. This component of an environmental sample can also be categorized as drinking water, non-potable water, and solid and chemical materials.

The **Method** is the scientific technique used to perform testing or analysis on an environmental sample.

A **Reagent** is a substance added to a system in order to bring about a chemical reaction.

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.

Unit 3 Exercise:

1. A portion of a total amount of a solution is known as an:

a. Analysis

b. Analyte

c. Acid

d. Aliquot

2. We dilute a solution by adding a diluent.

a. True

b. False

3. If Potassium Hydroxide - KOH - is added to water, will it raise or lower the pH?

a.	Raise the pH

b. Lower the pH

4. A 1.5 mL of a 1.0 M salt-water solution is being diluted to make 3 mL of a 0.5 M salt-water solution. What is the concentration of the stock solution?

a. 1.5 mL

b. 1.0 M

c. 3 mL

d. 0.5 M

5. You have 5 mL of a 3 ppm standard. You dilute this solution to make 15 mL of a working solution at 1 ppm.

What is our stock solution concentration?

a. 1 ppm

b. 15 mL

c. 3 ppm

d. 5 mL

Unit 3 Key Points:

- Acids can usually be recognized by the “H” at the beginning of the chemical formula.
- Bases can usually be recognized by the “OH” at the end of their chemical formula.
- Adding an acid to water **lowers** the pH.
- Adding a base **raises** the pH.
- Solution concentrations are often expressed in units of Molarity (expressed as a capital “M”) or parts per million (ppm.)
- Reagent water may be prepared by distillation, deionization, adsorption, reverse osmosis or a combination thereof.

Unit 3 References:

- Acid and base definitions and information was taken from Module 2 of Pa. DEP's 1998 Corrosion Control Treatment Training for Operators.
- The pH definition and chart were taken from the Wikipedia page about pH at http://en.wikipedia.org/wiki/PH Information about acids and bases – including chemical formulas and uses - were taken from acid and base hyperlinks in that article.
- The titration definition was taken from Pa. DEP wastewater module 12 "Laboratory Overview."
- Acceptance criteria definition taken from Ch. 252.1
- Reagent water definition from § 252.1. Definitions and NELAC Vol. 1 (2011) pg. 98 1.7.3.5 (c)(i)
- The following definitions were taken from Wikipedia: Mole, Solute, Solvent, Stock Solution, and Aliquot
- Solution definition from http://en.wikipedia.org/wiki/Solution and Brady, James E. and Humiston, Gerard E. (1975). "General Chemistry Principles and Structure" (John Wiley & Sons, Inc.). pg. 18

  Dilution definition from Ch 1 Glossary pg. 1-5 of the Pa. DEP NPDES Lab Manual (1998),
- Standard Solution definition taken from Ch 1 pg. 1-5 of the Pa. DEP NPDES Lab Manual (1998), at http://www.dep.state.pa.us/dep/deputate/waterops/redesign/pages/Npdeslab.htm ; 2nd definition sentence from DVAction web site (from Northwest University and U at Illonois Urbana-Champaign) at http://dvaction.northwestern.edu/parentdetail.php?id=2
- Working solution definition from http://chemistry.about.com/od/chemistryglossary/a/workingsolution.htm
- Frozen concentration dilution concept from Austin Community College in Texas
- Matrix definition is from http://en.wikipedia.org/wiki/Matrix and from 025 Pa. Code § 252.1. Definitions at http://www.pacode.com/secure/data/025/chapter252/s252.1.html
- Analyte and Method definitions are taken from § 252.1. Definitions.
- [1]Mole definition taken from Wikipedia at http://en.wikipedia.org/wiki/Mole_(unit) Mole definition tie in with Molarity from AUS-e-TUTE web site at: http://www.ausetute.com.au/concsols.html
- Molarity explanation from Lesson 8: The Chemistry of Solutions at http://water.me.vccs.edu/courses/env211/lesson8_3.htm
- Molar concentration explanation & calculation taken from http://www.sparknotes.com/testprep/books/sat2/chemistry/chapter5section14.rhtml
- M solution dilution concentration statements created by W. Lloyd and amounts compared against http://www.sigmaaldrich.com/chemistry/stockroom-reagents/learning-center/technical-library/solution-dilution-calculator.html
- ppm solution dilution concentration statements created by W. Lloyd and amounts compared against http://www.physiologyweb.com/calculators/dilution_calculator_ppb_ppm_ppt_pph.html

Unit 4 – Solution Calculations

Learning Objectives

At the end of this unit, you should be able to:

- Perform solution dilution calculations.
- Perform solution concentration calculations.

(Note: If you feel you are able to perform both of the types of calculations listed above, you can always go directly to the Unit 4 Review Calculations – questions #1 through #3 - at the end of the unit and solve those.)

I. Solution Dilution Calculations

Dilution Calculation Theory and Formula

A common calculation is to determine how much of a more concentrated solution (the "stock" solution) must be used to create a more diluted (less concentrated) solution.

When determining what formula to use to calculate a dilution, look at units for the concentration and volume of the stock solution as well as for the diluted solution.

For example:

What volume of 6.0 M sulfuric acid (H_2SO_4) must be used to prepare 2.0 L of a 0.10 M H_2SO_4 solution?

- The concentration information we are given in this equation is that our stock solution consists of a 6.0 M (i.e. Molarity) sulfuric acid solution.
- The diluted solution is also given as a Molarity (0.10 M sulfuric acid) so our concentration units for the stock and diluted solutions are equivalent.
- Both the volume we are looking for and the volume we are given are in liters.

As a result, to solve this problem, we can use a commonly known dilution equation as follows:

$C_1 V_1 = C_2 V_2$ Spelled out, this is:

(Concentration of Mix solution 1)(Volume of solution 1) = (Concentration of Mix solution 2)(Volume of solution 2)

This dilution equation can be used whenever you have the following circumstances:

- The units of concentration of both the stock solution and the diluted solution are equivalent (e,g, Moles, ppm, etc.)
- The volume of both the stock solution and the diluted solution are equivalent (e.g., liters, mL, etc.)

Before we go on to solving this dilution word problem, let's look again at our Word Problem Solving Steps from Chapter 2.

Steps to Solving Word Problems:

Step 1: Make a list of what you know and what you don't

Step 2: Find the formula you will use.

Step 3: Determine if the units are consistent throughout the calculation. If they are not, but can be converted, use unit conversion to obtain the necessary units.

Step 4: Plug the information into the equation and work to isolate the unknown item on one side.

Step 5: Cancel out the units and calculate the answer.

(Hint: When finished, you should be able to plug your answer back into the original equation and have both sides equal each other.)

☞ Formula to Memorize: Solution Dilution Equation

You are expected to know a formula for diluting stock solutions.

If your stock and diluted solutions have concentrations in the same type of units and your volumes are in the same type of units, you can use the following formula:

$$C_1V_1 = C_2V_2$$

Note: In this unit, instead of using "X" for the unknown, we will use the formula terms. For example, if our unknown is V_1, we will use that term for the unknown when we set up our equation.

Solution Dilution - Example 1:

What volume of 6.0 M sulfuric acid (H_2SO_4) must be used to prepare 2.0 L of a 0.10 M H_2SO_4 solution?

Step 1: Let's make a list of what we know and what we don't.

Concentration of Stock Solution (Solution 1) = 6.0 M sulfuric acid (H_2SO_4)
Volume of Stock Solution (Volume 1) = unknown liters
Concentration of Diluted Solution (Solution 2) = 0.10 M sulfuric acid (H_2SO_4)
Volume of Diluted Solution (Solution 2) = 2.0 liters

Step 2: Find the formula you will use. To solve this problem, we can use the formula below since both our solution and dilution concentration units are in Molarity (moles per liter) and our stock and dilution volume units are also the same on both sides of the equation (in this case, they are in liters):

(Conc of Stock Solution 1) (Volume of Stock Solution 1) = (Conc of Diluted Solution 2) (Volume of Diluted Solution 2)

This formula is also written as $C_1V_1 = C_2V_2$

Step 3: Make sure concentration and volume units are consistent through the calculation; in this case they are. Then plug the numbers into the equation.

$$C_1 V_1 = C_2 V_2$$

$$(6.0\ \text{M}\ H_2SO_4)\ (V_1) = (0.10\ \text{M}\ H_2SO_4\ )\ (2.0\text{L})$$

Step 4: Isolate the unknown item on one side of the equation.

$$\frac{(6.0\ \text{M}\ \cancel{H_2SO_4})\ (V_1)}{6.0\ \cancel{\text{M}\ H_2SO_4}} = \frac{(0.10\ \text{M}\ H_2SO_4\ )\ (2.0\ \text{L})}{6.0\ \text{M}\ H_2SO_4} \longrightarrow V_1 = \frac{(0.10\ \text{M}\ H_2SO_4\ )\ (2.0\ \text{L})}{6.0\ \text{M}\ H_2SO_4}$$

Step 5: Cancel out the units and calculate the answer.

$$V_1 = \frac{(0.10\ \text{M}\ \cancel{H_2SO_4}\ )\ (2.0\ \text{L})}{6.0\ \text{M}\ \cancel{H_2SO_4}} = \frac{0.2\ \text{L}}{6.0} = 0.033\ \text{L}$$

Let's look at another example where we use the same equation to solve a different piece of the dilution puzzle – the volume of diluted solution we need to achieve a particular concentration. Also, in this equation our volume is in mL.

Solution Dilution - Example 2:

You have 5 mL of a 3.0 M aqueous sugar water solution. If you want to dilute the solution to 1.0 M of sugar water, what will be the volume of the diluted solution?

Step 1: Let's make a list of what we know and what we don't.
Concentration of Stock Solution (Solution 1) = 3.0 M sugar water
Volume of Stock Solution (Volume 1) = 5 mL
Concentration of Diluted Solution (Solution 2) = 1.0 M sugar water
Volume of Diluted Solution (Solution 2) = unknown

Step 2: Find the formula you will use. To solve this problem, we can again use the dilution formula below since both our stock and dilution concentration units are in Molarity (moles per liter) and our stock and dilution <u>volume</u> units are also the same on both sides of the equation (in this case, they are in mL):

(Conc of Stock Solution 1) (Volume of Stock Solution 1) = (Conc of Diluted Solution 2) (Volume of Diluted Solution 2)

This formula is also written as $C_1V_1 = C_2V_2$

Step 3: Make sure concentration and volume units are consistent through the calculation; in this case they are. Then plug the numbers into the equation.

$$C_1 V_1 = C_2 V_2$$

$$(3.0\text{ M})\ (5\text{ mL}) = (1.0\text{ M})\ (V_2)$$

Step 4: Isolate the unknown item on one side of the equation.

$$\frac{(3.0\text{ M sugar water})\ (5\text{ mL})}{1.0\text{ M sugar water}} = \frac{(1.0\text{ M sug}\cancel{\text{ar water)}}\ (V_2)}{1.0\text{ M }\cancel{\text{sugar wate}}\text{r}}$$

Step 5: Cancel out the units and calculate the answer.

$$\frac{3.0\text{ M s}\cancel{\text{ugar wate}}\text{r (5 mL)}}{1.0\text{ M s}\cancel{\text{ugar water}}} = V_2 \longrightarrow \frac{15\text{ mL}}{1} = 15\text{ mL}$$

You will add water to make 15 mL of the diluted sugar water solution.

Hint: You should be able to go back and plug your numbers into both sides of the equation and have them equal on either side: $M_1V_1 = M_2V_2 \longrightarrow (3.0\text{ M})\ (5\text{ mL}) = (1.0\text{M})\ (15\text{ mL})$

$$15 = 15$$

Unit 4, Practice 1 – Solution Dilution Calculations:

(Note: Practice answers can be found in the answer key located after Unit 10.)

1. You have 1 L of a 0.13 M aqueous solution of salt water. You want to dilute the solution to 0.05 M of salt water; what will be the volume of the diluted solution?

a. 1.67 liters

b. 26 liters

c.16.7 liters

d. 2.6 liters

2. What volume of a 1,000 mg/L NH_3 stock solution must be used to create 1 liter of a 25 mg/l NH_3 diluted solution?

a. 0.025 L

b. 2.5 L

c. 0.4 L

d. 40 L

Let’s look at a third example where our units are in ppm and mg/L.

Solution Dilution - Example 3:

You have a standard with a concentration of 80 ppm. You need to make 8 ml of a working solution at 2 ppm. How many mL of standard will you need?

Step 1: Make a list of what is known and what is not:

- Concentration of Stock Solution (C 1) = 80 ppm
- Volume of Stock Solution (V 1) = unknown
- Concentration of Diluted Solution (C 2) = 2 ppm
- Volume of Diluted Solution (V 2) = 8 mL

Step 2: Find the formula you will use. Since both solution concentration units are the same – they are both ppm units - and both volumes are in milliliters (mL), we can use $C_1V_1 = C_2V_2$

(Conc of solution 1)(Volume of solution 1) = (Conc of solution 2)(Volume of solution 2)

Step 3: Plug the numbers into the equation.

$(80\ \text{ppm})\ (V_1) = (2\ \text{ppm})\ (8\ \text{mL})$

Step 4: Isolate the unknown item on one side of the equation

$$\frac{(80\ \cancel{\text{ppm}})\ (V_1)}{80\ \cancel{\text{ppm}}} = \frac{(2\ \text{ppm})\ (8\ \text{mL})}{80\ \text{ppm}} \longrightarrow \frac{16\ \text{mL}}{80}$$

= 0.2 mL of standard stock solution is needed.

II. Solution Concentration Calculations

Solution Concentration Theory and Formula

When preparing solutions from dry chemicals, we can calculate how much of a reagent we will need to create a certain volume of a certain concentration.

For example:

You want to make 2 L of a 0.5 mg/L sugar water solution. How many milligrams (mg) of sugar will you need to use?

- You are given the Concentration of the solution in mg/L
- You are given the Volume of the solution in L.

- You need to find the mass of the reagent you will add to create the solution.

To solve this problem, we can use a common solution concentration equation as follows:

$$C = \frac{M}{V}$$

Spelled out, this means:

$$\text{Solution Concentration} = \frac{\text{Mass (of Solute)}}{\text{Volume (of Solution)}}$$

Let's go ahead and use this equation to answer our original question.

Solution Concentration - Example 1: You want to make 2 L of a 0.5 mg/L sugar water solution. How many milligrams (mg) of sugar will you need to use?

Step 1: Let's make a list of what we know and what we don't.
Solution Concentration = 0.5 mg/L sugar water
Volume of Solution = 2 L
Mass of Solute = unknown

Step 2: Find the formula you will use. Since we are dealing with a solution concentration, solution volume, and solute mass, we use the formula that has those 3 items.

$$\text{Solution Concentration} = \frac{\text{Mass (of Solute)}}{\text{Volume (of Solution)}} \longrightarrow C = \frac{M}{V}$$

Step 3: Make sure the concentration units are equivalent to the mass over volume units. In this case, the concentration units are in mg/L. On the other side of the equation, the mass unit is in mg, and the volume unit is in liters, so we don't have to change any units. We can go ahead and plug our numbers into the equation.

$$\frac{0.5\text{ mg}}{1\text{ L}} = \frac{M\text{ mg}}{2\text{ L}}$$

Step 4: Isolate the unknown item on one side of the equation.

$$2\text{L} \times \frac{0.5\text{ mg}}{1\text{ L}} = \frac{M\text{ mg}}{\cancel{2\text{L}}} \times \cancel{2\text{L}}$$

= 1 mg of sugar will be used

☞ Formula to Memorize: Solution Concentration Equation

You are expected to know a formula for calculating the mass, volume or concentration involved in solution concentrations.

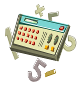
If you have two of the three items in the equation below – and the mass, volume, and concentration units correspond to each other - you can calculate the third item.

$$\text{Solution Concentration} = \frac{\text{Mass (of Solute)}}{\text{Volume (of Solution)}}$$

This equation is abbreviated as follows:

$$C = \frac{M}{V}$$

(Note: If the units correspond to each other but are in different gradations – for example, your concentration is in mg/L but your final volume is in mL or your mass is in grams, you will need to convert units to be equivalent.)



Unit 4, Practice #2 - Solution Concentration Calculation:

You want to make 8 L of a 24 mg/L salt water solution. How many mg of salt will you need?

a. 3 mg

b. 0.333 mg

c. 19.2 mg

d. 192 mg

Solution Concentration Formula and Unit Conversion

Let’s look at a solution concentration problem where we need to convert units.

Solution Concentration - Example 2:

How many grams of magnesium oxide (MgO) would you need if you want to make 250 mL of a 2000 mg/L MgO solution?

Step 1: Let's make a list of what we do know and what we don't.

Solution concentration = 2,000 mg/L
Volume of solution = 250 mL
Mass of solution = unknown

Step 2: Find the formula you will use. Since we are dealing with solution concentration, mass, and volume, we will use the following formula:

$$\text{Solution Concentration} = \frac{\text{Mass (of Solute)}}{\text{Volume (of Solution)}} \longrightarrow C = \frac{M}{V}$$

Step 3: Make sure the units are equivalent. In this case, they are not, but can be converted.
Because we have solution concentration units in mg/L and volume concentration units in mL, we will need to use unit cancellation to convert the volume concentration mL to L.

$$X\ \text{L} = \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} \times 250\ \cancel{\text{mL}}$$

$$X\ \text{L} = \frac{(1\ \text{L})(250)}{1000} = 0.25\ \text{L}$$

Here is our new list of what we know and what we don't.
Solution concentration = 2,000 mg/L
Volume of solution = 0.25 L
Mass of solution = unknown

Now we can go ahead and plug our numbers into the equation.

$$2000\ \text{mg/L} = \frac{x\ \text{mg}}{0.25\ \text{L}}$$

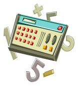
Step 4: Isolate the unknown item on one side of the equation.

$$0.25\ \text{L} \times 2000\ \text{mg/L} = \frac{x\ \text{mg}}{\cancel{0.25\ \text{L}}} \times \cancel{0.25\ \text{L}} \longrightarrow = 500\ \text{mg}$$

Since our answer in is mg and we are to calculate grams, let's do that unit conversion.

1,000 mg = 1 gram

$$\frac{1\ \text{g}}{1{,}000\ \cancel{\text{mg}}} \times 500\ \cancel{\text{mg}} = x\ \text{grams} \longrightarrow$$ 0.5 grams of magnesium oxide is needed.



Unit 4, Practice #3 - Solution Concentration Calculation:

You want to make 800 mL of a 3,000 mg/L $CaCl_2$ solution. How many grams of $CaCl_2$ will you need?

a. 0.192 grams

b. 2.4 grams

c. 37 grams

d. 3.75 grams

For a diagram on solution preparation, as well as more types of solution equations, go to the Flinn Scientific, Inc. laboratory solution preparation web page at:
http://www.flinnsci.com/media/396156/labsolutionprep.pdf

Unit 4 Practice Quiz:

(Note: Answers to the questions below can be found in the answer key located after Unit 10.)

1. What volume of a 10.0 M aqueous salt water stock solution must be used to prepare 3.0 L of a 4.0 M salt water solution?

a. 7.5 liters

b. 1.2 liters

c. 0.1 liters

d. 0.7 liters

2. You have a 4000 ppm standard. You need to make 200 mL of a 40 ppm working solution. How many ml of standard will you need?

a. 4 mL

b. 2 mL

c. 40 mL

d. 20 mL

3. How many grams of sugar would you need if you want to make 450 mL of a 2500 mg/L sugar water solution?

a. 1.125 grams

b. 5.557 grams

c. 180 grams

d. 2.95 grams

Unit 4 Key Points:

- When solving a solution dilution problem if the concentration units are equivalent and the volume units are equivalent, use the formula $M_1V_1 = M_2V_2$

- When solving a solution concentration problem, if you have 2 of the 3 formula variables (of concentration, mass, and volume), and the units correspond to each other or can be converted, use the formula $C = \frac{M}{V}$

Unit 4 References:

- Acceptance criteria definition taken from Ch. 252.1
- Matrix definition is from http://en.wikipedia.org/wiki/Matrix and from 025 Pa. Code § 252.1. Definitions at http://www.pacode.com/secure/data/025/chapter252/s252.1.html
- Analyte and Method definitions are taken from § 252.1. Definitions.
- Solution concentration formula taken from: http://clearviewregional.edu/docs/hs/depar/scien/hsscience/TeachRes/ProbSol/PrbSlv09.pdf
- Molar concentration explanation & calculation taken from http://www.sparknotes.com/testprep/books/sat2/chemistry/chapter5section14.rhtml
- Dilution explanation (using M & L), 1st equation and example 1 taken from SparkNotes web site at http://www.sparknotes.com/testprep/books/sat2/chemistry/chapter5section14.rhtml (Various steps created by W. Lloyd)
    - Explanation of how concentration and volume can be in any units as long as the units are equivalent on both sides of the equation taken from http://water.me.vccs.edu/courses/env211/lesson8_4.htm
- Dilution 1st practice and unit exercise (both using M & L) both created by W. Lloyd and checked against Sigma Aldrich solution dilution calculator at http://www.sigmaaldrich.com/chemistry/stockroom-reagents/learning-center/technical-library/solution-dilution-calculator.html
- Dilution 2nd equation taken from http://files.dep.state.pa.us/Water/BSDW/OperatorCertification/TrainingModules/both29_Chemistry_WB_Final_Updated042513.pdf pg 3-4
- Dilution Problems with Molarity concentration checked against Sigma Aldrich solution dilution calculator at http://www.sigmaaldrich.com/chemistry/stockroom-reagents/learning-center/technical-library/solution-dilution-calculator.html
- Molarity Calculation: http://chemconnections.org/crystals/ppt/calc/tsld010.htm
- Dilution problems with ppm concentration and mL volume checked against PhysiologyWeb dilution calculator at http://www.physiologyweb.com/calculators/dilution_calculator_ppb_ppm_ppt_pph.html
- Solution concentration calculations created by W. Lloyd and checked against calculator at http://www.physiologyweb.com/calculators/mass_per_volume_solution_concentration_calculator.html
- Ppm solution dilution from http://www.ehow.com/how_8668884_calculate-solution-parts-per-million.html
- Solution concentration Example 2 magnesium oxide idea is from practice problem 2 at http://clearviewregional.edu/docs/hs/depar/scien/hsscience/TeachRes/ProbSol/PrbSlv09.pdf
- Also used the following: http://chemistry.about.com/od/lecturenotesl3/a/concentration.htm

Unit 5 – Laboratory Operation & Maintenance

Learning Objectives

At the end of this unit, you should be able to:

- List items to document during sample acceptance.
- Identify holding times for some drinking water and wastewater sample parameters.
- State calibration frequencies for common laboratory equipment and instruments.
- List monitoring frequencies for common laboratory equipment.
- Review some basic laboratory safety principles.

I. Sample Acceptance

Environmental laboratories need to implement procedures for checking and recording the following for all received sample containers:

- The client/project name
- Sample date
- Sample time
- Location of sample collection
- Preservation type
- Sample type
- Name of sample collector and field identification code
- Date and time of laboratory receipt
- A unique laboratory ID code
- Identification of the person making the entries (i.e. receiving the samples)

In addition, laboratories should have a sample acceptance policy that states the circumstances under which samples are accepted or rejected. The sample acceptance policy should include the information recorded for received sample containers (listed previously in this section.) In addition, the following information should be included in this policy:

- Adherence to holding times
- Sufficient sample volume (to perform the necessary analysis and QA/QC)

- Procedures to be used when samples show signs of damage, contamination or inadequate preservation.

Importance of Sample Integrity

In 2013, a northeast U.S. water system manager was convicted of tampering with drinking water bacterial samples. The town's water system was on a boil-water notice. Feeling the pressure to get the drinking water boil water lifted, the manager tampered with six drinking water samples by adding a form of chlorine to the samples. He then submitted these tampered samples to a local lab for testing. On the "chain of custody" forms, he also falsely certified the integrity of the samples.

A laboratory analyst was instrumental in determining the samples had been tampered with during their normal course of analytical duties. A report to the state environmental agency resulted in a follow-up investigation and conviction which resulted in the manager serving jail time.

Sample Holding Times

It is critical that drinking water and wastewater samples do not exceed maximum holding times between collection and analysis.

Holding time: The storage time allowed between sample collection and sample analysis when the required preservation and storage techniques are followed.

Let's look at holding times for some commonly performed drinking water and wastewater analysis.

Holding Times for some Drinking Water & Wastewater Parameters / Methods (listed by increasing holding time)		
Parameter/Method	Drinking Water or Wastewater	Maximum Sample Holding Time
pH	Drinking Water / Wastewater	Immediately
Residual Disinfectant	Drinking Water	Immediately
Temperature	Drinking Water	Immediately
Total or E. Coli Bacteria	Drinking Water / Wastewater	30 Hours
Fecal Coliform Bacteria	Wastewater	8 Hours
Nitrate (non-chlorinated)	Drinking Water	48 Hours
Turbidity	Drinking Water	48 Hours
o-Phosphate	Wastewater	48 hours
Biochemical Oxygen Demand (BOD)	Wastewater	48 Hours

Holding Times for some Drinking Water & Wastewater Parameters / Methods (continued) (listed by increasing holding time)		
Parameter/Method	Drinking Water or Wastewater	Maximum Sample Holding Time
Solids (TDS)	Wastewater	7 Days
Alkalinity	Drinking Water / Wastewater	14 Days
Synthetic Organic Chemicals (SOC's) Method 525.2	Drinking Water	14 Days (see method for exceptions)
Volatile Organic Chemical (VOC's) Method 524.2	Drinking Water	14 Days
Nitrogen (Ammonia and TKN)	Wastewater	28 Days
Chemical Oxygen Demand (COD)	Wastewater	28 Days
Metals (except Hg)	Drinking Water	6 Months

II. Equipment and Instrument Calibration

Laboratories need to assure that test instruments consistently operate within the specifications required of the application for which the equipment is used. Equipment also needs to be properly maintained, inspected and cleaned.

If any of the following occur, a piece of equipment needs to be taken out of service:

- The equipment has been subjected to overloading,
- The equipment has been mishandled,
- The equipment gives suspect results,
- The equipment has been shown to be defective

Once the equipment is taken out of service, the status of being out of service needs to be clearly identified until it has been repaired and shown by calibration, verification or test to perform satisfactorily.

Any previous testing or analysis performed using the piece of equipment that was taken out of service needs to be examined.

Calibration Frequency & Methods

Equipment and instruments must be calibrated within certain time frames and using certain methods. See the calibration chart on the next page with this information. We will talk a bit more about instrument calibration later in this section.

As the laboratory supervisor, you are responsible for making sure these calibrations are completed.

Equipment Calibration Chart		
Equipment or Instrument	Calibration Frequency	Calibration Specifics
Certified NIST-reference thermometer.	Calibrate at least once every 5 years	Recalibrate at the temperatures of use.
Glass, liquid filled thermometers	Calibrate every 12 months	Calibrate at the temperature used against a certified NIST-reference thermometer
Dial and electronic thermometers	Calibrate every 3 months (after one year with NIST certificate)	Calibrate at the temperature used against a certified NIST-reference thermometer
ASTM class 1, 2 or 3 (Class S or S-1) certified reference weights.	Recertify at least once every 5 years	Recertify to ASTM standards
Analytical or pan balances	Calibrate daily or before each use *(whichever is less frequent)*	• Calibration must be verified using a minimum of three ASTM class 1, 2 or 3 (Class S or S-1) certified reference weights that bracket the effective range of the balance's use. • Analytical balances must be serviced and calibrated once a year by a qualified person
pH meter	Calibrate daily or before each use *(whichever is less frequent)*	• Calibrate with three standard buffers at least three pH units apart which bracket the expected pH range of the samples OR • Calibrate with a pH 7.0 and either a pH 4.0 or 10.0 standard buffer (whichever range covers the desired pH range of use.)
Conductivity meter	Calibrate daily or before each use *(whichever is less frequent)*	• With certified and traceable standard solutions within the range of interest OR • By determining the cell constant utilizing the method described in currently approved editions of *Standard Methods for the Examination of Water and Wastewater*

Analytical Balance Calibration
Analytical balances (like the one shown to the right) must be verified daily or before each use *(whichever is less frequent)*

Analytical Balance Photo by US DEA
at http://en.wikipedia.org/wiki/File:Analytical_balance_mettler_ae-260.jpg

pH Meter Calibration:
A pH meter (see equipment picture to the left) should be calibrated daily or before each use *(whichever is less frequent.)*

pH Photo by Datamax at http://en.wikipedia.org/wiki/File:PH_Meter.jpg

Instrument Calibration

The calibration chart you just reviewed included requirements for calibrating pH meters and conductivity meters.

One of the more complex instruments used in many drinking water and wastewater laboratories is the spectrophotometer. We mentioned in Unit 1 that this device is used to analyze samples of test material by passing light through the sample and reading the intensity of the wavelengths.

Some important information to remember about spectrophotometer calibration is:

- The visible light spectrophotometer should have the ability to work in the 400 to 700 nanometer wavelength range.
- Whenever the concentration of one or more analytes exceeds the spectrophotometer calibration range, samples must be diluted and re-analyzed.
- Wavelength settings on spectrophotometers should be verified at least annually with color standards.
- Refer to the individual method and 252.402 for additional requirements.

III. Equipment Monitoring

Equipment monitoring must be performed. See the chart on the next page with this information.

As the laboratory supervisor, you are responsible for making sure this equipment monitoring is performed.

Equipment Monitoring	
Equipment	Monitoring Frequency
Incubators	record temperatures once a day or twice a day, four hours apart for microbiology (for each day in use for all laboratory activities)
Water baths	record temperatures once a day or twice a day, four hours apart for microbiology (for each day in use for all laboratory activities)
Heating blocks	record temperatures once a day (for each day in use for all laboratory activities)
Ovens	record temperatures once a day (for each day in use for all laboratory activities)
Refrigeration equipment and freezers	Record calibration-corrected temperatures once a day for each refrigerator and freezer for each day in use
Autoclave	• Record continuous temperature or maximum temperature device during each autoclave cycle. • Verify the autoclave sterilization capability by utilizing appropriate biological indicators (for example, spore strips or ampoules) once a month. • Note: If the biological indicator fails to become properly sterilized, be sure to investigate and take corrective action.

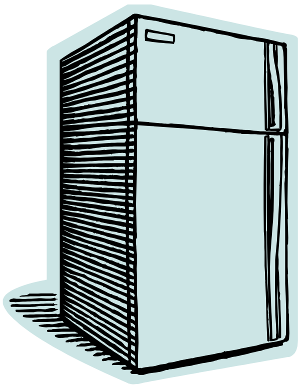


Image of refrigerator with freezer

<u>Refrigeration Monitoring Frequency:</u>
Refrigerator and freezer temperatures should be recorded once a day *(for each day in use)*

Incubator Monitoring Frequency:
Incubator temperatures (see equipment picture to the right) should be recorded once a day or twice a day, four hours apart for microbiology *(for each day the equipment is in use for all laboratory activities.)*

Bacteriological Incubator Photo by Microrao at
http://en.wikipedia.org/wiki/File:Bacteriological_incubator.jpgm

Autoclave Photo from Wikipedia at
http://en.wikipedia.org/wiki/File:ExampleAutoclave.jpg

Autoclave Monitoring Frequency:
Continuous or maximum autoclave temperatures should be recorded during each autoclave cycle.

- Verify the autoclave sterilization capability by utilizing appropriate biological indicators once a month.
- Autoclaves must reach 121 °C and hold that temperature for sterilization time of the particular equipment.

Volumetric Dispensing Checks

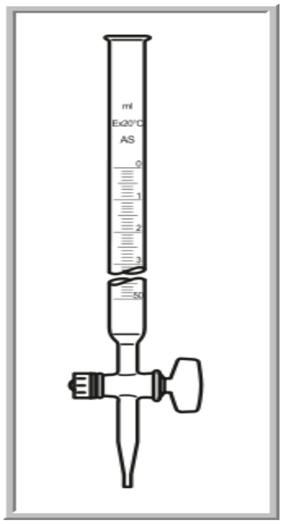
Except for Class A glassware, delivery volumes of mechanical volumetric dispensing devices need to be checked at least once every 3 months. This includes mechanical volumetric dispensing devices such as burettes, autopipetors and dilutors. Note that this equipment must be of sufficient sensitivity for the application. See the chart below with the information on frequency of checking delivery volumes.

- Note that glassware that is used to determined sample volume must be checked when not Class A.
- All glassware must be verified at the volumes used.

As the laboratory supervisor, you are responsible for making sure these volumetric dispensing checks are performed.

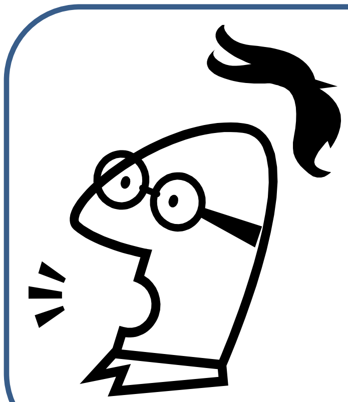
Volumetric Dispensing Checks
(Not Required for Class A Glassware)

Equipment	Dispensing Check Frequency
burettes	Check delivery volumes once every 3 months
autopipetors	Check delivery volumes once every 3 months
dilutors	Check delivery volumes once every 3 months
graduation marks on filter funnels	Verify and document the accuracy of the volume of use for each lot or at least once per year *(whichever is more frequent)*
graduation marks on sample bottles	Verify and document the accuracy of the volume of use for each lot or at least once per year *(whichever is more frequent)*
graduation marks on labware	Verify and document the accuracy of the volume of use for each lot or at least once per year *(whichever is more frequent)*



Burette Image created by Lucasbosch
at http://en.wikipedia.org/wiki/File:Burette_vertical.svg

Volumetric Dispensing Checks:
Devices that deliver volume (like the burette pictured on the left) – that are not Class A glassware - must have the delivery volume checked once every 3 months



In preparation for an audit, Harry looks at his equipment calibration records and panics when he thinks he may have waited too long to calibrate his laboratory's certified NIST-reference thermometer. However, after his 2nd cup of coffee, he looks at Chapter 252 (§252.306) - and breathes a sigh of relief - it only needs calibrated once every 5 years.

IV. Laboratory Safety

Laboratory Safety

In addition to overseeing that employees carry out their individual responsibilities, a laboratory supervisor must also ensure that employees are following safety principals.

Drinking water and wastewater laboratories include the following safety risks:
- Corrosive and toxic chemicals
- Toxic fumes,
- Hot glassware and
- Disease-causing organisms in samples

These items alone pose threats of fire, chemical burns, toxicity and disease to laboratory workers.

Safety Equipment

At a minimum, the following safety equipment should be provided and be readily available in the environmental laboratory to ensure a safe work place[1]:

- Eye wash device
- Emergency deluge shower
- Fire blanket
- Safety glasses/goggles
- Laboratory apron/coat
- Surgical or rubber gloves
- Fire extinguisher (A,B, & C Fires)
- Spill clean-up kit

Appendix D discusses some further laboratory safety considerations.

Unit 5 Exercise:

Multiple Choice: Choose one best answer unless otherwise indicated.

(Note: Answers to all module questions are in the answer key which follows unit 10.)

1. Fill in the letter of the correct maximum sample holding time for the parameter. Selections can be used more than once.

a. no max holding time; analyze immediately b. 30 hours c. 14 days d. 6 months

______________________ Total Coliform Bacteria

______________________ Chlorine Residual

______________________ temperature

______________________ Alkalinity

______________________ Metals (except Hg)

______________________ pH

2. Under Chapter 252, for heating blocks and ovens, temperatures are to be recorded once a ____________ .

a. day

b. week

c. month

3. Calibrate pH meter and conductivity meters weekly.

a. True

b. False

Unit 5 Exercise Continued:

In the table below, circle the letter of the correct amount of calibration or monitoring time.

4. Check *burette delivery volume *If not Class A glassware*	A = once a day B = once a week C = once a month D = once every 3 months E = once every 12 months
5. Record refrigerator temperatures	A = once a day B = once a week C = once a month D = once every 3 months E = once every 12 months
6. Calibrate conductivity meter	A = once a day B = once a week C = once a month D = once every 3 months E = once every 12 months
7. Calibrate glass, liquid filled thermometers	A = once a day B = once a week C = once a month D = once every 3 months E = once every 12 months
8. Record incubator temperature	A = once a day, four hours apart B = once a week C = once a month D = once every 3 months E = once every 12 months
9. Verify the autoclave sterilization capability (by utilizing appropriate biological indicators)	A = once a day B = once a week C = once a month D = once every 3 months E = once every 12 months

Unit 5 Key Points:

- There is no maximum holing time for chlorine residual, pH, and temperature analysis. There parameters must be taken and recorded immediately upon sampling (within 15 minutes).
- Record equipment temperatures daily.
- Verify balances and calibrate meters daily.
    - 3 weights must be used to calibrate an analytical balance.
    - pH meters must be calibrate with three standard buffers. pH standard buffers should not be used for longer than 1 analysis day.
- The ASTM class certified reference weights that are used to calibrate laboratory equipment must be recertified at least once every 5 years.
- Thermometers that are used to calibrate laboratory equipment must be calibrated as per the required schedules in Chapter 252:
    - Dial and electronic thermometers need calibrated every 3 months after 1 year with NIST certificate.
    - Glass, liquid filled thermometers need calibrated every 12 months.
    - Certified NIST-reference thermometers need calibrated every 5 years.
- Verify autoclave sterilization capability by utilizing appropriate biological indicators (for example, spore strips or ampoules) once a month.
    - Autoclaves must reach 121°C and hold that temperature for the particular equipment being sterilized.
    - If the biological indicator fails to become properly sterilized, be sure to investigate and take corrective action.

Unit 5 References:

- Procedures for receiving sample containers taken from Ch. 252.401 (f)
- "Holding time" definition taken from the Pa. NPDES Lab Manual (1998) Chapter 1 Glossary pg. 1-5
- Drinking Water sample holding times taken from EPA's Manual for the Certification of Laboratories Analyzing Drinking Water Table IV-6 (starts on page IV-23) and Pa. DEP Field Staff Sample Collection & Preservation Procedures (2002 - L. Daniels) and checked against EPA's 2-2014 Analytical Support Branch Laboratory Operations and Quality Assurance Manual Chapter 3 sample tables pages 10-15 at http://www.epa.gov/region4/sesd/asbsop/asb-loqam.pdf
- Equipment Maintenance information was taken from Chapter 252, Section 252.306 (c) through (e) on Equipment, supplies and reference materials
- Equipment Calibration & Monitoring information was taken from Chapter 252, Section 252.306 on Equipment, supplies and reference materials
- Spectrophotometer information taken from EPA's Manual for the Certification of Laboratories Analyzing Drinking Water page IV-5 item 7.1.4 and page V-6 item 3.17
- Laboratory Facility standards taken from EPA's Manual for the Certification of Laboratories Analyzing Drinking Water , pg. IV-1
- Laboratory Safety information taken from:
  - EPA's Manual for the Certification of Laboratories Analyzing Drinking Water , pg. IV-1
  - EPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories, pg. 14-6
- [1] List of recommended safety equipment taken from the Pa. NPDES Lab Manual (1998) Chapter 1 Section 6, pg. 1-6

For further information:

- Laboratory standard operating procedures:
  - http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095
  - http://files.dep.state.pa.us/RegionalResources/Labs/LabsPortalFiles/2010-0610%20Chapter%20252.pdf
- Massachusetts Criminal Prosecution May 17, 2013 bacterial sample tampering case found at EPA Summary of Criminal Prosecutions at http://cfpub.epa.gov/compliance/criminal_prosecution/index.cfm (click on left hand link "Criminal Enforcement", then icon picture box for "Criminal Prosecutions", then right hand link for "Search the Summary of Criminal Prosecutions", then enter the fiscal year 2013 and hit search; then look under MA.

Unit 6 – Laboratory Quality Assurance and Quality Control

Learning Objectives

At the end of this unit, you should be able to:

- Review common laboratory QA/QC terms and procedures.
- Examine selected Chapter 252 QA/QC requirements for accredited laboratories.
- Explain analyst requirements for demonstrating initial and continued performance.
- Be aware of data integrity concerns.

Pennsylvania environmental laboratories are required to have a quality assurance and quality control program.

Throughout this unit we will review several QA/QC terms and concepts.

I. Quality Assurance

First, let's look at three quality assurance definitions.

Quality Assurance is the activity of systematically monitoring and evaluating the various aspects of a laboratory program to ensure that standards of quality are being met.

A **Quality Manual** (aka **"QM"**) is defined in Pa.'s Chapter 252 as a document that states, or makes reference to, the policies, objectives, principles, responsibilities, accountability, implementation plans, methods, operating procedures or other documents of an environmental laboratory for ensuring its testing and analysis.

A **Standard Operating Procedure** (aka “SOP”) is a written laboratory document that provides detailed instructions for the performance of all aspects of a test, analysis, operation or action.

One of the ways that accredited Pa. environmental laboratories demonstrate their quality assurance methods is by keeping a written document called the “Quality Manual” (aka “QM”.) This manual must be available to and used by all laboratory personnel. The purposes of the Quality Manual are to:

- Contain the policies, objectives and principles for ensuring the quality of the testing performed by a laboratory.
- To state (or reference) the methods performed by the laboratory.
- To describe the laboratory’s quality assurance (“QA”) and quality control (“QC”) plans.
- To identify the laboratory personnel responsible for implementing laboratory policies, reviewing data, and ensuring that the laboratory generates legally defensible data of known quality.
- To provide a reference for lab personnel when they are uncertain how to proceed in circumstances that can affect data quality.

Quality Manual Sections

The 16 sections of the Quality Manual sections are listed below. Optional sections are labeled as such; more details about each section are noted in Appendix E.

(Note: sampling terms are defined in the quality control segment later in this unit.)

1. **Cover Page**: Include the laboratory name, address, telephone number, and laboratory supervisor.
2. **Revision History**: Describes the changes made during each revision.
3. **Distribution List** ***(Optional)***: Recommended to help keep track of who has a copy of the Quality Manual.
4. **Ethics Training Procedure:** Includes procedures for educating and training lab personnel in their ethical and legal responsibilities.
5. **Ethics Policy:** Describes the code of conduct for the laboratory and its staff.
6. **Document Control System:** A written procedure for the control and maintenance of all laboratory documents.

   ➢ NOTE: All records generated by the laboratory must be maintained for a **minimum of 5 years** from the date of the last entry (for logbooks) or date of retire (for SOPs, quality assurance manual, etc.)
7. **Personnel Records:** Document the training and competency of lab employees through personnel records.
8. **Permitting Departures from Established Lab Procedures:** Documents a procedure for permitting

departures from documented policies and procedures (contained in the QM, SOPs, reference methods, etc.) when such departures are necessary.

9. **Detecting Departures from Established Procedures:** Documents established procedures for detecting when non-permitted, unrealized, and unintentional departures from laboratory procedures have occurred.

10. **Prevention and Detection of Improper Practices:** The laboratory must develop and implement procedures to detect and prevent improper, unethical or illegal actions. These procedures are to be proactive to focus on preventing improper practices (instead of simply correcting them after they have occurred. Examples of such practices are:

    - Internal Proficiency Testing (PT or QC samples)
    - Post analysis electronic data and magnetic tape audits or reviews
    - Laboratory SOPs
    - Internal Laboratory Audits
    - Corrective Actions for improper, unethical or illegal actions

11. **Sample Handling Procedures** – Documents sample collection procedures, sample preservation and hold times, as well as laboratory procedures for accepting and handling samples.

12. **Sample Acceptance Policy**: Describes the circumstances under which samples are rejected or accepted for analysis.

13. **Reporting Data:** The laboratory develops written procedures for reporting data and identifying the individuals authorized to approve and report data.

14. **Monitoring the Quality of Analysis:** Procedures for monitoring the quality of analysis are stated. For some analyses these may involve quality controls specific to the analytical method; for other analyses this will involve the laboratory defining their own Quality Control.

    Examples of Quality Monitoring may include: Batch QC samples, Blanks, Laboratory Control Samples, Duplicates, Matrix Spikes, PT Studies, Split Samples, Secondary Source Standards, Replicate Testing, Retesting, and Correlation of Results.

15. **Recordkeeping:** The laboratory develops a written procedure describing how and where records are maintained.

16. **Equipment Listing *(Optional)*:** Labs may choose to include an equipment listing in their Quality Manual. If equipment is not listed, records of each item of equipment significant to the testing or analysis performed must be maintained. (See Appendix E for more information about this.)

In addition to Appendix E, more information on the details of the 16 sections of this manual can be found in the document "Writing a Quality Manual for PA State (Chapter 252) Accreditation" which is located on the Pa. DEP Bureau of Laboratories Accreditation web site. The steps to finding this web site are:

- Type the following web address into the internet address search: www.depweb.state.pa.us

- Click on the left hand link labeled “DEP Programs A-Z”
- From the top line of alphabet linked letters that appear, click on the letter “L”
- Click on the first highlighted word on the list: “LABORATORY ACCREDITATION PROGRAM”
- Scroll down the page to the “Compliance Assistance” heading
- Look for the linked heading about writing a Quality Manual for Pa State (Chapter 252) Accreditation

Before we go any further, let’s answer a few questions.

Unit 6, Exercise #1 - QA and Quality Manual Questions:

(Note: Exercise answers can be found in the answer key located after Unit 10.)

Choose the best answer to fill in the blank.

1. A quality manual must be kept by all ________________ Pa. laboratories.

a. operating

b. accredited

c. wastewater

2. A written laboratory document that provides detailed instructions for the performance of all aspects of a test, analysis, operation or action is known as a (an) _______.

a. SOP

b. QCP

c. QAP

d. OPS

II. Quality Control Samples

Quality Control is the collection of technical activities the measure the laboratory performance against defined standards designed to ensure adequate quality.

Analytical quality control is important in an environmental laboratory because the concentration of chemicals in a sample may be extremely low and close to the detection method of the analytical method.

Laboratories often perform quality control by introducing random samples of known amounts into the sample analysis stream or by way of spiked samples.

Environmental laboratories employ a variety of quality control samples to prove that the results are reliable. Some quality control samples are required by the specific analysis method. Others are introduced inside the laboratory as per the laboratory's quality control program. Still others are introduced from outside the laboratory through participation in inter-laboratory comparisons or analysis of split samples by different laboratories.

Let's look at some of the definitions associated with various types of quality control samples.

(Note: Remember that the terms aliquot, analyte, and matrix were defined in Unit 3.)

Blank sample – A sample that lacks the parameters of interest. A blank sample result is used to detect contamination during sample handling, preparation, and/or analysis. Examples of a blank sample include deionized water or a blank certified standard reference material.

Sample duplicate - Replicate aliquots of the same sample taken through the entire analytical procedure.

Spike - A known and verified mass or activity of the target analyte of interest added to reagent water or an environmental sample to determine recovery efficiency or for other quality control purposes.

Reference sample – A quality assurance sample composed of standard reference material. The data from this sample is used to evaluate laboratory accuracy.

Now let's look at some definitions related to quality control analysis procedures.

Single blind sample –An external quality assurance sample that is identified as a quality assurance sample to the contract laboratory performing the analyses, but the concentrations of the parameters of concern are unknown to laboratory personnel.

Double blind sample – An external quality assurance sample disguised as a production sample through appropriate labeling and identification. It is not identified as a quality assurance sample to the laboratory performing the analyses.

Before we go any further, let's do an exercise on the definitions we have covered so far.

Unit 6, Exercise #2 - QC Sample Definitions:

1. QC Sample Definition Matching Exercise Table:

Directions: Fill in the left hand column of the table with the name of the QC sample beside the proper description

a. Blank Sample b. Sample duplicate c. Spike d. Reference sample

Directions: Insert Letter of Correct Sample Title	Description
i. ___________	Replicate aliquots of the same sample taken through the entire analytical procedure.
ii. ___________	A sample that lacks the parameters of interest.
iii. ___________	A quality assurance sample composed of standard reference material.
iv. ___________	A known and verified mass or activity of the target analyte of interest added to reagent water or environmental sample to determine recovery efficiency or for other quality control purposes.

Choose the best answer.

2. A double blind sample is identified as a quality assurance sample to the contract laboratory performing the analyses, but the concentrations of the parameters of concern are unknown to laboratory personnel.

- a. True
- b. False

Now let's look at some additional definitions related to quality control analysis sampling procedures.

Blank spike – Measured aliquots of known concentrations of specific parameters are added by the laboratory QA/QC team to a measured volume of deionized water. A blank spike sample result is used to evaluate laboratory accuracy.

Matrix Spike – A quality assurance sample that has one or more measured aliquots of specific parameters at known concentrations added to it. This type of sample is taken through all the same preparation and analytical steps in the method being used for the parameters of interest. A matrix spike allows laboratory accuracy to be determined from a sample that may cause matrix interference.

Method blank - A sample of a known matrix, similar to the associated samples, and known to be free of the analyte of interest and that is taken through all preparation and analytical steps in the method.

Laboratory Control Sample (aka **"LCS"**) - A sample of a controlled matrix known to be free of the analyte of interest, to which a known and verified concentration of analyte has been added and that is taken through all preparation and analytical steps in the method.

Proficiency Testing Sample (aka **"PT Sample"**) - A sample for which the composition is unknown to the environmental laboratory and the analyst.

Important Note: For the purposes of learning the basics about various types of QA/QC samples, the 11 sample terms in this unit have been discussed. There are other types of samples that you may see listed in other circumstances (i.e. such as field QA/QC, approved methods for sample analysis, etc.)

Unit 6, Exercise #3 – More QC Sample Definitions:

1. Sample duplicates are useful for analyzing laboratory performance, but PT samples are not.

   a. True

   b. False

2. Analytical quality control is important in an environmental laboratory because the concentration of chemicals in a sample may be extremely low and close to the detection method of the analytical method.

   a. True

   b. False

III. General Laboratory Quality Control

General Laboratory Quality Control Requirements

Pa. environmental laboratories are required to implement procedures to monitor the quality of the laboratory's analytical activities. Examples of these procedures are:

- Internal quality control procedures using statistical analysis.
- Participation in proficiency testing, other inter-laboratory comparisons, or round robin testing.
- Analysis of split samples by different laboratories.
- Use of certified reference materials or in-house quality control using secondary reference materials, or both.
- Replicate testing using the same or different test methods.

Before beginning the analysis of compliance samples, the analyst must adhere to any required QC procedures specified in the methods for blanks, precision, accuracy, sensitivity, specificity and satisfactory analysis on unknown samples.

Laboratory Performance

The laboratory should periodically analyze an external QC sample, such as a proficiency testing sample, when available. The laboratory should review results, correct unsatisfactory performance, and record corrective actions.

As noted in Chapter 252, in order to receive and maintain full certification for an analyte, the laboratory must analyze PT samples (if available) at least once every 12 months for each analyte and by each method used to analyze compliance samples. For example, at a laboratory that analyzes inorganics using an ion selective electrode and spectrometer, the lab must run PT samples using both technologies. Results from analysis of the PT sample must be within the acceptable limits established by The NELAC Institute.

In Unit 8 we will look further at determining if certain results meet given acceptance criteria standards.

Detecting Departures from Lab Procedures

All Pa. accredited drinking water and wastewater laboratories are required to have procedures that enable the laboratory management to detect when departures from the laboratory's procedures occur.

Recommended procedures might include the following:

- Second level review of laboratory data.
- Internal audits

- Internal proficiency testing.

Review of analysis quality control data such as method blanks, laboratory control samples, matrix spikes, duplicates, and calibration verifications is required.

Each analyst should be responsible for reviewing the quality control data from their analyses prior to reporting the data. In addition, a second level review should occur once a week. The laboratory supervisor or QA officer should select random data from each analyst and review all quality control and calculations.

Method Blank Requirements

Under Chapter 252, Pa. accredited laboratories have certain method blank requirements. Key requirements are as follows:

- A method blank must be processed along with and under the same conditions as the associated environmental samples including all steps of the analytical procedure.
- A method blank must be analyzed at a minimum of one per preparation batch.
- When no separate preparation method is used (example: ammonia digestion), the batch shall be defined as no more than 20 environmental samples.
- A method blank must consist of a matrix that is similar to the associated environmental samples and is free of the analytes of interest (when this type of matrix is unavailable, reagent water or an artificial or simulated matrix may be used).
- To the extent possible, any environmental samples associated with a contaminated method blank shall be reprocessed for analysis.
- In addition, if the contaminant is detected in the method blank, the source of contamination shall be investigated and measures shall be taken to minimize or eliminate the contamination.

Unit 6, Exercise #4 - General Laboratory QC:

1. In an analytical run, what is the highest amount of samples that can be contained in sample batch?

a. 5

b. 10

c. 15

d. 20

IV. Analyst Performance

Analyst Performance and IDOC

Initial DOC (aka **IDOC**): An Initial Demonstration of Capability must be conducted before using any method, any time there is a change in an instrument type, personnel or method or at any time that a method has not been performed by the laboratory or analyst in a 12 month period.

Pa's Chapter 252 requires than an IDOC (initial demonstration of capability) be performed by each analyst for each method that relates to their job responsibilities.

- An initial demonstration of capability is required prior to the use of any method.
- An initial demonstration of capability must be completed each time there is a change in instrument type, personnel or method.
- An initial demonstration of capability must include all sample preparation and analytical steps contained in the method.

If the method or State or Federal regulations specify a procedure for the initial demonstration of capability, that procedure should be followed.

If there is no procedure specified in the method, then an initial demonstration of capability should be performed as follows (note that some of the calculation items in #3 and #4 are discussed in the Unit 8):

1. The analyte must be diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified in the method. If the method does not specify a concentration, the concentration must be approximately ten times the detection limit.

2. At least four aliquots of the quality control sample will be prepared and analyzed according to the method.

3. Using all of the results, calculate the mean recovery and the standard deviation of the mean recovery for the population sample in the same units used to report environmental samples. When it is not possible to determine mean and standard deviation, such as for presence-absence and logarithmic values, the environmental laboratory will assess method performance using criteria from the method or other established and documented criteria.

4. Compare the information from item 3 above to the corresponding acceptance criteria for precision and accuracy in the method. To be considered acceptable, an initial demonstration of capability must meet all acceptance criteria.

Note 1: In case you are wondering about the term “Mean Recovery” as it is used above, for the purpose of performing an initial demonstration of capability, the mean (or average) recovery is calculated by determining the percent recovery for each aliquot (this is discussed in unit 8) and then calculating the mean.

Note 2: “Population Sample” - for the purpose of performing an initial demonstration of capability, the population sample is considered to be the number of aliquots analyzed.

Demonstrating Continued Performance

Chapter 252 also requires than analysts continue to demonstrate proficiency – every 12 months – for each method that relates to their job responsibilities. They can demonstrate their proficiency through one of the following 5 methods:

- Another initial demonstration of capability.
- Acceptable analysis of blind performance samples (single blind to the analyst).
- Successful analysis of blind proficiency test samples on a similar test method using the same technology.
- At least four consecutive laboratory control samples with acceptable levels of precision and accuracy.
- Analysis of at least ten authentic samples with results statistically indistinguishable from those obtained by another trained analyst. The samples must include samples free of the analyte of interest and samples containing the analyte of interest at measurable concentrations.

Data Integrity[1]

It is important for environmental laboratory employees to understand the importance of data integrity. Infractions of laboratory data integrity procedures can result in a detailed investigation that could lead to very serious consequences. These consequences may even include termination, debarment (through EPA's management authority to suspend and or debar individuals and entities) or civil/criminal prosecution.

Unit 6 Review Exercise:

Multiple Choice: Choose one best answer unless otherwise indicated.

1. Any time that a method has not been performed by the laboratory or analyst in a ______ month period, an IDOC must be performed.

a. 3 months
b. 6 months
c. 9 months
d. 12 months

2. A Laboratory Control Sample (LCS) is a sample of a controlled matrix known to be free of the analyte of interest, to which a known and verified concentration of analyte has been added and that is taken through a few, but not all, of the preparation and analytical steps in the method.

a. True
b. False

3. Proficiency Testing (PT) samples must be analyzed at least once every ____ ________ for each analyte and by each method used to analyze compliance samples.

a. 3 months
b. 6 months
c. 9 months
d. 12 months

4. Any environmental samples associated with a contaminated method blank shall be reprocessed for analysis. In addition, the source of contamination of the method blank shall be:

a. Disregarded since it was just the method blank, not the actual sample

b. Investigated and measures taken to minimize or eliminate the contamination.

c. Ignored, since these types of contaminant sources can never be determined anyway

Unit 6 Key Points:

- Any time that a method has not been performed by the laboratory or analyst in a 12 month period, an Initial Demonstration of Capability must be performed.

- Laboratory performance can be evaluated by use of internal (known by the laboratory but not the analyst) and external (unknown by the laboratory) quality control samples. PT samples, method blanks, laboratory control samples, duplicates and spike recovery samples can all be useful in detecting departures from lab procedures.

- If an environmental sample is found to be associated with a contaminated method blank, corrective action and investigation should be performed by way of reprocessing the sample for another analysis.

- Any environmental samples associated with a contaminated method blank shall be reprocessed for analysis. In addition, the source of contamination of the method blank shall be investigated and measures taken to minimize or eliminate the contamination.

Unit 6 References:

- Quality Assurance definition: http://www.merriam-webster.com/dictionary/quality%20assurance
- Quality Control definition: combined from Merriam Webster at http://www.merriam-webster.com/dictionary/quality%20control and from the U.S. Department of the Interior at http://www.usbr.gov/mp/mp150/mp157/QA/Definintions.html ; further explanation taken from http://en.wikipedia.org/wiki/Analytical_quality_control
- For QA/QC information, see: http://www.epa.gov/ogwdw/methods/pdfs/manual_labcertification.pdf
- Method blank, Sample Duplicate, Spike, and SOP definitions are taken from § 252.1. Definitions
- Matrix Spike definition from both § 252.1. Definitions and http://www.usbr.gov/mp/mp150/mp157/QA/Definintions.html
- Blank spike and Reference sample, single blind and double blind sample definitions and blank sample definitions from http://www.usbr.gov/mp/mp150/mp157/QA/Definintions.html
- IDOC information from Pa. Chapter 252 Section 252.304(b)(3)(vi.) Demonstration of continued performance from Pa. Chapter 252 Section 252.304(b)(3)(vii.)
- Mean recovery and population sample explanations from V. Hunsberger and Y. Creason both from the Pa. DEP BoL Accreditation Section.
- [1] NELAC EL Vol 1 pg. 39 - Section 5.2.7 - Data Integrity Training
- Method Blank Requirements – Bullets 1-4 taken from Chapter § 252.402(g); Bullet 5 taken from § 252.402(f)(7)
- DOC definition – NELAC Environmental Laboratory Sector Vol 1 pg. 2.
- LCS Definition – Chapter 252 pg. 252-3

Unit 7 – Laboratory Accreditation Basics

Learning Objectives

At the end of this short unit, you should be able to:

- Define some of the terms associated with seeking a new field of accreditation.
- List the steps a laboratory takes to apply for a new field of accreditation.

State or NELAP Accreditation

All Pennsylvania environmental laboratories performing testing or analysis of Drinking/Potable Water for compliance with the Pennsylvania Safe Drinking Water Act or of Non-Potable Water (Wastewater), for compliance with the Clean Streams Law must be accredited by the Pa. DEP (or the National Environmental Laboratory Accreditation Program - "NELAP").

I. Laboratory Accreditation Definitions

Accreditation - A determination by the Pa. DEP that an environmental laboratory is capable of performing one or more classes of testing or analysis of environmental samples in accordance with Chapter 252.

Method: The scientific technique used to perform testing or analysis on an environmental sample. ((Note: We defined this back in Unit 4, but repeated it here again since it is used in adjacent definitions.)

NELAC (abbreviation for **National Environmental Laboratory Accreditation Conference**) was established on February 16, 1995 by State and Federal officials as an accreditation standards setting organization. The primary objective of NELAC was to develop and adopt laboratory accreditation standards to support a **National Environmental Laboratory Accreditation Program** (abbreviated **NELAP**).

Technology: The scientific technique (which is often abbreviated in accreditation documents) used to perform testing or analysis on an environmental sample. An example would be ion selective anode.

II. Adding a Field of Accreditation

5 Steps for Adding a Field of Accreditation

Pa. accredited environmental laboratories may choose to seek additional fields of accreditation through Pa's state program Chapter 252 or through NELAP. Both State and NELAP accreditation are available for the Drinking Water, Non-Potable Water, and Solid and Chemical Materials matrices.

Once the laboratory determines whether they are seeking an additional field of accreditation under 252 or NELAP, they follow the steps below:

1. The first step is for a laboratory to select an approved method and/or technology for the field of accreditation

- Along with the method and/or technology, determine the specific matrix (such as drinking water or non-potable water) and analyte (or associated group of analytes) for the field in which the laboratory wishes to obtain accreditation. Examples are as follows:
    - Nonpotable water; ion selective electrode, SM 4500-NH_3 D; Ammonia as N.
    - Drinking water; membrane filtration, SM 9222B; Total Coliform Bacteria.

- If the test method is not mandated by regulation, the laboratory will need to develop a method for accreditation.

2. The second step is for the laboratory to gather together their SOP

- The laboratory must provide copies of SOPs that meet the Chapter 252 requirements, based on the type of accreditation sought.

- If an SOP for the method is not currently in existence, it will need to be developed. Pa. DEP has details about writing an SOP at the Pa. link listed below under the "Compliance Assistance" heading.

3. The third step is to complete an Initial Demonstration of Capability

- The laboratory must provide copies of IDOC summary sheets. The Department may request the raw data prior to making a final decision.

- The IDOCs must be analyzed **before** the proficiency testing samples otherwise the PTs are invalid for accreditation purposes.

4. The fourth step is to complete Proficiency Testing Studies

- Laboratories must complete Proficiency Testing Studies for all requested fields of Accreditation listed on the applicable Fields of Proficiency Testing Tables (which – as mentioned previously - can be located at the Pa. link listed below under the “Proficiency Testing” heading.)
- The PT studies must be analyzed **after** successful completion of the IDOCs.
- PT samples need to be obtained from an approved PT provider (a list can also be found at the same Pa. link below) and the results of the analysis need to be submitted to the PT provider for scoring.
- The laboratory must obtain **passing** PT study results as required by Chapter 252.

5. The Fifth (and final) step is to submit the accreditation application to Pa.

- Fill out the application as per the instructions.
- Include the required attachments (SOPs, IDOCs and PTs)
- Be sure to include a check for the appropriate application fee

Accreditation Links:

State Accreditation: Pa. DEP’s Bureau of Laboratories Accreditation program details the steps for state accreditation on their various forms at the link below: http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095

NELAC Accreditation: The 2003 NELAC standard (at http://www.nelac-institute.org/docs/2003nelacstandard.pdf) details the steps for NELAC accreditation. A one page flow-chart of NELAC accreditation steps is available at http://www.nelac-institute.org/docs/FAQFlowchart.pdf

Unit 7 Exercise:

(Note: Exercise answers can be found in the answer key located after Unit 10.)

Multiple Choice: Choose one best answer unless otherwise indicated.

1. Your lab is going to obtain an additional field of accreditation from the state of Pennsylvania. You perform PT studies (which you pass) and then do an IDOC analysis. Is this the acceptable order for performing this testing? Choose the best answer below.

    a. Yes, you are supposed to do PT studies prior to an IDOC analysis.
    b. Yes, because you really only need PT studies, not any IDOC analysis.

c. Yes, because you really only need an IDOC analysis, not any PT studies.

d. No, you are supposed to do an IDOC analysis prior to PT studies

2. Before your laboratory does the aforementioned testing in question #1, what other 2 steps should it do?

a. Choose an approved method and develop a SOP

b. Choose an approved method and send in the application for the requested Field of Accreditation

c. Send in the application for the requested field of Accreditation and develop a SOP

3. All Pennsylvania environmental laboratories performing testing or analysis of wastewater for compliance with the Clean Streams Law must be accredited by the Pa. DEP.

a. True

b. False

Unit 7 Key Points:

- All Pennsylvania environmental laboratories performing testing or analysis of Drinking/Potable Water for compliance with the Pennsylvania Safe Drinking Water Act or of Non-Potable Water (Wastewater), for compliance with the Clean Streams Law must be accredited by the Pa. DEP.

- There are **5 steps** to obtaining an additional field of accreditation:
  1 - Select an approved method,
  2 - Gather together or develop a SOP,
  3 - Analyze IDOCs,
  4 - Complete and pass PT studies, and finally,
  5 - Submit the accreditation application.

Unit 7 References:

- Accreditation definition obtained § 252.1. Definitions
- Steps for Accreditation taken from the Pa. DEP's Bureau of Laboratories Accreditation web page at http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095 Part 4 Addition of FOA
    - First step of determining the applicable field of accreditation mentioned on page 37 of the 2003 NELAC standards and on the flowchart.
    - Second step of PT samples taken from page 64 item 2.2.3

Unit 8 – Quality Control Calculations & Analysis

Learning Objectives

At the end of this unit, you should be able to:

- Review and practice general EPA rules for rounding and determining significant digits.
- Be aware that some data is submitted to Pa. DEP without being rounded.
- Calculate relative percent difference
- Determine if results fit within a range of acceptable criteria.
- Be familiar with the uses for a calibration curve.
- Review information on how to locate an Internet graphical package to create a trend chart.

I. EPA Rounding Rules

Let’s look at some of the federal Environmental Protection Agency rules for basic rounding of drinking water and wastewater compliance calculations.

Rounding Decimals

Find the place value you want (the "rounding digit") and look at the digit just to the right of it.

- If that digit is less than 5, do not change the rounding digit but drop all digits to the right of it.
- If that digit is 5 or more, add one to the rounding digit and drop all digits to the right of it.

Rounding Decimals - Example 1:

Round 3.234 to one decimal point = 3.2.

Rounding Decimals - Example 2:

Round 2.45 to one decimal point = 2.5.

Round 2.449 to one decimal point = 2.4.

Round 2.55 to one decimal point = 2.6.

Rounding Whole Numbers and Decimals to Whole Numbers

Find the place value you want (the "rounding digit") and look to the digit just to the right of it.

- If that digit is less than 5, do not change the rounding digit but change all digits to the right of the rounding digit to zero.
- If that digit is 5 or more, add one to the rounding digit and change all digits to the right of the rounding digit to zero.

Rounding Whole Numbers - Example 1:

Round 5,763 to the nearest hundred = 5,800.

Rounding a Decimal to a Whole Number - Example 1:

Round 25.501 to a whole number = 26.

Rounding a Decimal to a Whole Number - Example 2:

Round 16.499 to a whole number = 16.

Unit 8, Practice #1 – Rounding Calculations:

(Note: Practice answers can be found in the answer key located after Unit 10.)

1. Round 9.875 to two decimal points.

2. Round 9,637 to the nearest thousand.

3. Round 9,637 to the nearest hundred.

4. Round 9,637 to the nearest tens.

When to Round Pa. DEP Compliance Data

When you are submitting data for Pa. DEP compliance purposes, laboratories usually do not round the data. Instead, laboratories submit the data using as many decimal places as given by the instrument.

- Pa. DEP regulatory detection/reporting limits are used to establish the number of significant digits required for reporting purposes.

- At the very least, submit data that is 2 significant digits more than the detection/reporting limit.

If you are submitting Pennsylvania **drinking water** data, do not round it, since it will be automatically rounded by a computer system called PADWIS (Pennsylvania's Drinking Water Information System.)

If you are submitting Pennsylvania **wastewater** data, the entity you are submitting it to determines if you should round it or not.

- If you are submitting wastewater data **to a permitee** who will then be rounding the data for compliance purposes and submitting the data to the eDMR system, **laboratories should submit data using as many decimal places as available.**

- If you are switching out of the laboratory role and **into the role of the "entity for the permittee"** and rounding the data for direct submission to the eDMR system, **you then need to round the data based on the eDMR data rules.**

Having established the fact that as a laboratory you probably will not be rounding the data you are reporting, let's look at how the Pa. DEP drinking water and wastewater compliance systems round the data to determine if a particular regulated system is in compliance.

How Pa. DEP’s PADWIS system rounds drinking water data for compliance purposes.

The PADWIS system uses EPA’s rules of rounding for drinking water compliance purposes:

- If the digit to the right is 5 or more, round the value up for compliance purposes.
- If the digit to the right is less than 5, the value is rounded down.

When averaging data, round at the end of the calculation.

Step 1: Without rounding, use the data to compute the average.

Step 2: Find the Pa. DEP compliance limit and determine the number of significant digits.

(a) Go one number past the last significant digit and underline that number, which you will use for rounding.

(b) Cross out any other digit past the one significant digit, since they are not used in the rounding calculation.

(c) To round, if the number past the significant digit is 5 or more, round your compliance number up; if not, keep the number as is and report with the proper number of significant digits.

Let’s look at an example on the next page.

Rounding an Average Example:

A Pa. DEP drinking water nitrate MCL = 10 mg/L. The last significant digit is $\underline{0}$.

Sample results are as follows:

- 10.49 mg/l
- 9.46 mg/L
- 10.9 mg/L
- 11 mg/L

Recommendation: Write down numbers and calculation for better analysis

Step 1: Average the unrounded results

$$\frac{10.49\text{ mg/L} + 9.46\text{ mg/L} + 10.9\text{ mg/L} + 11\text{ mg/L}}{4} = \frac{41.85}{4} = 10.46$$

Step 2:

(a) Go one number past the last significant digit and underline that number, which you will use for rounding.
(b) Cross out any other digit past the one significant digit, since they are not used in the rounding calculation.
(c) To round, if the number past the significant digit is 5 or more, round your compliance number up; if not, keep the number as is and report with the proper number of significant digits.

Use the digit to the right of the last significant digit of the compliance number, and round the answer.

$10.\,\underline{4}\,\cancel{6} \longrightarrow 10$ (Note: this is not an MCL exceedance.)

The 6 gets ignored.

4 is less than 5, so the number 10 does not get rounded higher.

Reporting Raw Data

For the data that is being reported for compliance purposes (that will be processed through a Pa. DEP information system such as PADWIS) data should be submitted using as many decimal places as available.

Unit 8, Practice #2 – Rounding an Average:

1. A Pa. DEP wastewater permit was issued with an average monthly limit of 3.0 mg/L for ammonia-nitrogen.

Sample results for the monitoring period are as follows:

- 2.10mg/L
- 3.52 mg/L
- 2.71 mg/L
- 3.56 mg/L

What is the average rounded result for the monitoring period?

a. 2.9 mg/L
b. 3.1 mg/L
c. 2.0 mg/L
d. 3.0 mg/L

2. A Pa. DEP drinking water system performed arsenic monitoring for 4 quarters; the drinking water MCL for arsenic is 0.010 mg/L.

Arsenic sample results for the monitoring period are as follows:

- Quarter 1 = 0.0163 mg/L
- Quarter 2 = 0.0162 mg/L
- Quarter 3 = 0.0104 mg/L
- Quarter 4 = 0.0100 mg/ L

What is the average rounded result for the monitoring period?

a. 0.014 mg/L
b. 0.013 mg/L
c. 0.012 mg/L
d. 0.031 mg/L

What if a sample measures non-detect?

EPA has set detection/reporting limits for many of the regulated contaminants; Pennsylvania incorporates the limits by reference.

Drinking Water:

For drinking water results, where results are non-detected and the minimum detection limit has been met, the lab should report the results as zero (0).

Wastewater:

For wastewater, check with the Pa. DEP staff that review or can give you guidance with the types of reports which you are filling out. Sometimes, when an analysis of an effluent sample indicates no detectable levels for a parameter not covered by the permit provision, the level of detection achieved must be used for that sample result in determining reportable maximum and average values (and a zero (0) may not be used.) We will discuss more in Chapter 9 about where wastewater data is submitted to and processed by at Pa. DEP.

II. Quality Control Calculations

We looked at quality assurance and quality control in the last chapter.

Now let’s look at two quality control calculations: Relative Percent Difference and Acceptance Criteria.

Relative Percent Difference

We defined duplicate samples back in unit 6 as a type of quality control sample that involves taking replicate aliquots of the same sample through the entire analytical procedure.

The analysis of a duplicate sample indicates how precise the first result was. We can use a calculation – known as the “Relative Percent Difference” – to compare the two duplicate sample results and see how close in accuracy (how precise) they are to each other.

Various published analytical procedures or laboratory standard operating procedures (SOPs) have specific acceptance criteria for the acceptable relative percent difference of duplicate samples.

Let’s look at a formal definition for relative percent difference.

Relative Percent Difference (sometimes abbreviated **“RPD”**) is a comparison of 2 duplicate results to determine how precise they are to each other. The comparison is expressed as a ratio; multiplying the ratio by 100 allows for the ratio to be expressed as a percentage.

A common way to express the formula for calculating relative percent difference is:

$$\text{RPD} = 100 \times \left[\frac{|\text{result 1} - \text{result 2}|}{\text{average of result 1 and result 2}} \right] \quad \text{OR} \quad \text{RPD} = 100 \times \left(\frac{|\text{result 1} - \text{result 2}|}{(\text{result 1} + \text{result 2}) \div 2} \right)$$

Let’s look at an example.

Relative Percent Difference Example:

You perform a duplicate analysis of a sample and obtain the readings of 6 mg/L and 9 mg/L. What is the relative percent difference of these results?

Step 1: We determine what we know and what we don't know.

RPD = unknown

result 1 = 6 mg/L

result 2 = 9 mg/L

Step 1: We find our formula:

$$\text{RPD} = 100 \text{ x } \left[\frac{\text{result 1} - \text{result 2}}{\text{average of result 1 and result 2}} \right]$$

Step 3: We plug our numbers into the equation:

$$\text{RPD} = 100 \text{ x } \left[\frac{6\text{mg/L} - 9 \text{ mg/L}}{(6 \text{ mg/L} + 9 \text{ mg/L}) \div 2} \right]$$

Step 4: We make sure our unknown is on one side of the equation (which it is)

Step 5: We follow the rules for performing complex calculations, so we take this a step at a time:

$$\text{RPD} = 100 \text{ x } \left[\frac{3 \text{ mg/L}}{(6 \text{ mg/L} + 9 \text{ mg/L}) \div 2} \right]$$

Note: The numerator result will always be an absolute number (not positive or negative)

$$\text{RPD} = 100 \text{ x } \left[\frac{3 \text{ mg/L}}{7.5 \text{ mg/L}} \right]$$

RPD = 100 x 0.4

RPD = 40 %

From Chapter 2: A reminder of the rule #4 to remember when performing complex calculations:

- Perform all arithmetic within parentheses prior to arithmetic outside the parentheses
- Perform all multiplication and division above the line (in the numerator) and below the line (in the denominator); then proceed with the addition and subtraction. Finally divide the numerator by the denominator.

☞ **Formula to Memorize: Calculating Relative Percent Difference**

You are expected to know the formula for calculating RPD (Relative Percent Difference.) The basic formula for calculating Relative Percent Difference is:

$$\text{RPD} = 100 \times \left[\frac{\text{result 1} - \text{result 2}}{\text{average of result 1 and result 2}} \right]$$

Another simplified way of expressing the same thing is RPD% = [X1 - X2}/Xave x 100

! Important Note: Be sure to perform ALL 5 of the arithmetic steps involved in calculating the relative percent difference. It is very easy to hurry through the calculation and leave one of those 5 steps out. If you have to write the equation down a few times on paper as you work through the steps, then do so.

Unit 8, Practice #3 – Relative Percent Difference:

A duplicate analysis of a sample found results of 12 mg/L and 13 mg/L. What is the relative percent difference of these results?

a. 20%

b. 200%

c. 8%

d. 0.08%

Let's use the RPD calculation from the previous section to determine if the relative percent difference of two duplicate samples is acceptable.

Unit 8, Practice #4 – Is the RPD Acceptable?

An effluent sample is tested twice for a contaminant and the results obtained are 0.109 mg/L and 0.115 mg/L. The relative percent difference for duplicate samples of this contaminant is required to be less than 10%. Is the % difference between these duplicate levels acceptable?

a. Yes

b. No

Acceptance Criteria

First, let's define this term:

Acceptance criteria are specified limits that are placed on a measurement, quality control sample or process. For example, the Standards Methods 2320B for the determination of alkalinity in a water sample sets the LCS QC standard acceptance criteria at +/- 5 %.

Now let's look at how LCS recovery results are compared to established acceptance criteria for the method.

LCS and Acceptance Criteria

Laboratory Control Samples are prepared and analyzed as one of the methods for assessing laboratory performance.

- A laboratory control sample is spiked with the analyte of interest at the project-specific action level and carried throughout the entire sample preparation and analytical process.
- The percent recovery is then calculated.
- The percent recovery is then compared to the established acceptance criteria for the method.

Let's look at an example of how we determine if the % recovery we found in our laboratory control sample results meets the acceptance criteria for the method.

In these types of circumstances, you will have a known LCS value for the method (in the example we are looking at on the next page, this value is 50 mg/L) and acceptance criteria for the method (in our example it is +/- 5%.) It is important to be able to determine if a certain LCS sample that you run for a method in your laboratory meets the acceptance criteria.

To perform this calculation we will be using the % formula that we used back in unit 2: $\% = \frac{\text{Part}}{\text{Whole}} \times 100$

First we calculate "What is 5% of 50 mg/L?" We then add and subtract our results from 50 mg/L.

Let's go ahead and look at the example.

LCS and Acceptance Criteria Determination Example

Using Standards Methods 2320B for the determination of alkalinity in a water sample the LCS QC standard acceptance criteria is +/- 5 %. If the known value of the LCS is 50 mg/L of $CaCO_3$, which of the following LCS samples meets the acceptance criteria? (Directions: choose one)

a. 56.15 mg/L
b. 44.17 mg/L
c. 49.253 mg/L
d. 55.32 mg/L

Step 1: We determine we know and what we don't know:

- LCS = 50 mg/L
- Acceptance Criteria = +/- 5%
- 5% of 50 = unknown

Step 2: We find our formula (the % calculation from Chapter 2.)

$$\% = \frac{\text{Part}}{\text{Whole}} \times 100$$

- % = 5%
- Part = unknown
- Whole = 50

Step 3: We plug our numbers into the equation.

$$5\% = \frac{\text{Part}}{50} \times 100$$

Step 4: We make sure our unknown is on one side of the equation. Since it's not, we work to cancel items out from one side to the other.

$$50 \times 5\% = \frac{\text{Part}}{\cancel{50}} \times 100 \times \cancel{50}$$

$$\frac{250\text{ mg/L }\%}{100} = \frac{\text{Part}}{\cancel{100}} \times \cancel{100}$$

Part = 2.5

Therefore, 5% of 50 is 2.5

To determine + 5% of 50, we add 2.5 to 50:
50 + 2.5 = 52.5

To determine - 5% of 50, we subtract 2.5 from 50:
50 – 2.5 = 47.5

c. 49.253 mg/L is between 47.5 and 52.5, thus it would qualify as meeting the +/- 5% criteria

Unit 8, Practice #5 – Acceptance Criteria Determination:

Using Standard Method 2540 C for total dissolved solids the acceptance criteria for the LCS is +/- 15%. The laboratory LCS known concentration is 25 mg/L.

Which of the following LCS samples meets the acceptance criteria?

a. 29.1 mg/L

b. 22.3 mg/L

c. 21.05 mg/L

d. 32.23 mg/L

LCS Frequency

Note that for Pa. accredited laboratories, there are quality control requirements in Chapter 252 for how often laboratory control samples must be prepared and analyzed.

- Each individual laboratory control sample must be compared to the acceptance criteria in the methods.
- The Pa. DEP acceptance criteria for various methods for proficiency testing can be found at the following bureau of laboratories link: http://www.portal.state.pa.us/portal/server.pt/community/labs/13780/laboratory_accreditation_program/590095 (Note: Look under the NELAC Institute heading.
- If there are no established criteria in a method, the environmental laboratory will need to determine internal criteria and document the procedure used to establish the limits.

III. Data Analysis

Data analysis is the process of inspecting and modeling data with the goal of discovering useful information, suggesting conclusions and supporting decision making. Two visual formats into which laboratory data is often placed for analysis are a calibration curve and a trend chart.

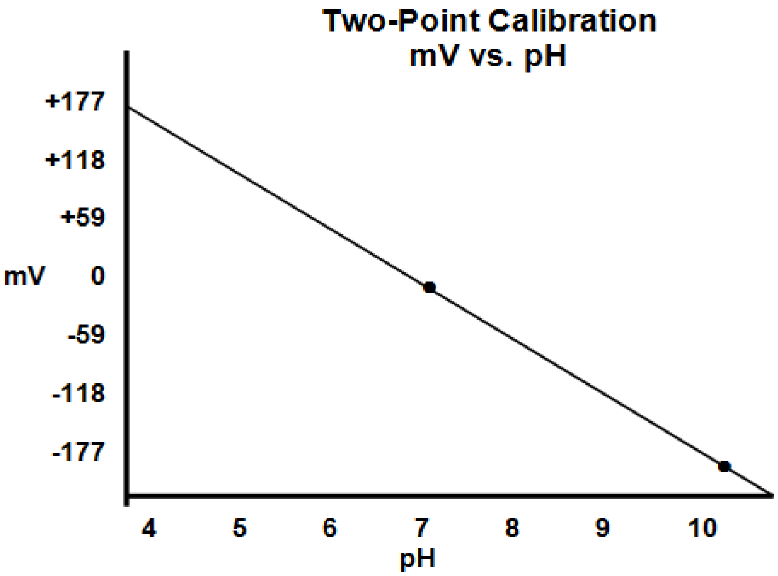
Calibration Curve

A **Calibration Curve** (aka "**Standards Curve**") is a graph of known concentrations used to determine the concentrations of the unknown or to verify the proper functioning of an analytical instrument.

By graphing multiple samples of certain known properties, other properties can be determined by interpolation using the graph.

Calibration curves may be used to:

- Determine the concentration of a substance
- Verify the proper functioning of an analytical instrument or a sensor device
    - One example would be verifying the function of an ion selective electrode
    - Another example would be to determine a standard calibration curve for many inorganic materials for use on UV spectrophotometer instruments.



The example 2-point pH calibration curve shown above is taken from the 1998 Pa. DEP CCT Workbook.

- The two standard buffers used to construct this calibration curve were the pH 7.0 and 10.0 buffers.
- For every pH unit difference, an electrical potential of ≈ 59 mV is produced.
- The pH meter measures the mV potential and then converts the mV potential into pH units.
- Once the calibration curve is constructed, it then provides a reference point from which to read the pH of a sample.

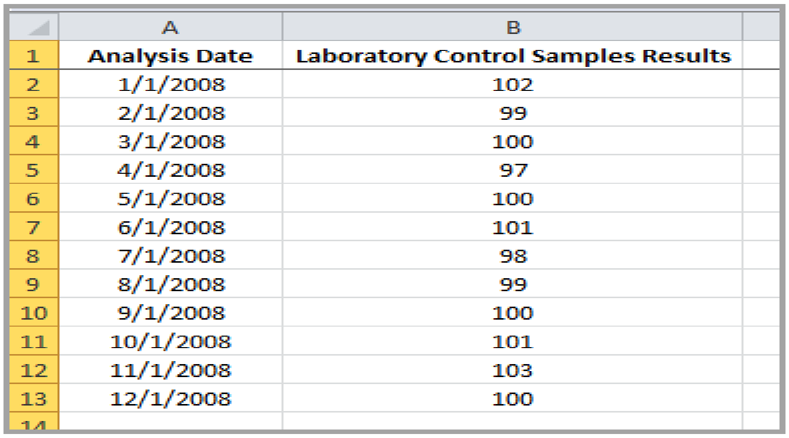
The number of points that are needed for a particular calibration curve are dependent upon the standard operating procedure for calibrating the particular piece of equipment or for the method being used.

A computer search on the phrase “Creating a Standard Curve” will bring up an instructional YouTube video on creating a standard curve for laboratory results in Excel.

Trend Chart

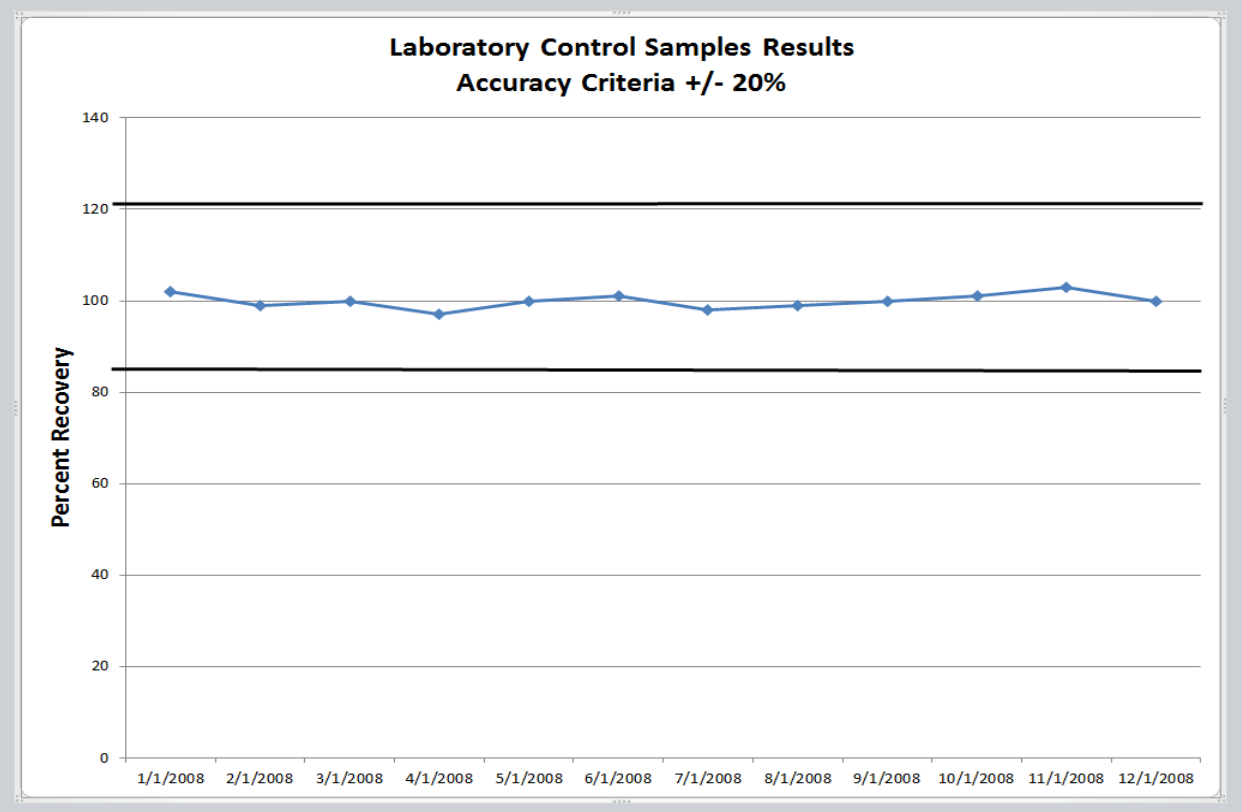
A **Trend Chart** consists of quantitative plots representing laboratory sample results for specific contaminants of concern over time. (Note: Basically the chart allows you to visually look for data trends over a period time.) An example trend chart (after the accompanying data list) is shown below.

Data for Trend Chart:



	A	B
1	Analysis Date	Laboratory Control Samples Results
2	1/1/2008	102
3	2/1/2008	99
4	3/1/2008	100
5	4/1/2008	97
6	5/1/2008	100
7	6/1/2008	101
8	7/1/2008	98
9	8/1/2008	99
10	9/1/2008	100
11	10/1/2008	101
12	11/1/2008	103
13	12/1/2008	100

Trend Chart:



Trend charts may be a useful screening tool for laboratory managers for monitoring data quality for specific contaminants of concern.

- They produce a quick visual method for use in assessing quality assurance activities over time.
- Core QC elements may be tracked in the field and laboratory. Laboratories produce the data used in preparing these charts, with most producing charts upon request.
- Trend chart use may be extended to quantify results of performance evaluation samples, field laboratory audits, and data validation.
    - They permit one to see trends in a timely manner, for corrective action when needed.
    - Due to their ease in interpretation, they permit improved oversight and control of data quality, for corrective action when needed.
    - The chemist should be consulted when making a critical decision based on the data provided in the trend charts.
- Any graphical package may be used to produce trend charts.
    - Microsoft Excel is often used, primarily due to its ability to accept data and present it in graphical format.
    - A computer search on the phrase “How to Create A Trend Chart in Excel” will bring up various how-to articles (and even instructional YouTube videos.)
    - These how-to articles and videos will explain (and some even show) how the data needs to look in the Excel computer spreadsheet in order to obtain the chart you want.

Calibration Verification Standards

Pa. accredited environmental laboratories need to analyze a calibration verification standard at the beginning and end of each analysis day. In addition, a calibration verification standard is to be analyzed after every ten samples.

Laboratories also need to verify the calibration curve of each analytical batch with calibration verification standards at a low and a high level as follows:

- The concentration of the low calibration verification standard needs to be within the lower 20% of the calibration curve and not more than five times the lowest quantitation level.
- The concentration of the high calibration verification standard needs to be within the upper 20% of the calibration curve.

Details of the calibration verification procedure (including calculations, integrations, acceptance criteria and associated statistics) needs to be included or referenced in the laboratory’s standard operating procedure.

Raw data records also need to be retained to permit reconstruction of the calibration verification

Unit 8 Exercise:

1. In order to produce a trend chart, data needs to be entered into a computer spreadsheet contained in a graphical package such as Excel.

a. True

b. False

2. A standards curve is a graph of known concentrations that can be used to determine the concentrations of the unknown.

a. True

b. False

3. The permit limit for a particular NPDES permit parameter is 1.0. Using EPA rounding principals, is a calculated parameter of 1.06 a violation?

a. Yes, because it rounds to 1.1

b. No, because it rounds to 1.0

4. A duplicate analysis of a sample found results of 3 mg/L and 5 mg/L. What is the relative percent difference of these results?

a. 50%

b. 0.08%

c. 80%

d. 0.05%

5. The standard method for a contaminant has an acceptance criteria for the LCS of +/- 5 %. If the known value of the LCS is 30 mg/l, which of the following LCS sample results meets the acceptance criteria?

a. 36 mg/l

b. 35 mg/l

c. 29 mg/l

d. 25 mg/l

Unit 8 Key Points:

- Pa. DEP regulatory detection/reporting limits are used to establish the number of significant digits required for reporting purposes. However, as a Pa. drinking water or wastewater laboratory, it is important to determine whether you should round the data you are reporting or submit it using as many decimal places as possible.

- Pa. Drinking Water Laboratories should submit data using as many decimal places as available if the data will be rounded for compliance purposes by the Pa. DEP PADWIS system.

- Pa. Wastewater Laboratories should submit data using as many decimal places as available if the data is being submitted to a permitee who will then round the data prior to submitting it to the eDMR system.

- Use the RPD formula to calculate relative percent difference for duplicate samples.

- Use the % calculation formula from chapter 2 to determine if LCS results are within acceptance criteria.

- The number of points that are needed for a particular calibration curve (aka “standards curve”) are dependent upon the standard operating procedure for either the equipment or the method being used.

Unit 8 References:

- General "Rules for Rounding" taken from the Pa. DEP "Overview of Basic Math" Module #28 workbook pp. 1-10, 1-11.
    - Chapter exercise question #3 taken from p.28 of the EPA NPDES Reporting Handbook at http://www.deq.state.ok.us/wqdnew/forms/DMR-Manual.pdf

- Drinking Water "Calculating Averages for Pa. DEP Compliance Purposes" Explanation and Example from Drinking water General Update training; calculation #2 from DW General Update Training WB page 2A-31 (IG p. 42)

- Calculating drinking water averages when a sample measures non-detect from 2007 Pa. DEP DW General Reporting IG Ch. 2 p.9

- Wastewater calculation #1 from Pa. DEP document 3800-BK-DEP3047 on "Discharge Monitoring Reports Overview and Summary" p. 6 example 1 (W. Lloyd changed numbers a bit for teaching about rounding concepts)

- "Converting within the Metric System" pp. 1-13 through 1-16 (problems #1 & #2 created by W. Lloyd)

- Relative percent difference

    - Written definition taken from Wikipedia at http://en.wikipedia.org/wiki/Relative_change_and_difference
    - Calculation taken from US EPA web page Radon Glossary of Terms http://www.epa.gov/radon/glossary.html + Bill McNamara (Pa. DEP BSDW)

- Acceptance criteria:
    - Acceptance criteria definition taken from Ch. 252.1
    - Explanation taken from EPA's Manual for the Certification of Laboratories Analyzing Drinking Water – Fifth Edition (2005) pg. IV-5 section 7.2

- LCS and Acceptance criteria taken from Ch. 252 pg. 44 section 252.402(h)(6) and EPA's "Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry" pg. 7473-6 section 9.4

- Standard Curve definition from internet article Hendrix College (Conway, AR) Cell Biology Laboratory Manual "Graphing – Standard Curves" at http://www2.hendrix.edu/biology/CellWeb/Techniques/GRAPhstdcrv.html and Wikipedia "Standard Curve" at http://en.wikipedia.org/wiki/Standard_curve

    - A YouTube video on how to create an Excel 2010 standard curve for laboratory results can be found at http://www.youtube.com/watch?v=stp_zj9RRJU

- Spectrophotometer standard absorption curve information from Pg 3-10 of EPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories (1979.)

- Data analysis definition from http://en.wikipedia.org/wiki/Data_Interpretation

- Trend Chart information taken from EPA's Region 9 QA Office on-line article entitled "Data Quality Screening Using Trend Charts" (10-2011) at http://www.epa.gov/region9/qa/pdfs/TrendCharting.pdf

    - Much of the description is taken from the conclusion on page 16.
    - A YouTube video on how to create an Excel 2007 graph for a Lab Report can be found at http://www.youtube.com/watch?v=EloFn0IWtms

- Relative Percent Difference:
    - Equation from: http://www.deq.state.or.us/lab/wqm/docs/DataEvaluation.pdf
    - Explanation from: http://fscimage.fishersci.com/cmsassets/downloads/segment/Scientific/pdf/WaterAnalysis/Log113TipLaboratoryDuplicatesMatrixSpikeDuplicates.pdf
    - Example taken from http://www.mathsisfun.com/percentage-difference.html (scroll down to see "what if the difference is negative?")
    - Practice and unit problems created by W. Lloyd and checked in percent difference calculator at http://www.calculatorsoup.com/calculators/algebra/percent-difference-calculator.php

- Acceptance Criteria:
    - Statement about laboratory control samples and LCS relationship taken from NELAC, Volume 1 (item 1.7.3)
    - Practice Type equation here.problems created by B. Titler. Calculation step explanations and unit problem created by W. Lloyd and checked in percent difference calculator at http://www.calculatorsoup.com/calculators/algebra/percent-difference-calculator.php

Unit 9 – Laboratory Reporting

Learning Objectives

At the end of this unit, you should be able to:

- Refer to Chapter 252 for the required laboratory result reporting information.
- Review the flow of data for Pa. drinking water compliance reporting and be able to access more information to report electronically.
- Review the flow of data for Pa. wastewater compliance reporting and be able to access more information to report electronically.

This short unit covers a few points about Pa. drinking water and wastewater compliance monitoring reporting requirements.

I. Required Lab Test Report Information

Chapter 252 requires that the reporting of data by environmental laboratories be done under the direct supervision of a laboratory supervisor.

II. Pennsylvania Compliance Reporting Systems

Generally, laboratories will submit compliance drinking water data directly to Pa. DEP on behalf of the drinking water facility.

Wastewater data, on the other hand, is generally submitted directly from the wastewater facility to Pa. DEP. The wastewater facility obtains sample data from their laboratory to include with the other compliance data collected at their facility.

Let’s start this section off by looking at a few definitions.

DWELR (abbreviation for the **Drinking Water Electronic Lab Reporting** web application) is a Pennsylvania electronic reporting system that allows laboratories to securely submit drinking water sample data to Pa. DEP over the Internet.

PADWIS (abbreviation for the **Pennsylvania Drinking Water Information System**) is a Pennsylvania electronic data system that that performs monthly compliance processing on regulated drinking water data. Regulated drinking water data are received from Pa. accredited laboratories through the electronic DWELR system. PADWIS submits drinking water compliance monitoring results to the federal EPA.

DMR (abbreviation for **Discharge Monitoring Report**): Most wastewater facilities are required to submit a monthly Discharge Monitoring Report (DMR) to the Pa. DEP that summarizes effluent monitoring results.

eDMR (abbreviation for **Electronic Discharge Monitoring Report**) provides an alternative way for facilities to submit wastewater discharge monitoring reports electronically to Pa. DEP instead of submitting a paper form.

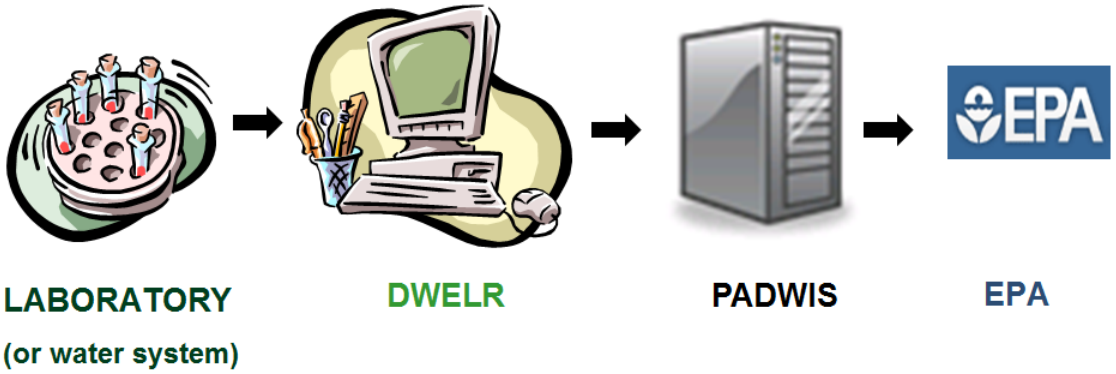
Pa. Drinking Water Compliance Monitoring Data Systems

Pennsylvania's Drinking Water Electronic Lab Reporting (DWELR) web application allows laboratories to securely submit drinking water sample data over the internet to Pa. DEP. Laboratories (or water systems) must have a DEP laboratory identification number (Lab ID) to submit sample results using DWELR.

On the 10th of each month as required by Chapter 109 of Title 25 of the Pennsylvania Code, all data is cleared from DWELR and passed to PADWIS (the electronic Pennsylvania Drinking Water Information System) for monthly compliance processing.

PADWIS electronically submits drinking water compliance monitoring results to EPA.

The flow of data is as follows:



Flow of Drinking Water Compliance Data

More information about using the DWELR system can be found on the DWELR web page. The steps to finding this web page are:

- Type the following web address into the internet address search: www.depweb.state.pa.us
- Click on the left hand link labeled “DEP Programs A-Z”
- From the top line of alphabet linked letters that appear, click on the letter “D”
- Find the word “DWELR” near the bottom of the 2nd column of the list and click on it

Reporting Wastewater Compliance Monitoring Data

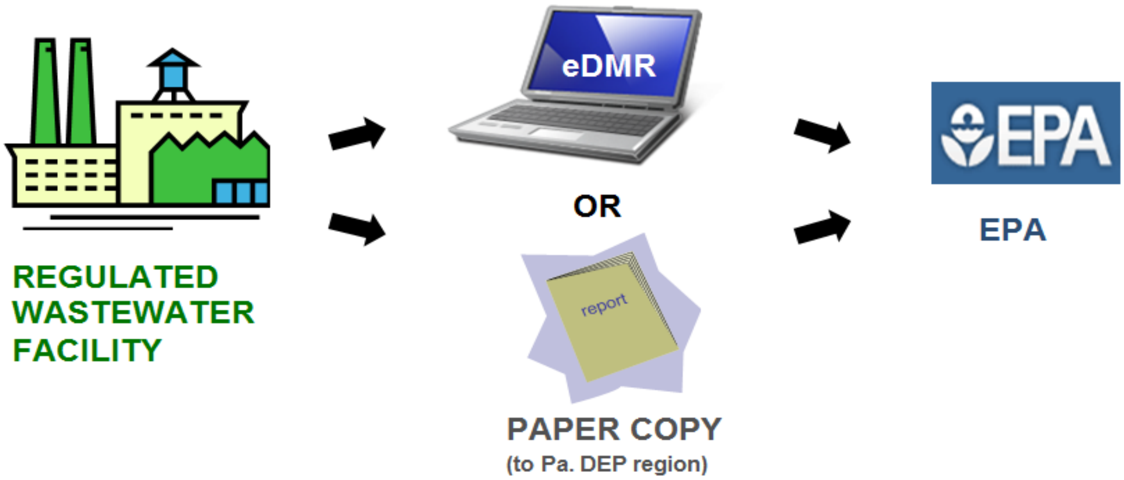
Regulated wastewater facilities are required to send Discharge Monitoring Reports (DMRs) to the Pennsylvania DEP to summarize effluent monitoring results.

DMRs must be submitted by any facility that has been issued an NPDES permit that requires sampling and monitoring (typically sewage treatment plants and industrial facilities with a wastewater or storm water discharge to surface waters). DMRs may also be required for Water Quality Management permits with land application of effluent.

An Electronic DMR (eDMR) provides an alternative way for facilities to submit these wastewater reports electronically instead of submitting a paper form.

In most cases, DMRs for NPDES permits must be received by the applicable Pa. DEP regional office by the 28th day of the month following the monitoring period. For example, the September DMR must be received in the appropriate DEP’s regional office by October 28. Different due dates may apply for WQM permits.

Flow of Wastewater Compliance Data



More information about using the eDMR system can be found on the eDMR web page. The steps to finding this web page are:

- Type the following web address into the internet address search: www.depweb.state.pa.us
- Click on the left hand link labeled "Water"
- Click on the left hand link labeled "Bureau of Point and Non-point Source Management"
- Click on the right hand link labeled "Wastewater Management"
- Click on the right hand link labeled "eDMR"

Importance of Laboratory Ethics

Fraudulent Flood Water Test Results

In 2012, a northeastern U.S. laboratory - along with the laboratory director and owner – that performed analytical testing of environmental samples of water and wastewater, caused environmental test reports to be prepared and mailed to customers which falsely stated that proper EPA methods were followed when they weren't. The test results then were false, inaccurate and unreliable. For example, they prepared and mailed false and fraudulent test results for flood water samples which were required by EPA to be tested for contamination by various pollutants. In addition, fake results were reported in testing imported fruit for potential contamination.

The laboratory director was sentenced to nine months in prison and the laboratory was sentenced to five years of probation. In addition, both defendants were ordered to share the cost of restitution in the amount of $14,000.00.

Unit 9 Exercise:

(Note: Practice answers can be found in the answer key located after Unit 10.)

Multiple Choice: Choose one best answer unless otherwise indicated.

1. In most cases, DMRs for NPDES permits must be received by the applicable Pa. DEP regional office by the ______ day of the month following the monitoring period.

a. 1st
b. 10th
c. 28th

2. On the ____ day of each month as required by Chapter 109 of Title 25 of the Pennsylvania Code, all drinking water data is cleared from DWELR and passed to PADWIS for monthly compliance processing.

a. 1st
b. 10th
c. 28th

Unit 9 Key Point:

- Deadlines for reporting of Pennsylvania drinking water data and wastewater data are at different times of the month, since Pennsylvania deadlines are based on the requirements of the particular environmental regulation.

Unit 9 References:

- United States Department of Justice, United States Attorney's Office Eastern District of Pennnsylvania September 10, 2012 sentencing found at http://www.justice.gov/usao/pae/News/2012/Sep/bluemarsh_release.htm .

- DWELR information taken from Pa. DEP's DWELR web page at: http://www.portal.state.pa.us/portal/server.pt/community/public_drinking_water/21162/Drinking_Water_Electronic_Lab_Reporting_System/1258975 ; in addition, there was consultation with Jennifer brock of the Pa. DEP PADWIS section.

- DMR information taken from Pa. DEP's DMR web page at http://www.portal.state.pa.us/portal/server.pt/community/discharge_monitoring_report_information/21375

- eDMR information taken from Pa. DEP's eDMR web page at http://www.portal.state.pa.us/portal/server.pt/community/edmr/17879

Unit 10 – Laboratory Recordkeeping

Learning Objectives

At the end of this unit, you should be able to:

- List general recordkeeping requirements for supplies and chemicals
- Explain the procedures for correcting data.
- Identify key record maintenance requirements.
- List the main types of documentation that a laboratory needs to present during an audit.
- Identify records required for drinking water and wastewater accredited laboratories.
- State the time frame for the submission of a corrective action report to Pa. DEP

I. General Supply Records

Standard, reagent and laboratory supply receipt records need be maintained and include the following:

- date of receipt,
- vendor,
- lot number,
- amount received,
- expiration date, and
- certificates of analysis or purity (if available)

Purchased chemicals, solutions, standards, media and laboratory supplies need to be labeled with date of receipt, expiration date and the date when the container is opened.

- Purchased chemicals, solutions and standards without an expiration date on the original container shall be discarded after 10 years from the date they are received.

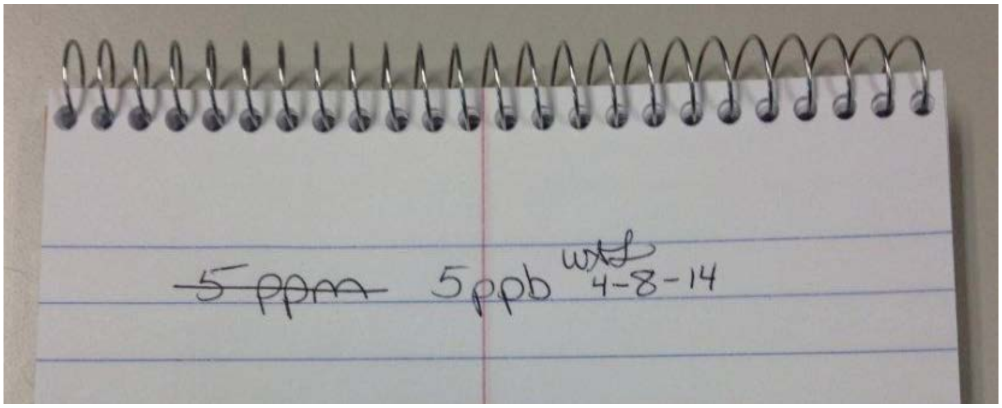
- Standard and reagent preparation records must also be kept.

II. Record Editing & Maintenance

Record Editing

All generated data needs to be recorded promptly and be readable in permanent ink or in an electronic format.

When changes are made to laboratory records, the original entry must remain visible by drawing a single line through the original entry and entering the new information beside it (see picture below.) The individual making the change shall sign or initial and date the correction.



Picture taken by Pa. DEP

These criteria also apply to electronic records unless they involve data generated by automated data collection systems. Electronic records need to be maintained in a way that tracks changes to the original record. All laboratory information management systems (LIMS) will have this feature. Additionally, the Microsoft Office suite includes features to track changes.

Record Maintenance

Environmental laboratories need to maintain records in an organized fashion. Note that records need to be accessible by the Pa. DEP.

Original handwritten records are also to be kept so that reconstruction of the following can occur:

- all sample testing and analysis
- proficiency test (PT) samples,
- initial demonstration of capability (aka initial DOC or IDOC)
- demonstration of continued proficiency

Records shall be maintained for a minimum of **five years** unless otherwise specified in regulation.

- A change in ownership, merger, or closure of a laboratory does not cancel this requirement.
- This includes all raw data, calculations, and quality control data.
- These data files may be either hard copy, microfiche or electronic. Electronic data should always be backed up by protected tape or disk or hardcopy.

Environmental laboratories need to have a written plan that specifies how records will be maintained or transferred if the laboratory transfers ownership or terminates operations.

Sally kept all the laboratory records for 5 years like she was supposed to.

III. Equipment Records

Equipment Records

Environmental laboratories need to maintain records for each piece of equipment. These records must document the following:

- The equipment name
- The manufacturer's name, type identification, and serial number (or other unique identification)
- The date received and date placed in service (if available)
- The current location (when appropriate)
- Condition when received (for example, new, used or reconditioned, if available)
- A copy of the manufacturer's instructions (where available)
- The dates and results of calibrations or verifications.

- The manufacturer's instructions (if available, or reference their location)
- The details of maintenance performed.
- A history of damage, malfunction, modification or repair.

Equipment Calibration Records

The following equipment calibration records need to be kept:

- *Certified NIST-reference thermometer:* Retain a certificate documenting traceability of the calibration to NIST standards.
- *Working thermometers (glass, liquid filled, dial and electronic thermometers):* Maintain records in a laboratory notebook for each working thermometer.
- *ASTM class 1, 2 or 3 (Class S or S-1), or better certified reference weights:* Maintain a certificate documenting traceability of the calibration to ASTM standards.
- *Analytical or pan balances:* Maintain records in a laboratory notebook of balance calibrations. Records of annual service shall be maintained and the service date shall be recorded on the balance.
- *pH meter:* Maintain records of pH meter calibration in a laboratory notebook.
- *Conductivity meter:* Maintain records of conductivity meter calibrations in a laboratory notebook.
- *Refrigeration equipment and freezers:* Record calibration-corrected temperatures for each refrigerator and freezer once a day for each day in use for all laboratory activities.

See Chapter 252, § 252.306 (f) for more details on items to record.

Equipment Monitoring Records

Calibration-corrected temperatures for the following need to be recorded once a day for each day in use for all laboratory activities:

- each incubator
- water bath
- heating block or oven

(Note: When used as an incubation unit for microbiology, the calibration-corrected temperature shall be recorded at least twice per day in use with the readings separated by at least 4 hours.)

Even though she was a perfectionist and didn’t like to see crossed out and corrected results, the surveillance camera NEVER found Madge shredding incorrect bench sheets...OR using white-out (because she never did either!)

IV. Training Records

Training Records

As mentioned in Unit 1, all laboratory personnel must have ethics and legal training every 14 months.

Accredited laboratories need to keep the following training records:

- Records that show employees have attended ethics training (whether it be attended in-house or as an outside formal training session.)
- A signed statement on file to indicate that the employee acknowledges and understands his/her personal ethical and legal responsibilities, including potential punishments for unlawful or unethical behavior.

V. Pa. Quality Manual Records Retention

Pa. Quality Manual

In Unit 1 we reviewed how Pennsylvania laboratories that are accredited under Chapter 252 must develop and maintain the written document called a “Quality Manual.” This manual must be available to and used by all laboratory personnel. A few of the quality manual sections specific to records retention are again listed below.

More information about quality manual sections can be found in Appendix E.

- **Document Control System:** A written procedure for the control and maintenance of all laboratory documents. This includes recordkeeping procedures for storing laboratory records and making changes to documents.

- **Personnel Records:** Documents the training and competency of lab employees through personnel records.

- **Recordkeeping:** The laboratory develops a written procedure describing how and where records are maintained.

NOTE: All records generated by the laboratory must be maintained for a **minimum of 5 years** from the date of the last entry (for logbooks) or date of retire (for SOPs, QA manual, etc.)

VI. Records available for an Audit

Availability of Documents

The laboratory's QA plan and appropriate Standard Operating Procedures (SOPs) should be readily available for inspection by auditors. Pa.-accredited labs will have a Quality Manual as their QA plan.

- All quality control information should be readily available for inspection by auditors.

- Adequate information should be available to allow the auditor to reconstruct the final results for compliance samples and PT samples.

A highlight of some of the records that may be requested during an audit is included in Appendix F. It would be good to review the checklist to see if your laboratory has the applicable information available for the next upcoming audit. Note that this list is not all-inclusive, since additional audit items will be added based on the specific types of equipment and tests used by your laboratory.

Onsite Assessments

Pa. DEP may conduct announced or unannounced onsite assessments of an environmental laboratory to ensure compliance with the conditions of accreditation. The environmental laboratory will be provided with an onsite assessment report documenting any deficiencies found by the Department.

If deficiencies are found, an environmental laboratory shall submit a corrective action report to the Department within *60 calendar days* from receipt of an onsite assessment report from the Pa. DEP. The corrective action report must document the corrective action taken by the laboratory to correct each deficiency.

Unit 10 Exercise:

(Note: Practice answers can be found in the answer key located after Unit 10.)

Multiple Choice: Choose one best answer unless otherwise indicated.

1. Unless otherwise specified in regulation, how long must records required under Chapter 252 be maintained?

   a. 1 year
   b. 3 years
   c. 5 years
   d. 10 years

2. To avoid confusion, records should be edited in a way that the erases the original entry.

   a. True
   b. False

3. Records are to be kept electronically in an organized fashion, which allows laboratories to dispose of original handwritten records.

   a. True
   b. False

4. An environmental laboratory shall submit a corrective action report to the Department within *60 business days* from receipt of an onsite assessment report from the Pa. DEP where deficiencies have been found.

a. True

b. False

5. Laboratory supply receipt records need be maintained and include which of the following:

a. Date received

b. Vendor

c. Amount received

d. Expiration date

e. a through d

f. c and d

6. Which of the following need to be recorded once a day for each day in use for all laboratory activities?

a. incubator temperatures

b. water bath temperatures

c. refrigerator temperatures

d. freezer temperatures

e. all of the above

7. On April 5, 2013, Annette pulled an unopened laboratory chemical bottle off the shelves and saw it did not have an expiration date, but someone noted it had been purchased over 5 years prior during 1-2006; she went ahead and used it in her chemical analysis. Was this chemical considered too old to be used?

a. Yes
b. No

8. The laboratory's QA plan should be readily available for inspection by auditors. On the other hand, the Standard Operating Procedures (SOPs) do not need to be available, since the auditors would never look at this information.

a. True
b. False

Unit 10 Key Points

- Records shall be maintained for a minimum of **five years** unless otherwise specified in regulation
- Original handwritten records are to be kept so that sample and proficiency reconstruction can occur.
- Environmental laboratories need to maintain their records in an organized fashion that is accessible by the Pa. DEP.
- Changes to records need to occur in a way that the original entry remains visible.
- Laboratory supply receipt records need be maintained and include the following: date received, vendor, lot number, amount received, expiration date, and (if available) certificates of analysis or purity.
- Once the Pa. DEP sends an environmental laboratory an assessment report with deficiencies, the laboratory has 60 calendar days to submit a corrective action report to the Pa. DEP.
- Both the laboratory's QA plan and appropriate Standard Operating Procedures (SOPs) should be readily available for inspection by auditors.

Unit 10 References:

- Laboratory supply recordkeeping information taken from Chapter 252, section 252.306 (h)(4)
- Recordkeeping information; taken from page IV-9 of EPA's Manual for the Certification of Laboratories Analyzing Drinking Water: http://www.epa.gov/ogwdw/methods/pdfs/manual_labcertification.pdf
- Record Maintenance and Record Editing information was taken from Chapter 252, Section 252.706 Recordkeeping. Electronic record editing information provided by V. Hunsberger and Y. Creason from Pa. DEP BoL Accreditation Section.
- Equipment Records information was taken from Chapter 252, Section 252.306(b) on Equipment, supplies and reference materials
- [2]"Writing a Quality Manual for PA State (Chapter 252) Accreditation"" http://files.dep.state.pa.us/AboutDEP/Labs/LabsPortalFiles/2010_0709%20-%20QM%20%20Rev%208.pdf
- Onsite assessment information was taken from Chapter 252, Section 252.601e.
- Availability of QA, SOP & QC control information for an audit taken from EPA's Manual for the Certification of Laboratories Analyzing Drinking Water – Fifth Edition (2005) at http://www.epa.gov/ogwdw/methods/pdfs/manual_labcertification.pdf
- Checklist of audit information from V -40 of EPA's Manual for the Certification of Laboratories Analyzing Drinking Water – Fifth Edition (2005)