Water Treatment Laboratory Workshop

Week 1

Course # 2112

Fleming Training Center

Fleming Training Center
Your Partner in Clean Water

TDEC
TENNESSEE DEPARTMENT OF ENVIRONMENT AND CONSERVATION

State of Tennessee

Water Treatment Laboratory
Week 1
Course # 2112

Monday

8:30	Registration	Amanda Carter
9:00	Basic Lab Skills/Safety/Lab Equip	Amanda
11:30	Lunch	
12:30	QA/QC	Amanda

Tuesday

8:30	pH	Amanda
9:30	Specific Gravity	Amanda
11:00	Lunch	
12:00	Potassium Permanganate Residual	Amanda
12:30	Chlorine, Free Residual & Total	Amanda

Wednesday

8:30	Bacteriological Testing	Amanda
11:30	Lunch	
12:30	Turbidity	Amanda
1:30	Jar Testing	Amanda

Thursday

8:30	Corrosion Control	Amanda
11:30	Lunch	
12:30	Tour - To Be Announced	

Friday

8:30	Lead & Copper	Amanda
9:30	Review	Amanda
11:00	Lunch	
12:00	Course Evaluation and Exam	Amanda

Fleming Training Center
2022 Blanton Dr.
Murfreesboro, TN
37129

Phone: 615-898-6507
Fax: 615-898-8064
E-mail:
Amanda.Carter@tn.gov

Water Treatment Laboratory
Week 1
Course # 2112

Section 1	Basic Lab Skills / Safety / Lab Equipment	3
Section 2	QA / QC Program	43
Section 3	pH	61
Section 4	Specific Gravity	77
Section 5	Potassium Permanganate Residual	85
Section 6	Chlorine Residual and Demand	91
Section 7	Bacteriological Testing	123
Section 8	Orthophosphates and Corrosion Control	167
Section 9	Lead and Copper Sampling	191
Section 10	Turbidity	201
Section 11	Jar Test	213

Section 1

Basic Lab Skills / Safety / Lab Equipment

Lab Policies

1. No horse play.
2. No shorts or open-toed shoes.
3. No smoking, eating, dipping or drinking in the lab.
4. Put broken glass in broken glass container, NOT IN THE TRASH.
5. Do not pipet by mouth.
6. Each day after class:
   - All used glassware will be washed in hot soapy water, rinsed in tap water, then distilled water.
   - All counter tops will be wiped clean with disinfectant.
   - Balance room must be clean.
7. Used pipets are placed in containers containing detergent immediately after use, tip up.
8. Acid spills must be cleaned up immediately.
9. Pipet bulbs must be cleaned immediately after overpipeting.
10. Wear safety glasses when performing any experiment.
11. Wear aprons in the lab at all times.
12. Wear gloves when performing any experiment or washing glassware.
13. Wash your hands before leaving the laboratory.
14. Know where the eye wash stations are located and how to use them.
15. Know where the emergency shower is and how to use it.
16. Know where each fire extinguisher is located and how to use them.
17. Read carefully the Material Safety Data Sheets for all chemicals used in the laboratory.

Periodic Table of the Elements

KEY

Atomic Mass → 12.011

Symbol → C

Atomic Number → 6

Electron Configuration → 2-4

← Selected Oxidation States: –4, +2, +4

Relative atomic masses are based on ^{12}C = 12.000

Note: Mass numbers in parentheses are mass numbers of the most stable or common isotope.

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	1.00794 +1 −1 **H** 1 1																	4.00260 0 **He** 2 2
2	6.941 +1 **Li** 3 2-1	9.01218 +2 **Be** 4 2-2											10.81 +3 **B** 5 2-3	12.0111 −4 +2 +4 **C** 6 2-4	14.0067 −3 −2 −1 +1 +2 +3 +4 +5 **N** 7 2-5	15.9994 −2 **O** 8 2-6	18.998403 −1 **F** 9 2-7	20.179 0 **Ne** 10 2-8
3	22.98977 +1 **Na** 11 2-8-1	24.305 +2 **Mg** 12 2-8-2											26.98154 +3 **Al** 13 2-8-3	28.0855 −4 +2 +4 **Si** 14 2-8-4	30.97376 −3 +3 +5 **P** 15 2-8-5	32.06 −2 +4 +6 **S** 16 2-8-6	35.453 −1 +1 +3 +5 +7 **Cl** 17 2-8-7	39.948 0 **Ar** 18 2-8-8
4	39.0983 +1 **K** 19 2-8-8-1	40.08 +2 **Ca** 20 2-8-8-2	44.9559 +3 **Sc** 21 2-8-9-2	47.88 +2 +3 +4 **Ti** 22 2-8-10-2	50.9415 +2 +3 +4 +5 **V** 23 2-8-11-2	51.996 +2 +3 +6 **Cr** 24 2-8-13-1	54.9380 +2 +3 +4 +7 **Mn** 25 2-8-13-2	55.847 +2 +3 **Fe** 26 2-8-14-2	58.9332 +2 +3 **Co** 27 2-8-15-2	58.69 +2 +3 **Ni** 28 2-8-16-2	63.546 +1 +2 **Cu** 29 2-8-18-1	65.39 +2 **Zn** 30 2-8-18-2	69.72 +3 **Ga** 31 2-8-18-3	72.59 −4 +2 +4 **Ge** 32 2-8-18-4	74.9216 −3 +3 +5 **As** 33 2-8-18-5	78.96 −2 +4 +6 **Se** 34 2-8-18-6	79.904 −1 +1 +5 **Br** 35 2-8-18-7	83.80 0 +2 **Kr** 36 2-8-18-8
5	85.4678 +1 **Rb** 37 2-8-18-8-1	87.62 +2 **Sr** 38 2-8-18-8-2	88.9059 +3 **Y** 39 2-8-18-9-2	91.224 +4 **Zr** 40 2-8-18-10-2	92.9064 +3 +5 **Nb** 41 2-8-18-12-1	95.94 +3 +6 **Mo** 42 2-8-18-13-1	(98) +4 +6 +7 **Tc** 43 2-8-18-14-1	101.07 +3 **Ru** 44 2-8-18-15-1	102.906 +3 **Rh** 45 2-8-18-16-1	106.42 +2 +4 **Pd** 46 2-8-18-18	107.868 +1 **Ag** 47 2-8-18-18-1	112.41 +2 **Cd** 48 2-8-18-18-2	114.82 +3 **In** 49 2-8-18-18-3	118.71 +2 +4 **Sn** 50 2-8-18-18-4	121.75 −3 +3 +5 **Sb** 51 2-8-18-18-5	127.60 −2 +4 +6 **Te** 52 2-8-18-18-6	126.905 −1 +1 +5 +7 **I** 53 2-8-18-18-7	131.29 0 +2 +4 +6 **Xe** 54 2-8-18-18-8
6	132.905 +1 **Cs** 55 2-8-18-18-8-1	137.33 +2 **Ba** 56 2-8-18-18-8-2	138.906 +3 **La** 57 2-8-18-18-9-2	178.49 +4 **Hf** 72 **18-32-10-2	180.948 +5 **Ta** 73 -18-32-11-2	183.85 +6 **W** 74 -18-32-12-2	186.207 +4 +6 +7 **Re** 75 -18-32-13-2	190.2 +3 +4 **Os** 76 -18-32-14-2	192.22 +3 +4 **Ir** 77 -18-32-15-2	195.08 +2 +4 **Pt** 78 -18-32-17-1	196.967 +1 +3 **Au** 79 -18-32-18-1	200.59 +1 +2 **Hg** 80 -18-32-18-2	204.383 +1 +3 **Tl** 81 -18-32-18-3	207.2 +2 +4 **Pb** 82 -18-32-18-4	208.980 +3 +5 **Bi** 83 -18-32-18-5	(209) +2 +4 **Po** 84 -18-32-18-6	(210) **At** 85 -18-32-18-7	(222) 0 **Rn** 86 -18-32-18-8
7	(223) +1 **Fr** 87 -18-32-18-8-1	226.025 +2 **Ra** 88 -18-32-18-8-2	227.028 +3 **Ac** 89 -18-32-18-9-2	(261) **Rf** 104	(262) **Db** 105	(263) **Sg** 106	(264) **Bh** 107	(265) **Hs** 108	(268) **Mt** 109	(269) **Uun**	(272) **Uuu** 111	(277) **Uub** 112		(285) **Uuq** 114				

**Denotes the presence of (2-8-) for elements 72 and above

*The systematic names and symbols for elements of atomic numbers above 109 will be used until the approval of trivial names by IUPAC.

140.12 +3 +4 **Ce** 58	140.908 +3 **Pr** 59	144.24 +3 **Nd** 60	(145) +3 **Pm** 61	150.36 +2 +3 **Sm** 62	151.96 +2 +3 **Eu** 63	157.25 +3 **Gd** 64	158.925 +3 **Tb** 65	162.50 +3 **Dy** 66	164.930 +3 **Ho** 67	167.26 +3 **Er** 68	168.934 +3 **Tm** 69	173.04 +2 +3 **Yb** 70	174.967 +3 **Lu** 71
232.038 +4 **Th** 90	231.036 +4 +5 **Pa** 91	238.029 +3 +4 +5 +6 **U** 92	237.048 +3 +4 +5 +6 **Np** 93	(244) +3 +4 +5 +6 **Pu** 94	(243) +3 +4 +5 +6 **Am** 95	(247) +3 **Cm** 96	(247) +3 +4 **Bk** 97	(251) +3 **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(260) **Lr** 103

Common Valences

1+	2+	3+
Ammonium, NH_4^+	Barium, Ba^{2+}	Aluminum, Al^{3+}
Cuprous, Cu^+	Calcium, Ca^{2+}	Chromic, Cr^{3+}
Hydrogen, H+	Cupric, Cu^{2+}	Ferric, Fe^{3+}
Hydronium, H_3O^+	Ferrous, Fe^{2+}	
Potassium, K^+	Lead, Pb^{2+}	
Silver, Ag^+	Magnesium, Mg^{2+}	
Sodium, Na^+	Mercuric, Hg^{2+}	
	Nickel, Ni^{2+}	
	Zinc, Zn^{2+}	

1–	2–	3–
Acetate, $C_2H_3O_2^-$	Carbonate, CO_3^{2-}	Phosphate, PO_4^{3-}
Bicarbonate, HCO_3^-	Chromate, CrO_4^{2-}	
Bromide, Br^-	Peroxide, O_2^{2-}	
Chlorate, ClO_3^-	Sulfate, SO_4^{2-}	
Chloride, Cl^-	Sulfide, S^{2-}	
Hydroxide, OH^-	Sulfite, SO_3^{2-}	
Iodide, I^-		
Nitrate, NO_3^-		
Nitrite, NO_2^-		
Bisulfate, HSO_4^-		

How many grams of Na_2CO_3 would it take to make a 1 Molar and a 1 Normal solution?

Step 1: Determine the molecular weight of Na_2CO_3.

$$Na_2CO_3 \rightarrow Na^+ + Na^+ + CO_3^{2-}$$

Na = 22.99 amu X 2 = 45.98 amu
C = 12.01 amu X 1 = 12.01 amu
O = 16 amu X 3 = 48.00 amu
Molecular weight = 105.99 amu

Molarity

Step 2: Calculate the number of moles

$$\# \text{ moles} = \frac{\text{total weight}}{\text{molecular weight}}$$

$$\# \text{ moles} = \frac{105.99 \text{ g}}{105.99 \text{ g/mole}}$$

$$\# \text{ moles} = 1$$

or

grams required = (#moles required)(grams/mole)
grams required = (1 mole)(105.99 grams/mole)
grams required = 105.99 g

Step 3: Calculate the Molarity of the solution.

$$\text{Molarity} = \frac{\text{\# of moles}}{\text{volume of solvent}}$$

$$\text{Molarity} = \frac{1 \text{ mole}}{1 \text{ liter of water}}$$

Molarity = 1M

Every 105.99 grams of Na_2CO_3 in 1 L of water gives a 1M solution.

Normality

Step 2a: Calculate the equivalent weight.

$$\text{equivalent weight} = \frac{\text{molecular weight}}{\text{\# of positive charges}}$$

$$\text{equivalent weights} = \frac{105.99}{2}$$

equivalent weights = 53 grams

Step 2b: Calculate the number of equivalent weights.

$$\text{\# equivalent weights} = \frac{\text{total weight}}{\text{equivalent weight}}$$

$$\text{\# equivalent weights} = \frac{105.99 \text{ g}}{53 \text{ g/equivalent}}$$

\# equivalent weights = 2

or

grams required = (# equivalent weights)(grams/equivalent weight)
grams required = (2 equivalent weights)(53 g/equivalent)
grams required = 106 g

Step 3: Calculate Normality

$$\text{Normality} = \frac{\text{\# of equivalents}}{\text{volume of solvent}}$$

$$\text{Normality} = \frac{2 \text{ equivalents}}{1 \text{ liter of water}}$$

Normality = 2N

Every 105.99 g of Na_2CO_3 in 1 L of water gives a 2N solution. To make a 1N solution, cut the grams in half.

Laboratory Equipment

Identification, Handling and Cleaning

Objectives

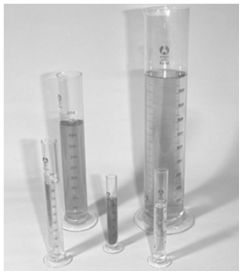
- Identify equipment commonly used in water treatment and wastewater laboratory
- Discuss accuracy and use of glassware
- Discuss how to maintain analytical equipment

Beakers

- Used for:
  - Mixing
  - Measuring approximate volumes
  - ~10% accuracy

Graduated Cylinders

- Accurate to ~1%
- Measures liquid volumes more accurately than beakers, but still not the most accurate
- Measure quicker



Volumetric Flasks

- Most accurate way to measure volume
- Disadvantage:
  - Only can measure one volume
  - Not used for storing or heating solutions

What Are Pipets?

- Pipets are glass or plastic tubes, usually open at both ends,which are used to transfer specific amounts of liquid from one container to another
- They are usually used for volumes between 1 and 100 milliliters

Types of Pipets

- Volumetric
- Measuring
  - Mohr
  - Serological

Volumetric Pipets

- Used to deliver a single specific volume of liquid, usually between 1 and 100 mL
- Shaped like rolling pins with a large belly, one blunt end, the neck, and one tapering end, the tip

Volumetric Pipets

- Used for accurate measurements, since it is designed to deliver only one volume and is calibrated at that volume
- Should be used when accuracy and reproducibility are crucial, because these can achieve accuracy to four significant figures

Specifications on a Volumetric Pipet

- When emptying a volumetric pipet, the liquid is allowed to drain out
  - It is <u>NOT</u> forced out
- After it is emptied, the small amount of liquid which remains in the tip should not be blown out
- Volumetric pipets are NOT blow-out pipets

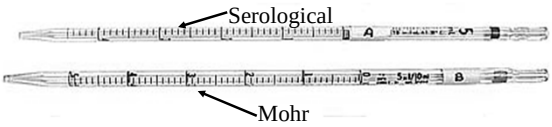
Measuring Pipets

- They are straight glass or plastic tubes with one tapering end
- Calibrated into small divisions so that various amounts of liquid can be measured with the same pipet
- Usually used to measure any amount between 0.1mL and 25.0mL
- They are not as accurate due to the fact that any imperfection in their internal diameter will have a greater effect on the volume delivered

Mohr and Serological Pipets

- Measuring pipets are divided into:
  - Mohr Pipets
    - Graduations on these always end before the tip
  - Serological Pipets
    - Graduation marks continue to the tip

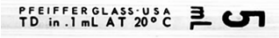
Examine pipets A and B.
Which is the serological and which is the Mohr?



Specifications on a Measuring Pipet

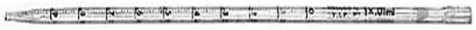
- Maximum volume of liquid that can be transferred
- Size of the divisions on the pipet
- Temperature at which calibrations were made
- If the pipet is a “to deliver”(TD) or “to contain”(TC) pipet.

5 mL in 1/10 mL TD 20°C



- Specifications on a pipet as shown above indicate that the pipet is calibrated in 1/10 mL divisions and will deliver up to 5.0 mL within published tolerance levels at 20°C

1 mL in 1/100 mL TD 20°C



- These specifications indicate that the pipet is calibrated in 1/100 mL divisions and it will deliver up to 1.00 mL within published tolerance levels at 20°C

Handling and Disposing of Pipets

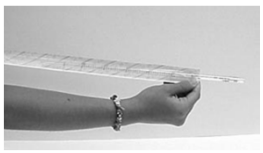
- Chipped and cracked pipets should be replaced as they are unsafe and may affect the accuracy of measurements
- NEVER mouth pipet
- Hold the pipet by the upper third of the tube and keep the tip from touching anything

Handling and Disposing of Pipets

- Dispose dirty pipets by placing in soapy water solution in a tray or pipet washer
- Place disposable pipets in a cardboard holder
- Do not leave pipets on counters or sinks

Handling Sterile Pipets

- When using sterile pipets, be sure to use proper sanitary techniques
- If you have a sterile package of disposable pipets, tear only a small corner of the package open and push one pipet out of this opening, then immediately close the package to prevent contamination



Handling Sterile Pipets

- If you are using sterile pipets in a pipet canister, place the canister on its side, slide off the cover, pull out one pipet and replace the cover immediately

Transferring a Precise Volume of Liquid

- A pipet bulb is used to draw liquid up into the pipet
- There are many types of pipet bulbs

Transferring a Precise Volume of Liquid

- You should observe the meniscus at eye-level
- Touch the tip of the pipet to the inside of the container when the meniscus is at the desired level

Transferring a Precise Volume of Liquid

- Squeeze bulb and touch it to the mouth of the pipet
- Place other end of the pipet in liquid to be transferred and slowly release pressure on bulb
- Draw liquid up past desired level, quickly replacing bulb with index finger

Transferring a Precise Volume of Liquid

- Let liquid drain until bottom of meniscus lines up with desired level on pipet
- Touch tip of pipet to inside of beaker to remove any adhering drops
- Transfer liquid to second beaker and touch tip to inside of beaker and let liquid drain out of pipet

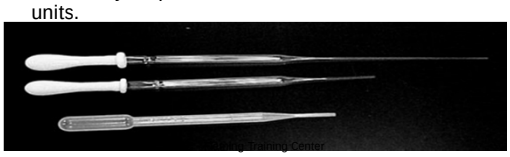
Other Pipet Bulbs

Other pipet bulbs that are often used include the Vadosa pipet filler, seen on the left, and the pipet Pumper, on the right

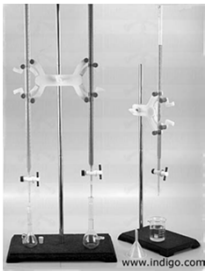
TDEC - Fleming Training Center 25

Other Pipet Types

- Transfer of uncalibrated volumes up to 2.5 mL can be accomplished using glass "transfer" or "Pasteur" pipets shown below. These may be sterilized before use.
- Roughly calibrated volumes of 1 and 2 mL can be transferred with the one piece plastic transfer pipets which may be purchased as sterile or non-sterile units.



Burettes and Titrations



- Burettes
  - Used for titrations
  - Treat like a Mohr pipet, do not let liquid completely drain out
  - Also, make sure to remove air bubble in tip before titrating

TDEC - Fleming Training Center 27

Flasks

- Distilling Flask

- Florence (Flat Bottom) Flask

TDEC - Fleming Training Center 28

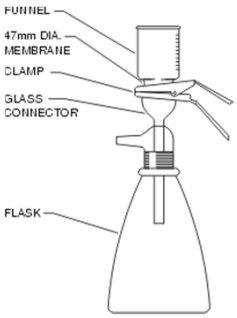
Flasks

- Erlenmeyer Flasks

- Filter Flask

TDEC - Fleming Training Center 29

Filter Apparatus



- Vacuum Pump

TDEC - Fleming Training Center 30

Bottles

- Dilution Bottle
- Sample Bottles

TDEC - Fleming Training Center 31

Bottles

- Reagent Bottle
- Weighing Bottles

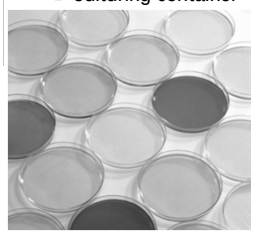
TDEC - Fleming Training Center 32

Funnels

- Separatory
- Buchner
- General

TDEC - Fleming Training Center

- Petri Dish
  - Culturing container
- Desiccators
  - Dust and moisture free



TDEC - Fleming Training Center

- Evaporating Dish
- Crucible

TDEC - Fleming Training Center 35

Centrifuge

- Used to separate materials of different density

TDEC - Fleming Training Center 36

Autoclave

- Pressure cooker used to sterilize glassware, bottles, membrane filter equip, culture media and contaminated material to be discarded.
- Standard temperature is set at121°C and 15 PSI

TDEC - Fleming Training Center 37

Refrigerators

- Sample storage should maintain between 1-5 °C
- Never store samples and chemicals together

Explosion proof

Walk-in cooler

TDEC - Fleming Training Center 38

Incubators

- Artificially heated container used for growing bacteria cultures
- Dry-Heat types hold temperatures to ± 0.5°C
- For E. coli and Total coliform = 35 ± 0.5°C
- Water Bath for fecals = 44.5 ± 0.2°C

TDEC - Fleming Training Center 39

Incubators

- For BOD incubation at 20 ± 1 °C
- Do not store chemical solutions and samples in same refrigerator

TDEC - Fleming Training Center 40

UV Sterilizer

- Use in Bac'T Lab to sterilize test equipment

TDEC - Fleming Training Center 41

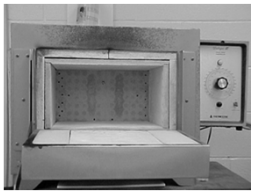
Drying Oven

Used more often in wastewater labs

For some solids testing set oven at 103-105°C

TDEC - Fleming Training Center 42

Muffle Furnace



- High temp oven used to ignite or burn solids.
- Usually operate at temps of 550°C.
- More often used in Wastewater lab work.

Fume Hood

- Can prevent serious accidents
- Use whenever heat is used in a test procedure
- Fumes vented out of lab
- Use when harmful smoke, gas, vapors, splashes or fumes are possible

Water Still

- Produces distilled water for lab tests and rinsing washed glassware
- Removes dissolved minerals, organic and inorganic nonvolatile compounds
- Does not sterilize

Heating and Stirring Samples

- Combo Heat/Stir Plate
  - Can be used to stir or heat and stir samples
  - Safer than heating with an open flame
- Gas Burner
  - Uses natural gas

Balances

- Top Loading
  - Weighs to the nearest 0.01 g
- Analytical
  - Precise to 0.0001 g

pH Meter

- Use buffer solutions to calibrate
- Store electrodes properly
- Calibrate daily
- Maintain records on daily calibrations

Spectrophotometer

- HACH DR 6000
  - Factory pre-set programs for lab chemical analysis
- Very versatile

TDEC - Fleming Training Center 49

Colorimeters

- Determine the concentration of many chemicals
- Most commonly used is chlorine type colorimeter
- Portable and battery powered

TDEC - Fleming Training Center 50

Amperometric Titrator

- Chlorine analysis
- Accurate and unaffected by sample color or turbidity
- Takes greater skill to use than DPD method with colorimetric devices

TDEC - Fleming Training Center 51

Turbidimeter

- Desk top and continuous on-line monitoring
- Position away from direct sunlight and have extra light bulb on hand
- Ensure sample bottles maintained; no scratches; acid clean if necessary

TDEC - Fleming Training Center 52

Chemical Storage

- Do not store volatile chemicals together
- Have separate storage cabinets for acids and bases/caustics

TDEC - Fleming Training Center 53

Flammable Cabinet

- Flammable chemicals should be kept in a flammable cabinet.

TDEC - Fleming Training Center 54

Safety Equipment

PPE (Personal Protective Equipment):

Goggles

Gloves

Aprons

Wear safety clothing.

Eye Wash and Shower

Cleaning Glassware

- Just because it looks clean does not mean residues are not left behind
- Results need to be accurate to use data for process control and/or reporting to the State
- Detergents, such as Alconox, may be sufficient
  - Should be phosphate-free

Cleaning Glassware

- Residues of minerals and other substances can build up on glassware, causing erroneous test results

Steps for Washing

- Clean glassware using laboratory detergent (phosphate-free)
- Rinse with tap water
- Rinse at least three times with distilled water
- Let air dry

Steps for Acid-Washing

- Clean glassware using laboratory detergent (phosphate-free)
- Rinse with tap water
- Rinse with 1:1 hydrochloric acid or nitric acid
  - 1:1 means equal parts distilled water and acid
- Rinse well with distilled water
- Let air dry

Note: always use gloves and goggles when handling acids

Before Lab Work, Get to Know:

- Hazards of materials and their prescribed safety procedures
- Learn the lay-out of the building
  - location of emergency exits
  - emergency exit routes
  - emergency telephones
  - emergency ventilation system
  - fire-fighting equipment and how it works
  - emergency shower
  - first aid equipment

TDEC - Fleming Training Center 2

Communication

- Emergency 911 number sticker on telephone set
- Emergency notification procedures, contacts, and phone numbers are posted
- Emergency procedures and Updated Fire Escape Route posted

TDEC - Fleming Training Center

General Preparedness

- Emergency ventilation switch (in laboratory) unobstructed and function properly
- Exit signs readily visible/ illuminated
- Hazardous materials not stored along exit route and exit route free from obstruction
- Two well-separated exits, doors swing outward for chemistry laboratories or other high hazardous laboratories

TDEC - Fleming Training Center 4

Chemical Spill

- Chemical spill kit, cleanup procedures available and training provided if considered necessary by departmental plan
- Safety showers and eyewashes (inspected monthly) easily accessible/ unobstructed

TDEC - Fleming Training Center 5

First Aid

- First aid box easily accessible and adequately stocked
- First-aider name posted on first aid box
- First aid box contain a copy of first aid instructions
- Medication items not stored in first aid box

TDEC - Fleming Training Center 6

First Aid

- When a major injury occurs:
  - Call the emergency contact number, e.g. 911.
  - Keep the victim warm, lying down, and quiet until medical assistance arrives.
  - It is better NOT to move the injured person unless he or she is immediately threatened by further injury.

TDEC - Fleming Training Center 7

First Aid

- While waiting for the response personnel to arrive:
  - Treat acid and alkali burns with running water for 20-30 minutes
    - Use emergency eyewash/shower if necessary.
    - Do not attempt to neutralize.
    - Take care not to contaminate yourself.
  - Irrigate burned (heat or cryogenic) areas with cold water.

TDEC - Fleming Training Center 8

First Aid

- While waiting for the response personnel to arrive:
  - Remove contact lenses, if present
    - Use eyewash for 15 minutes to cleanse eye after chemical splash.
  - Treat major bleeding with direct compression of the wound using a clean cloth.
  - Expose anyone who has inhaled toxic materials to fresh air.

TDEC - Fleming Training Center 9

Safety Data Sheets

- SDS
- Keep on file for all chemicals purchased
  - According to the Americans with Disabilities Act of 1990, SDS's should be kept for a minimum of 30 years
- Includes all information shown on a chemical label and more

TDEC - Fleming Training Center 10

Safety Data Sheet

- OSHA moving from HCS (Hazard Communication Standard) to GHS (Globally Harmonized System)
- Revised criteria for chemical hazard classification, labeling & new format for Safety Data Sheets (SDS)
- Final rule effective May 25, 2012 but compliance dates are phased in:
  - Complete training on new label formats: 12/1/13
  - Comply with label and SDS requirements: 6/1/15
  - Update Hazcom programs: 6/1/16

TDEC - Fleming Training Center 11

TDEC - Fleming Training Center

Minimum Info for SDS

- Product identification
- Hazard Identification
- Composition/info on ingredients
- First-aid measures
- Fire-fighting measures
- Accidental release measures
- Handling and storage
- Exposure controls
- Physical/chemical properties
- Stability & reactivity
- Toxicological information
- Ecological information*
- Disposal considerations*
- Transport information*
- Regulatory information*
- Other information (including date of SDS or last revision)*

* Non mandatory

12

OSHA Pictograms

TDEC - Fleming Training Center

GHS Degree of Hazard

- 1→ extreme
- 2 → serious
- 3 → moderate
- 4→ minimal

TDEC - Fleming Training Center 14

NFPA

- National Fire Protection Association
- Chemical hazard label
  - Color coded
  - Numerical system
    - Health
    - Flammability
    - Reactivity
  - Special precautions
- Labels are required on all chemicals in the lab

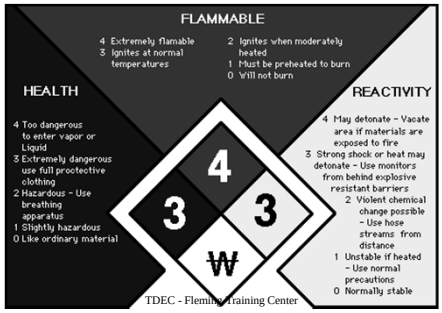
TDEC - Fleming Training Center 15

Degrees of Hazard

- Each of the colored areas has a number in it regarding the degree of hazard
  - 4 → extreme
  - 3 → serious
  - 2 → moderate
  - 1 → slight
  - 0 → minimal

TDEC - Fleming Training Center 16

Chemical Label



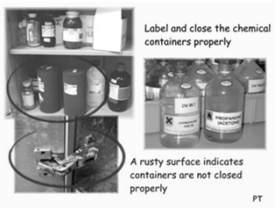
TDEC - Fleming Training Center 17

Special

- W
  - Water reactive
- Ox
  - Oxidizing agent

TDEC - Fleming Training Center 18

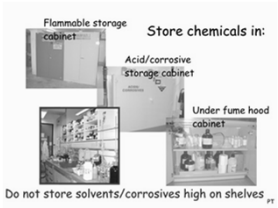
Chemical Safety - Storage



- Current chemical inventory available
- No expired chemicals.
  - Disposed of out-dated chemicals
- Chemical containers properly labeled, in good condition and closed properly
- Only compatible chemicals are stored together
  - Everything *not* stored in alphabetical order

Chemical Safety - Storage

- Secondary containment for stored chemicals as necessary.
  - Polyethylene trays for separate storage of acids and bases
- Chemicals stored at safe levels, in cabinets or on stable shelving (but not on high levels)



Chemical Safety - Flammables

- Stored in flammable cabinet and/or explosion-proof or flammable storage refrigerator
- Stored away from sources of heat and ignition
- Not stored along path of egress or in aisle space

Lab Hygiene

- Food and drink are not to be stored or prepared in laboratories or chemical storerooms
- Use appropriate personal protective equipment and wash your hands regularly when working with chemical reagents, especially before meals or snacks.
- Smoking in laboratories is prohibited.

Lab Hygiene

- Loose sleeves are a hazard and should not be worn in the lab.
- If you have long hair, ensure that it is properly tied back.
- Wearing of contact lenses in the lab is strongly discouraged.
  - If it is unavoidable, advise your supervisor and co-workers so that this information is known in the event of a chemical splash in the eyes.

Personal Practices

- No inappropriate clothing and shoes (shorts, sandals, slippers, etc.)
- Gloves removed before handling telephone, door handle or leaving laboratory
- No pipeting by mouth

Personal Practices

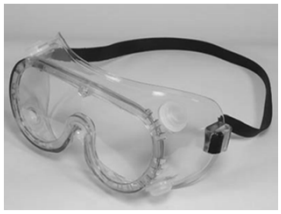
- Lab coats and safety glasses/ goggles worn by all where necessary
- Proper gloves are used as needed
- Other personal protective equipment used properly as needed

Safety Glasses

- Unbreakable lenses of plastic or tempered glass
- For light-to-moderate work
- Can be prescription glasses
- Do not interfere with contact lenses

Goggles

- Work with significant risk of splash of chemicals or projectiles
- Can be worn over prescription glasses



Face Shield

- Work with significant risk of splash on face or possible explosion
- Face shield protects face adequately but not eyes
  - Should be worn with safety glasses and/or goggles to protect eyes

Pregnancy

- Women who are pregnant should discuss their work assignments with their supervisors to seek alternate work assignments if the potential for exposure to teratogens exist
  - Teratogens are reproductive toxins that may cause damage to the fetus
  - THM Plus method by Hach for determining Trihalomethanes deals with chloroform, a teratogen

Fume Hood

- All work generating toxic/hazardous vapor, fume, or aerosol performed in hood
- Front sash at appropriate level when hood is in use/ not in use
- Storage within the hood minimized and containers kept sealed

Fume Hood

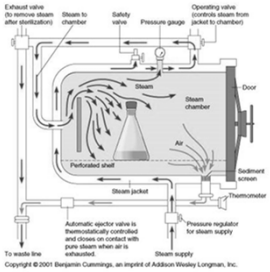
- Verify that the fume cupboard is working properly.
- Locate work at least 6 inches inside the hood.
- Do not block the face of the hood, e.g. with shielding or large equipment.
- Do not block the space between tapered metal front lip and the work surface.
- Do not block rear exhaust slot. Place bulky items to rear and sides.
- Secure papers and other light weight materials to prevent their entrainment in the exhaust.

Autoclave

- Because an autoclave uses saturated steam under high pressure to achieve sterilizing temperatures, proper use is important to ensure operator safety.

Autoclave

- Racks of test tubes, stacks of culture media and trays of used needles awaiting sterilization prior to disposal were splattered across the room by the tremendous concussion.
- Metal shrapnel penetrated the walls.
- A few minutes sooner or later and those projectiles could have easily struck a lab worker.
- Luckily, the room was unoccupied at the critical moment.



Autoclave

- Prevent injuries when using the autoclave by observing the following rules:
  - Wear heat resistant gloves, eye protection, closed toed shoes and a lab coat, especially when unloading the autoclave.
  - Prevent steam burns and shattered glassware by making sure that the pressure in the autoclave chamber is near zero before opening the door at the end of a cycle. Slowly crack open the autoclave door and allow the steam to escape gradually.

Autoclave

- Prevent injuries when using the autoclave by observing the following rules:
  - Allow items to cool for 10 minutes before removing them from the autoclave.
  - Never put sealed containers in an autoclave. They can explode. Large bottles with narrow necks may also explode if filled too full of liquid.
  - Never put solvents, volatile or corrosive chemicals (such as phenol, chloroform, bleach, etc.), or radioactive materials in an autoclave.

Lab Work Area

- The work bench is to be kept clean at all times, and free from chemicals and apparatus which are not required.
- Before starting an experiment, make sure you are familiar with all the procedures and the potential hazards of the starting materials and products.
  - Determine the appropriate safeguards and remedies.
  - Know the procedures for emergency shut off as well as the person and phone numbers to contact in case of emergency.
  - If anything unexpected occurs during your experiment, or if you are in any doubt, consult your supervisor immediately.

TDEC - Fleming Training Center 37

Handling Glassware

- Examine all glassware before use.
  - Discard any broken glass apparatus in the appropriate sharps container.
- Never store damaged glassware in cupboards.
  - Damaged glassware should either be sent for repair properly or disposed in a separate labeled container for sharps disposal.
- Use gloves when sweeping up broken glass, do not use bare hands.
  - Pick up fine glass particles with wet paper toweling.

TDEC - Fleming Training Center 38

Handling Glassware

- Cut ends of glass rods and tubing should always be fire-polished before use.
- Use a cloth for protection when inserting glass tubing, rods or thermometers into bungs or tubing
  - Use a lubricant or water where necessary.

TDEC - Fleming Training Center 39

Chemical Spills

- Small spills (generally less than 100 mL) can usually be cleaned up safely by the employees involved.
- The hazardous properties of the material must be considered when deciding whether it is a “small” spill or not, and therefore whether unassisted clean-up should be attempted.
- Employees must be trained in advance to handle cleanup of even small spills

TDEC - Fleming Training Center 40

Cleaning Glassware

We often overlook the importance of clean glassware in the lab. We think if it looks clean, it must be clean. But there may be residues on the glassware that can affect our results. Since we use those results for both running the plant and reporting water quality to the state, it is important that those results be as accurate as possible.

For many purposes in the water treatment lab, washing in a detergent such as Alconox is sufficient. However, some analyses and some glassware require special cleaning procedures to ensure removal of all residues. Residues of minerals and other substances can build up on glassware, causing erroneous test results. Always follow the recommendations for cleaning glassware and sample containers, and always use the suggested type of sample container.

The following is a partial list of special cleaning procedures for laboratory glassware used for chemical analyses:

Sample containers:

When collecting samples for metals analyses, special cleaning of the containers is necessary to prevent residues from affecting results. Clean the sample bottles by thoroughly washing with laboratory soap (preferably phosphate-free), followed by an acid wash and multiple rinses with distilled or deionized water. Do not use glass sample bottles for metals analysis.

Sample cells and cuvets:

Wash thoroughly using laboratory soap (preferably phosphate-free), followed by an acid wash and multiple rinses with distilled or deionized water. Allow to air dry or wipe with a Kim-wipe, don't use paper towels.

Flasks, beakers, etc used for metals analysis:

Wash thoroughly using laboratory soap (preferably phosphate-free), followed by an acid wash and multiple rinses with distilled or deionized water.

Pipets:

Soak overnight in a solution of Alconox. Rinse thoroughly using a pipet washer.

Procedure for Acid Washing Glassware

If acid washing is required, follow these steps:

- Clean the glassware using laboratory detergent (phosphate-free)
- Rinse with tap water
- Rinse with 1:1 hydrochloric acid solution or 1:1 nitric acid solution
- Rinse well with distilled water
- Air dry

❖ Note: always use gloves and safety goggles when handling acids

821 William D. Jones Blvd, Fayetteville TN 37334
888-542-8561 Fax - 931-438-2673
www.adc-chem.com

Material Safety Data Sheet

This Material Safety Data Sheet conforms to the requirements of ANSI z400.1.
This MSDS complies with 29 CFR 1910.1200 (Hazard Communication Standard)
Read this MSDS before handling & disposing of this product.

Section 1: Material Identification and Company Identification

Product Identity: **Chlorine**
Distributed By: American Development Corporation
Address: 821 William D. Jones Blvd.
City/State: Fayetteville TN 37334
Phone: 888-542-8561
Chem-Tel 800-255-3924

Section 2: Hazardous Ingredients

Component	CAS NO.	Concentration	Hazard
Chlorine	7782-50-5	99%	Corrosive

Section 3: Hazards Identification

Primary routes of exposure: Inhalation, skin or eye contact,

Potential Health Effects:

Eyes: Can cause severe burns and permanent damage to eyes.

Skin: Corrosive to the skin and all living tissue.

Ingestion: Unlikely. Gas at room temperature

Inhalation: Corrosive and irritating to the upper and lower respiratory tracts

The information appearing in this document is based upon data obtained from the product manufacturer and/or supplier. While the information is believed to be pertinent and accurate, no warranty expressed or implied is given to it's accuracy. This MSDS is to be used as a guideline for safe work practices and emergency response.

Section 4: First Aid Measures

Eye Contact: Flush with copious quantities of water. Part eyelids to assure complete flushing. Continue for 15 minutes. Seek immediate medical attention.

Skin Contact: Remove contaminated clothing. Flush affected area with copious quantities of water. Seek medical attention.

Ingestion: Not likely

Inhalation: Seek immediate medical attention. Rescue personal should wear SCBA. Medical treatment should be symptomatic and supportive.

Section 5: Fire Fighting Measures:

Extinguishing Media: Non-flammable. Use media for surrounding materials.

Hazardous combustion products: None
Sensitivity to mechanical shock: None
Sensitivity to static discharge: None

NFPA Rating:	
Health	3
Fire	0
Reactivity	0
Hazard	Corrosive

Section 6: Accidental Release Measures:

Evacuate all personal from affected area.
Only properly trained personnel equipped with protective clothing and respiratory protection should locate and stop release.

The information appearing in this document is based upon data obtained from the product manufacturer and/or supplier. While the information is believed to be pertinent and accurate, no warranty expressed or implied is given to it's accuracy. This MSDS is to be used as a guideline for safe work practices and emergency response.

Section 7: Handling and Storage:

Secure cylinder to protect from falling.
Store in well ventilated areas.
Keep protective cap on cylinder when not in use.

Section 8: Exposure Controls/Personal Protection

Control Measures: Provide adequate general and local exhaust ventilation to maintain concentration well below exposure limits.

Recommended Personal Protective Equipment:

Respirator: In case of leakage, use an approved self-contained breathing apparatus.

Eyes: Safety glasses or goggles.

Gloves: Impervious, resistant gloves

Clothing: Impervious coveralls, boots and/or other resistant clothing.

Other protective measures: Emergency eye wash and safety showers for first aid should be available near work area.

Section 9: Physical Properties

Appearance:	Yellow or green	**Specific Gravity**	Gas
Physical State:	Gas	**Boiling Point:**	-31º F
Odor:	Suffocating pungent odor	**Freezing Point:**	- 150º F
Odor Threshold:	0.08 - 0.4 ppm	**Flash Point**	n/a

The information appearing in this document is based upon data obtained from the product manufacturer and/or supplier. While the information is believed to be pertinent and accurate, no warranty expressed or implied is given to it's accuracy. This MSDS is to be used as a guideline for safe work practices and emergency response.

Section 10: Stability and Reactivity

Stability: Stable under normal conditions
Polymerization: Will not occur
Conditions to avoid: Storage in poorly ventilated areas. Storage near a heat source.

Incompatible materials: Chlorine reacts with reducing agents and combustibles. Materials such as acetylene, turpentine, hydrocarbons, ammonia, ether, must be kept away.
Hazardous decomposition products: Chlorine will react with steam and water to give HCl fumes.

Section 11: Toxicological Information

Medical conditions aggravated by exposure:

Heart conditions
Asthma

Section 12: Ecological Information

Chlorine is harmful at uncontrolled quantities to aquatic life. Keep out of water. Releases as a gas may damage green vegatation and may be hazardous to birds and mammals.

Section 13: Disposal Considerations

Subject to disposal regulations: U.S. EPA 40 CFR 262.
Hazardous Waste number D001.
Dispose in accordance with all applicable regulations.

The information appearing in this document is based upon data obtained from the product manufacturer and/or supplier. While the information is believed to be pertinent and accurate, no warranty expressed or implied is given to it's accuracy. This MSDS is to be used as a guideline for safe work practices and emergency response.

Section 14: Transportation Information

D.O.T. Proper Shipping Name: Chlorine

D.O.T. Hazard Class: 2.3 (poison)
Hazard zone B
UN number: 1017
D.O.T. Labels: **Primary:** Poison Gas **Subsidiary:** Corrosive
D.O.T. Placards: Poison Gas

2004 Emergency Response Guidebook Number 124

Section 15: Regulatory Information

TSCA Inventory Status:	Yes
SARA - 313 Listed Chemicals:	Yes
CERCLA:	Yes
Reportable Quantity:	10 lbs

Section 16: Other Information

CERCLA Comprehensive Environmental Response, Compensation and Liability Act of 1980
IARC International Agency for Research on Cancer
MSHA Mine Safety and Health Administration
NIOSH National Institute for Occupational Safety and Health
NTP National Toxicology Program
OSHA Occupational Safety and Health Administration
PEL-C OSHA Permissible Exposure Limit-OSHA Ceiling Exposure Limit
RCRA Resource Conservation and Recovery Act
SARA Superfund Amendments and Reauthorization Act of 1986
TLV-TWA Threshold Limit Value - Time Weighted Average
TSCA Toxic Substances Control Act

The information appearing in this document is based upon data obtained from the product manufacturer and/or supplier. While the information is believed to be pertinent and accurate, no warranty expressed or implied is given to it's accuracy. This MSDS is to be used as a guideline for safe work practices and emergency response.

1. Identification

Product identifier **CHLORINE**

Other means of identification Not available.

Recommended use Chlorinating and oxidizing agent, Water treatment chemicals, pharmaceutical, Synthesis, Disinfectants and general biocidal products, Plastics

Recommended restrictions None known.

Manufacturer / Importer / Supplier / Distributor information

Company name Olin Chlor Alkali Products
Address 490 Stuart Road, NE
Cleveland, TN 37312

Company name Pioneer Americas, LLC (d/b/a Olin Chlor Alkali Products)
Address 490 Stuart Road, NE
Cleveland, TN 37312

Company name Olin Canada ULC (d/b/a Olin Chlor Alkali Products)
Address 2020 University, Suite 2190
Montreal, Quebec H3A 2A5

General Information
Telephone (888) 658-MSDS (6737)
Website olinchloralkali.com
Contact person ORC MSDS Control Group
Emergency phone number CHEMTREC
US: 1-800-424-9300 Canada: 1-800-567-7455

2. Hazard(s) identification

Physical hazards	Oxidizing gases	Category 1
	Gases under pressure	Liquefied gas
Health hazards	Acute toxicity, inhalation	Category 2
	Skin corrosion/irritation	Category 1
	Serious eye damage/eye irritation	Category 1
	Specific target organ toxicity, single exposure	Category 3 respiratory tract irritation
	Specific target organ toxicity, repeated exposure	Category 1 (Lung)

OSHA defined hazards Not classified.

Label elements

Signal word Danger

Hazard statement May cause or intensify fire; oxidizer. Contains gas under pressure; may explode if heated. Causes severe skin burns and eye damage. Fatal if inhaled. May cause respiratory irritation. Causes damage to organs (lung) through prolonged or repeated exposure.

Precautionary statement

Prevention Keep/Store away from clothing//combustible materials. Keep reduction valves/valves and fittings free from oil and grease. Do not breathe gas. Use only outdoors or in a well-ventilated area. Do not eat, drink or smoke when using this product. Wear protective gloves/protective clothing/eye protection/face protection. Wear respiratory protection. Wash thoroughly after handling.

Response In case of fire: Stop leak if safe to do so. Get medical advice/attention if you feel unwell. If inhaled: Remove person to fresh air and keep comfortable for breathing. If swallowed: Rinse mouth. Do NOT induce vomiting. If on skin (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower. If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a poison center/doctor. Specific treatment is urgent. Wash contaminated clothing before re-use.

Storage Store in a well-ventilated place. Keep container tightly closed. Store locked up.

Disposal Dispose of contents/container in accordance with local/regional/national/international regulations.

Hazard(s) not otherwise classified (HNOC) Not classified.

Environmental hazards Hazardous to the aquatic environment, acute hazard Category 1

Supplemental information

Hazard symbol

Hazard statement Very toxic to aquatic life.

Precautionary statement

Prevention Avoid release to the environment.

Response Collect spillage.

3. Composition/information on ingredients

Substances

Chemical name	Common name and synonyms	CAS number	%
CHLORINE		7782-50-5	98-100

4. First-aid measures

Inhalation Move to fresh air. If breathing is difficult, give oxygen. If breathing stops, provide artificial respiration. Get medical attention immediately!

Skin contact Immediately flush with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention immediately! Chemical burns must be treated by a physician. Wash contaminated clothing before reuse.

Eye contact Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Get medical attention immediately.

Ingestion Ingestion is not a typical route of exposure for gases or liquefied gases. Contact with liquid form may cause frostbite. Immediately call a poison control center or doctor for treatment advice.

Most important symptoms/effects, acute and delayed Contact with this material will cause burns to the skin, eyes and mucous membranes. Unconsciousness. Cough, shortness of breath, headache, nausea, vomiting. May cause lung damage.

Indication of immediate medical attention and special treatment needed For liquid contact, treat the affected person for frostbite if necessary. If the product is ingested, probable mucosal damage may contraindicate the use of gastric lavage. Treat the affected person appropriately. Provide general supportive measures and treat symptomatically. Symptoms may be delayed.

General information Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves.

5. Fire-fighting measures

Suitable extinguishing media Use fire-extinguishing media appropriate for surrounding materials.

Unsuitable extinguishing media Direct water spray. Direct water spray jet.

Specific hazards arising from the chemical May cause fire or explosion; strong oxidizer. Contents under pressure. Pressurized container may explode when exposed to heat or flame. Contact with reactive metals e.g., aluminum, zinc and tin may result in the generation of flammable hydrogen gas. Water used for fire extinguishing, which has been in contact with the product, may be corrosive. Water spray on active leak may promote accelerated corrosion of container and accelerate rate of leakage.

Special protective equipment and precautions for firefighters Wear full protective clothing, including helmet, self-contained positive pressure or pressure demand breathing apparatus, protective clothing and face mask. Additional protective clothing must be worn to prevent personal contact with this material. Those items include but are not limited to: boots gloves, hard hat, splash-proof goggles, full face shield and impervious clothing, i.e. chemically impermeable suit. Compatible materials for response to this material are neoprene and butyl rubber.

Fire-fighting equipment/instructions In case of fire and/or explosion do not breathe fumes. Remove pressurized gas cylinders from the immediate vicinity. Cylinders can burst violently when heated, due to excess pressure build-up. Cool containers / tanks with water spray. Evacuate area and fight fire remotely due to the risk of explosion.

6. Accidental release measures

Personal precautions, protective equipment and emergency procedures

Immediately evacuate personnel to safe areas. Many gases are heavier than air and will spread along ground and collect in low or confined areas (sewers, basements, tanks). Keep people away from and upwind of spill/leak. Keep out of low areas. Keep unnecessary personnel away. Ventilate closed spaces before entering them. Wear appropriate protective equipment and clothing during clean-up. Local authorities should be advised if significant spillages cannot be contained.

For response to Chlorine gas it is recommended to use as a minimum level "B " protection that is compatible to Chlorine. For Liquid spills it is recommended to utilize as a minimum enhanced level "B" (Enhanced Level "B" is the addition of a splash hood). Do not touch damaged containers or spilled material unless wearing appropriate protective clothing. Responders can reference Chlorine Institute pamphlet #65 on PPE.

Methods and materials for containment and cleaning up

Extinguish all flames in the vicinity. Keep combustibles (wood, paper, oil, etc.) away from spilled material. Ventilate well, stop flow of gas or liquid if possible. If possible, turn leaking containers so that gas escapes rather than liquid. Dike far ahead of spill for later disposal. Isolate area until gas has dispersed. Neutralize spilled material with crushed limestone, soda ash or lime. Collect spillage.

Never return spills to original containers for re-use. Clean up in accordance with all applicable regulations. For waste disposal, see section 13 of the MSDS.

Environmental precautions

Avoid discharge into drains, water courses or onto the ground. Contact local authorities in case of spillage to drain/aquatic environment.

7. Handling and storage

Precautions for safe handling

Avoid heat, sparks, open flames and other ignition sources. Keep away from clothing and other combustible materials. Use only chlorine-compatible lubricants. Do not use greases and oils. Do not breathe gas. Do not get in eyes, on skin, on clothing. Use in a sealed system and/or a well-ventilated area. Wear appropriate personal protective equipment. Observe good industrial hygiene practices. Avoid release to the environment.

Conditions for safe storage, including any incompatibilities

Contents under pressure. Keep away from heat, sparks and open flame. Secure cylinders in an upright position at all times, close all valves when not in use. Store in a well-ventilated place. Store away from incompatible materials.

Store at temperatures not exceeding 55°C/131°F. For the above specified temperature the system pressure is 225 psig (1551kPa).

8. Exposure controls/personal protection

Occupational exposure limits

US. OSHA Table Z-1 Limits for Air Contaminants (29 CFR 1910.1000)

Material	Type	Value
CHLORINE (CAS 7782-50-5)	Ceiling	3 mg/m3
		1 ppm

US. ACGIH Threshold Limit Values

Material	Type	Value
CHLORINE (CAS 7782-50-5)	STEL	1 ppm
	TWA	0.5 ppm

Biological limit values

No biological exposure limits noted for the ingredient(s).

Exposure guidelines

Check State and local regulations for other applicable exposure limits.

Appropriate engineering controls

Should be handled in closed systems, if possible. Provide adequate ventilation. Observe Occupational Exposure Limits and minimize the risk of inhalation. Eye wash facilities and emergency shower must be available when handling this product.

Individual protection measures, such as personal protective equipment

Eye/face protection

Wear goggles/face shield. Gas-proof goggles are recommended.

Skin protection

Hand protection

Wear cold insulating gloves. Suitable gloves can be recommended by the glove supplier.

Other

Wear appropriate chemical resistant clothing.

Respiratory protection

If engineering controls do not maintain airborne concentrations below recommended exposure limits (where applicable) or to an acceptable level (in countries where exposure limits have not been established), an approved respirator must be worn.

Thermal hazards

Wear appropriate thermal protective clothing, when necessary.

General hygiene considerations	Do not eat, drink or smoke when using the product. Always observe good personal hygiene measures, such as washing after handling the material and before eating, drinking, and/or smoking. Routinely wash work clothing and protective equipment to remove contaminants.

9. Physical and chemical properties

Appearance	Compressed liquefied gas.
Physical state	Gas Compressed, liquified.
Form	Liquefied gas.
Color	Yellow green.
Odor	Pungent.
Odor threshold	1.7 ppm
pH	Not available.
Melting point/freezing point	-149.8 °F (-101 °C) (1 atm)
Initial boiling point and boiling range	-29.27 °F (-34.04 °C) (1 atm)
Flash point	Not applicable.
Evaporation rate	Not available.
Flammability (solid, gas)	Not available.
Upper/lower flammability or explosive limits	
Flammability limit - lower (%)	Not applicable.
Flammability limit - lower (%) temperature	Not applicable.
Flammability limit - upper (%)	Not applicable.
Flammability limit - upper (%) temperature	Not applicable.
Explosive limit - lower (%)	Not available.
Explosive limit - upper (%)	Not available.
Vapor pressure	113 psia (25°C/77°F) 779 kPa (25 °C/77 °F) 4800 mm Hg (25°C/77°F)
Vapor density	2.5
Relative density	Not available.
Solubility(ies)	0.73 g/100g H20 (20°C/68°F) (760 mm Hg)
Partition coefficient (n-octanol/water)	Not available.
Auto-ignition temperature	Not available.
Decomposition temperature	Not available.
Viscosity	Not available.
Other information	
Bulk density	88.76 lb/ft³ 59.8 °F (15.6 °C)
Density	0.76 lb/ft³ 32 °F (0 °C) 53.51 psia
Heat of vaporization	123.9 BTU/lb
Molecular formula	Cl2
Molecular weight	70.906 g/mol

10. Stability and reactivity

Reactivity	Contact with combustible material may cause fire.
Chemical stability	Stable under normal temperature conditions and recommended use.
Possibility of hazardous reactions	Hazardous polymerization does not occur.

Conditions to avoid	Avoid heat, sparks, open flames and other ignition sources. Titanium will react vigorously, resulting in spontaneous ignition, when contacted by Dry Chlorine. Combustion will be supported in carbon steel systems and equipment containing a Chlorine environment at temperatures greater than 480 °F (248.9 °C). Properly purge systems and equipment PRIOR to conducting Hot Work.
Incompatible materials	Reducing agents. Organic material. Alkalis.
Hazardous decomposition products	Hydrogen chloride. Hypochlorous acid.

11. Toxicological information

Information on likely routes of exposure

Ingestion	Causes digestive tract burns.
Inhalation	Fatal if inhaled. Irritating to respiratory system.
Skin contact	Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling.
Eye contact	Contact with liquefied gas can cause damage (frostbite) due to rapid evaporative cooling. Can cause blurred vision, redness, pain, severe tissue burns and eye damage.
Symptoms related to the physical, chemical and toxicological characteristics	Contact with this material will cause burns to the skin, eyes and mucous membranes. Cough, shortness of breath, headache, nausea, vomiting. May cause lung damage. Unconsciousness.

Information on toxicological effects

Acute toxicity Fatal if inhaled.
Irritation Threshold: approximately 0.5 ppm
Immediately Dangerous to Life or Health: 10.0 ppm.

Product	Species	Test Results
CHLORINE (CAS 7782-50-5)		
Acute		
Inhalation		
LC50	Rat	293 ppm, 1 hr

Skin corrosion/irritation	Causes severe skin burns.
Serious eye damage/eye irritation	Causes serious eye damage.
Respiratory sensitization	No data available.
Skin sensitization	No data available.
Germ cell mutagenicity	No data available to indicate product or any components present at greater than 0.1% are mutagenic or genotoxic.
Carcinogenicity	This product is not considered to be a carcinogen by IARC, ACGIH, NTP, or OSHA.
Reproductive toxicity	No data available.
Specific target organ toxicity - single exposure	Not available.
Specific target organ toxicity - repeated exposure	Causes damage to organs (lungs) through prolonged or repeated exposure.
Aspiration hazard	Due to the physical form of the product it is not an aspiration hazard.
Chronic effects	Prolonged exposure may cause chronic effects.
Further information	Be aware that symptoms of lung edema (shortness of breath) may develop up to 24 hours after exposure.

12. Ecological information

Ecotoxicity Very toxic to aquatic life with long lasting effects.

Product		Species	Test Results
CHLORINE (CAS 7782-50-5)			
Aquatic			
Crustacea	LC50	Pacific oyster (Crassostrea gigas)	637.5 mg/l, 1 hours
		Water flea (Daphnia magna)	0.017 mg/l, 46 hours
Fish	LC50	Bluegill (Lepomis macrochirus)	0.44 mg/l, 96 hours
		Bullhead, catfish (Ictalurus sp.)	0.07 mg/l, 96 hours
		Yellow perch (Perca flavescens)	0.88 mg/l, 1 hours

Persistence and degradability	No data available.
Bioaccumulative potential	Will not bio-accumulate.

Mobility in soil	The Gas will disperse in the air. This product is miscible in water.
Other adverse effects	No data available.

13. Disposal considerations

Disposal instructions	Return the empty cylinder to the supplier. Disposal recommendations are based on material as supplied. Disposal must be in accordance with current applicable laws and regulations, and material characteristics at time of disposal.
Local disposal regulations	Dispose in accordance with all applicable regulations.
Hazardous waste code	D002: Waste Corrosive material [pH <=2 or =>12.5, or corrosive to steel]
Waste from residues / unused products	Dispose of in accordance with local regulations. Empty containers or liners may retain some product residues. This material and its container must be disposed of in a safe manner (see: Disposal instructions). Avoid discharge into water courses or onto the ground.
Contaminated packaging	Since emptied cylinders may retain product residue, follow label warnings even after cylinder is emptied.

14. Transport information

DOT

UN number	UN1017
UN proper shipping name	Chlorine
Transport hazard class(es)	2.3
Subsidiary class(es)	5.1, 8
Packing group	Not available.
Environmental hazards	
Marine pollutant	Yes
Special precautions for user	Read safety instructions, SDS and emergency procedures before handling.
Special provisions	2, B9, B14, N86, T50, TP19
Packaging exceptions	None
Packaging non bulk	304
Packaging bulk	314, 315

IATA

UN number	UN1017
UN proper shipping name	Chlorine
Transport hazard class(es)	2.3
Subsidiary class(es)	5.1, 8
Packaging group	Not available.
Environmental hazards	No
Labels required	Not available.
ERG Code	2CP
Special precautions for user	Read safety instructions, SDS and emergency procedures before handling.

IMDG

UN number	UN1017
UN proper shipping name	CHLORINE
Transport hazard class(es)	2.3
Subsidiary class(es)	5.1, 8
Packaging group	Not available.
Environmental hazards	
Marine pollutant	Yes
Labels required	Not available.
EmS	F-C, S-U
Special precautions for user	Read safety instructions, SDS and emergency procedures before handling.

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code	Not applicable.

15. Regulatory information

US federal regulations This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200.

TSCA Section 12(b) Export Notification (40 CFR 707, Subpt. D)

Not regulated.

US. OSHA Specifically Regulated Substances (29 CFR 1910.1001-1050)

Not listed.

CERCLA Hazardous Substance List (40 CFR 302.4)

CHLORINE (CAS 7782-50-5) LISTED

Superfund Amendments and Reauthorization Act of 1986 (SARA)

Hazard categories	Immediate Hazard - Yes Delayed Hazard - Yes Fire Hazard - No Pressure Hazard - Yes Reactivity Hazard - Yes
SARA 302 Extremely hazardous substance	Yes
SARA 311/312 Hazardous chemical	Yes

SARA 313 (TRI reporting)

Chemical name	CAS number	% by wt.
CHLORINE	7782-50-5	98-100

Other federal regulations

Clean Air Act (CAA) Section 112 Hazardous Air Pollutants (HAPs) List

CHLORINE (CAS 7782-50-5)

Clean Air Act (CAA) Section 112(r) Accidental Release Prevention (40 CFR 68.130)

CHLORINE (CAS 7782-50-5)

Clean Water Act (CWA) Section 112(r) (40 CFR 68.130)	Hazardous substance
Safe Drinking Water Act (SDWA)	4 mg/l 4.0 mg/l
Food and Drug Administration (FDA)	Not regulated.

US state regulations

US. Massachusetts RTK - Substance List

CHLORINE (CAS 7782-50-5)

US. New Jersey Worker and Community Right-to-Know Act

CHLORINE (CAS 7782-50-5) 100 lbs

US. Pennsylvania RTK - Hazardous Substances

CHLORINE (CAS 7782-50-5)

US. Rhode Island RTK

CHLORINE (CAS 7782-50-5)

US. California Proposition 65

This product is not listed, but it may contain elements known to the State of California to cause cancer or reproductive toxicity as listed under Proposition 65 Safe Drinking Water and Toxic Enforcement Act. For additional information, contact Olin Technical Services (800-299-6546).

US - California Proposition 65 - Carcinogens & Reproductive Toxicity (CRT): Listed substance

Not listed.

International Inventories

Country(s) or region	Inventory name	On inventory (yes/no)*
Australia	Australian Inventory of Chemical Substances (AICS)	Yes
Canada	Domestic Substances List (DSL)	Yes
Canada	Non-Domestic Substances List (NDSL)	No
China	Inventory of Existing Chemical Substances in China (IECSC)	Yes
Europe	European Inventory of Existing Commercial Chemical Substances (EINECS)	Yes
Europe	European List of Notified Chemical Substances (ELINCS)	No
Japan	Inventory of Existing and New Chemical Substances (ENCS)	No
Korea	Existing Chemicals List (ECL)	Yes
New Zealand	New Zealand Inventory	Yes
Philippines	Philippine Inventory of Chemicals and Chemical Substances (PICCS)	Yes
United States & Puerto Rico	Toxic Substances Control Act (TSCA) Inventory	Yes

*A "Yes" indicates this product complies with the inventory requirements administered by the governing country(s).
A "No" indicates that one or more components of the product are not listed or exempt from listing on the inventory administered by the governing country(s).

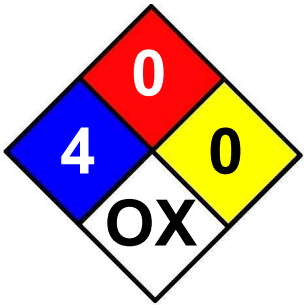
16. Other information, including date of preparation or last revision

Issue date 23-August-2013

Revision date -

Version # 01

NFPA Ratings



List of abbreviations

LD50: Lethal Dose, 50%.
LC50: Lethal Concentration, 50%.
EC50: Effective concentration, 50%.
TWA: Time weighted average.

References

EPA: AQUIRE database
HSDB® - Hazardous Substances Data Bank
US. IARC Monographs on Occupational Exposures to Chemical Agents
IARC Monographs. Overall Evaluation of Carcinogenicity
ACGIH Documentation of the Threshold Limit Values and Biological Exposure Indices

Disclaimer

This information is provided without warranty. The information is believed to be correct. This information should be used to make an independent determination of the methods to safeguard workers and the environment.

Section 2
QA/QC Program

Quality Assurance/Quality Control (QA/QC)

1

Terms

- A QA/QC program consists of procedures that ensure the precision and accuracy of tests performed on a daily basis.
- Precision – repeatability; being able to get the same results time after time
  - Shooting at a target and hitting the same spot repeatedly
- Accuracy – closeness of test results to the correct (known) value
  - Shooting at a target and hitting bull's eye

2

QA/QC Program

- Three phases:
  - Keeping records
  - Documenting that equipment is regularly calibrated and temperatures are correct
  - Perform QC tests to demonstrate precision and accuracy

3

Record Keeping

- Maintain a complete and accurate list of exact locations of all sampling sites
- Maintain a complete and accurate list of all test procedures used.
  - Record method numbers on bench sheets
- Write in pen
- Initial your entries
- Use a notebook that has numbered pages

4

Laboratory Conditions

- Lab equipment should be in good working condition
  - Calibrated
  - Checked against standards
- Lab quality distilled water and fresh, pure reagents must be on hand
- Lab temperature should be 68°F

5

Laboratory Conditions

- Glassware
  - Keep it clean
- pH meter
  - Calibrated daily w/ fresh buffers
- Spectrophotometer
- Incubator
  - Keep records of temperatures
- Balances
  - Checked at least annually for accuracy
  - Use ASTM Class 1 weights to check calibration

6

Laboratory Conditions

- Whenever repairs or maintenance are done on lab equipment, record those activities in a log book

7

Reagents

- Use only fresh ACS (American Chemical Society) Reagent Grade chemicals
- Check for expiration dates
- Mark chemicals with date arrived in lab, date opened and expiration date
- When solutions are mixed using dry reagents, record this in a reagent log
  - If standardization is required, include this information in the reagent log as well

8

Distilled or Deionized Water

- The quality of distilled or deionized water can greatly influence the quality of the test
- There should be no traces of chlorine, ammonia and total suspended solids
- TDS should be less than 1 mg/L
- Distilled is better than deionized
- Ultrapure is better than distilled

9

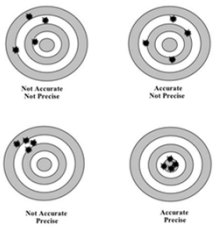
Quality Control Tests

- Duplicates
- Blanks
- Lab Standards
- Unknown Lab Standards
- Spikes

10

Precision and Accuracy

- Accuracy
  - Correctness
  - Checked by using a different method
  - Poor accuracy results from procedural or equipment flaws
- Precision
  - Reproducibility
  - Check by repeating measurements
  - Poor precision results from poor technique



11

Duplicates

- Simplest form of QC test
- Run two tests on one sample
  - This shows how precise the analyst's procedure is
  - Sample results should yield very close results (goal is to have no difference)
- General recommendation is to run a duplicate sample for every 10 samples

12

Duplicates

- Common sources of error:
  - Sample size (should be the same size)
  - Insufficient mixing
  - Dirty glassware
  - Calculation errors
  - Titration (misreading the burette)
  - Weighing
  - Calibration
  - Reagent water
  - Reagents

13

Duplicates

- Range
  - Difference between the test results
- RPD (Relative Percent Difference)
  - Calculate the average of the two results
  - Divide the range by the average

14

Duplicates

- You tested a sample for chlorine residual. The sample read 2.1 mg/L and the duplicate sample read 2.2 mg/L. What is the range and RPD?

Range = 2.2 mg/L – 2.1 mg/L = 0.1 mg/L
Average = (2.1+2.2)/2 = 2.15

$$RPD = \frac{range}{average} = \frac{0.1 mg/L}{2.15 mg/L} = 0.0465 = 4.7\%$$

15

Blanks

- Blanks can show test interferences
- Blanks should be treated as a sample
  - Take through all procedures
  - Add all reagents or incubate along with other samples
- Target value for blanks is zero

16

Blanks

- Positive blanks shows problem
  - Bad reagents
  - Bad technique
  - Unclean glassware
  - Bad distilled water
- Coliform Tests
  - A blank should never be positive
  - If the pre-sample blank has colony growth, the equipment was not properly sterilized
  - If the post sample blank has colony growth, the equipment was not cleaned well enough between samples

17

Laboratory Standards

- Determines accuracy
- If the test value agrees with the true value, the test has been performed accurately
- Mix onsite or purchased from a supplier
  - Purchased standards should be the preference, because this can reduce the possibility of having mixing errors; they also come with a certificate of analysis
- Perform along with dups., one every 10 samples

18

Unknown Laboratory Samples

- EPA quality control unknowns
- Commercially available
- Gives confidence to analyst
- Can show deficiencies in the testing procedure

19

Spikes

- Determines accuracy
- A known amount of standard is added to a sample
- The results should equal the sample value plus the added known amount
- Goal is to have 100% recovery of spike and sample
- If your sample result was 100 mg/L and you added 50 mg/L into the spiked sample, you should yield 150 mg/L

20

Spikes – Hach Example

- Ortho-Phosphate

1. After reading test results, leave the sample cell (unspiked sample) in the instrument. Verify the chemical form.
2. Touch Options. Touch Standard Additions. A summary of the standard additions procedure will appear.
3. Touch OK to accept the default values for standard concentration, sample volume, and spike volumes. Touch Edit to change these values. After values are accepted, the unspiked sample reading will appear in the top row. See *Standard Additions in the instrument manual for more information.*

21

Spikes – Hach Example

- Ortho-Phosphate

4. Open a Phosphate 10-mL Ampule Standard, 50-mg/L PO_4^{3-}.
5. Prepare a 0.1-mL sample spike by adding 0.1 mL of standard to the unspiked sample. Touch the timer icon. After the timer beeps, read the result.
6. Prepare a 0.2-mL sample spike by adding 0.1 mL of standard to the 0.1-mL sample spike. Touch the timer icon. After the timer beeps, read the result.

22

Spikes – Hach Example

- Ortho-Phosphate

7. Prepare a 0.3-mL sample spike by adding 0.1 mL of standard to the 0.2-mL sample spike. Touch the timer icon. After the timer beeps, read the result. Each addition should reflect approximately 100% recovery.
8. After completing the sequence, touch Graph to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch View: Fit, then select Ideal Line and touch OK to view the relationship between the sample spikes and the "Ideal Line" of 100% recovery.

23

Split Samples

- Some labs split samples with other labs to check the accuracy of the testing procedure
- If you are concerned that your contracted lab is getting wrong values, send in a known standard as a sample
  - This does double you cost, but you can see how close they are to the known value
  - Don't tell the contracted lab that the second sample is a known

24

40CFR136

Method Update Rule
For Backwash Lagoons that have Discharge Permits
May 10, 2013
Fleming Training Center

You Have Heard it All Before

* More Rules
* More Testing
* More Paperwork
* More Cost

* But everything we do is regulated.

2012 Update of 136

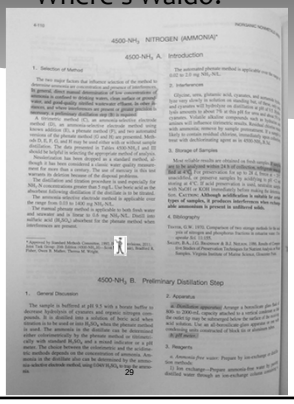
* Standard Methods approved by date not Edition
* Section 136.7 Quality Assurance and Quality Control.

Federal Register May 18, 2012

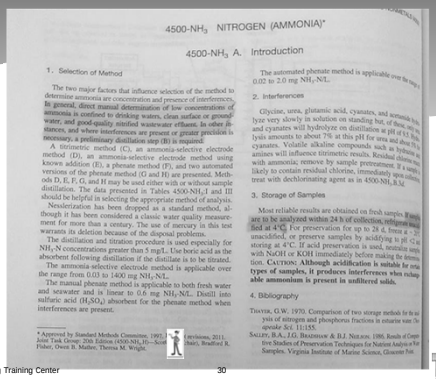
"Standard Methods" Changes

* Approved methods are not listed by the Edition of Standard Methods, but by the year the method was approved…

Where's Waldo?



THERE'S Waldo!



40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC/ Other
Chlorine-Total Residual, mg/L	Amperometric Direct	……	4500-Cl D-2000	D1253-08	
	Amperometric Direct (Low Level)	……	4500-Cl E-2000		
	Iodometric Direct	……	4500-Cl B-2000		
	Back Titration Ether End-Point[15]	……	4500-Cl C-2000		
	DPD-FAS	……	4500-Cl F-2000		
	Spectrophotometric, DPD	……	**4500-Cl G-2000**		
	Electrode	……	……	……	See Footnote [16]

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC/ Other
Hydrogen Ion (pH), pH units	**Electronic Measurement**	……	**4500---H^+ B-2000**	D1293-99 (A or B)	973.41, [3] I-1586-85.[2]
	Automated Electrode	150.2 (Dec. 1982)[1]	……	……	See Footnote, [21] I-2587-85[2]

TDEC - Fleming Training Center 32

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC /Other
Residue – Non-filterable (TSS), mg/L	**Gravimetric, 103-105° post washing of residue**	……	**2540 D-1997**	D5907-03	I-3765-85.[2]
Residue – Settleable, mg/L	**Volumetric, (Imhoff cone) or gravimetric**	……	**2540 F-1997**		
Temperature, °C	**Thermometric**	……	**2550 B-2000**	……	See Footnote.[32]

TDEC - Fleming Training Center 33

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC/ Other
Aluminum – Total, mg/L	**Digestion, followed by any of the following**				
	• AA direct aspiration	……	3111 D-1999 or 3111 E-1999	……	I3051-85
	• AA furnace	……	3113 B-2004		
	• STGFAA	200.9 Rev 2.2 (1994)			
	• ICP/AES	200.5 Rev 4.2 (2003), 200.7 Rev 4.4 (1994)	3120 B-1999	D1976-07	I-4471-97
	• ICP/MS	200.8 Rev 5.4 (1994)	3125 B-2009	D5673-05	993.14, I-4471-97
	• Direct Current Plasma (DCP)	……	……	D4190-08	
	• Colorimetric (Eriochrome cyanine R)	……	3500-Al B-2001		

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC/ Other
Iron – Total, mg/L	**Digestion, followed by any of the following**				
	• AA direct aspiration	……	3111 B-1999 or 3111 C-1999	D1068-05	974.27, I-3381-85
	• AA furnace	……	3113 B-2004	D1068-05	
	• STGFAA	200.9 Rev 2.2 (1994)			
	• ICP/AES	200.5 Rev 4.2 (2003), 200.7 Rev 4.4 (1994)	3120 B-1999	D1976-07	I-4471-97
	• ICP/MS	200.8 Rev 5.4 (1994)	3125 B-2009	D5673-05	993.14
	• Direct Current Plasma (DCP)	……	……	D4190-08	
	• Colorimetric (Phenanthroline)	……	3500-Fe-1997	D1068-05	

Three QA Options

- A. … follow equivalent EPA procedures
- B. Refer to QA/QC in consensus organization compendium. (Follow Standard Methods) didn't we have that on the previous slide?
- **C. Follow the 12 Steps where applicable.**

TDEC - Fleming Training Center 36

12 Quality Control Elements

1. DOC – demonstration of capability
2. MDL – method detection level
3. LRB/MB – method blank
4. LFB – laboratory fortified blank (standard)
5. LFM/LFMD – laboratory fortified matrix/duplicate (spike)
6. Internal standards, surrogate standards or tracer – ***only applies to organic analysis and radiochemistry***
7. Calibration- initial and continuing
8. Control charts or other trend analysis
9. Corrective action – root cause analysis
10. QC acceptance criteria
11. Definition of a batch (preparation and analytical)
12. Minimum frequency for conducting all QC elements
13. Unwritten 13th Step – SOP – Standard Operating Procedures need to be written and followed for all lab sampling and analyses

Not all of these items apply to all tests, there are many exceptions!

TDEC - Fleming Training Center 37

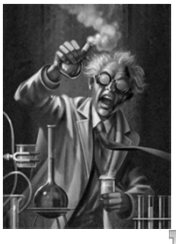
Can you defend what you do?

- How do you interpret your Permit language or the Rule?
- Can you defend that interpretation, will a judge or jury support you?
- What do Regulators say and what is written?
  - Is it clear?
  - Don't be afraid to ask Why?
  - Don't be afraid to ask for directives in writing.

TDEC - Fleming Training Center 38

Applicable Tests for Drinking Water

- Total Residual Chlorine
- pH
- TSS
- Settleable Solids
- Aluminum



TDEC - Fleming Training Center 39

What You Are Already Doing

- Most Labs are doing lots of QA/QC stuff
- Write down what you do….SOP
- Summarize QC Data
  - Table Form
  - Average, Max, Min.
  - Control Charts

TDEC - Fleming Training Center 40

Demonstration of Capability

- DOC
- Standard Methods 1020.B.1
  - As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 10 times the MDL and the midpoint of a calibration curve.
- Standard Methods 2020B.1.a, 4020B.1.a. & 5020.B.1.a
  - Run a laboratory-fortified blank (LFB) at least four times and compare to the limits listed in the method
  - LFB initial recovery limits = Mean ± (5.84xStandard Deviation)

TDEC - Fleming Training Center 41

Demonstration of Capability

- What tests does this apply to?
  - Chlorine, pH, TSS
  - Analyst needs to make up this standard, cannot be bought premade
  - Example: for chlorine, the analyst needs to make up 0.5 mg/L, not purchase pre-made 0.5 mg/L
    - Analyst can make 1 L of 0.5 mg/L by diluting down from 100 mg/L or 1000 mg/L and then pour up 4-100 mL aliquots

TDEC - Fleming Training Center 42

Demonstration of Capability

- How often?
  - Once for each analyst.
    - Recommended yearly for backup analyst who does not perform tests frequently
    - EPA highly recommends running every 2-3 years for every analyst
  - Each analyst should have a file kept on their training within and for the lab.
  - Something to keep along with these records is a signed form (documentation) that analyst has read and understands all appropriate SOPs and Methods.

Method Detection Level

- MDL
- Standard Methods 1020.B.4
  - As a starting point for selecting the concentration to use when determining the MDL, us an estimate of five times the estimated true detection level
  - Ideally, prepare and analyze at least seven portions of this solution over a 3-day period to ensure the MDL determination is more representative of routine measurements as performed in the laboratory

Method Detection Level

- Standard Methods 1020.B.4 - continued
  - Recommended that the replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50-150% , with RSD (relative standard deviation) values ≤ 20%
- Standard Methods 4020.B.1.b
  - Ideally use pooled data from several analysts rather than data from one analyst

Method Detection Level

- What tests does this apply to?
  - Chlorine
- How often?
  - Annually

What the heck IS an MDL study?

- It is a calculation that statistically gives the lowest concentration that a lab/facility can "see", that is detect an analyte
- Not practical for many analyses
- It is a bit tricky the first time, but KEEP RECORDS so next year it will be a breeze.
- Fresh samples prepared daily are preferred and it is recommended that samples are run over 3 days to give a more accurate account of how samples are run.

How MDL Studies are Performed

- Make seven very low level blank spikes (can be lower than the lowest point on your curve)
- Analyze all seven over several days and calculate the standard deviation
- Multiply the standard deviation by the "student t" for 7 values (3.14)
- You cannot "cherry pick" your results, they must be 7 samples in a row

MDL Calculations

- The result is the MDL (method detection level)
- The MDL must be greater than 1/10 the concentration of each spike
  - Example: if the spike was 3, the MDL cannot be lower than 0.3 (3 divided by 10)
- Keep up with the best spike value used for your MDL study so you don't have to go through several attempts each year

Good MDL Values for Cl_2

Date	Analyst	Number	True Value	Value Read	% Recovery (50-150%)
1/28/2013	SEP	1	0.05	0.09	180.00
1/28/2013	SEP	2	0.05	0.07	140.00
1/28/2013	SEP	3	0.05	0.07	140.00
1/30/2013	SEP	4	0.05	0.08	160.00
1/30/2013	SEP	5	0.05	0.08	160.00
2/1/2013	SEP	6	0.05	0.07	140.00
2/1/2013	SEP	7	0.05	0.08	160.00
			Standard Deviation	**0.007559289**	
	Relative Standard Deviation (RSD)			9.7990789	(Needs to be ≤ 20%)
			MDL	**0.0237362**	

MDL is NOT good because it is < 1/10th of the spike of 1.00. 1/10th of the spike is 0.10 mg/L and the calculated MDL is less than this and therefore unacceptable.

NOT Good MDL Values for Cl_2

Date	Analyst	Number	True Value	Value Read	% Recovery (50-150%)
1/28/2013	SEP	1	1.00	1.00	100.00
1/28/2013	SEP	2	1.00	0.99	99.00
1/28/2013	SEP	3	1.00	1.00	100.00
1/30/2013	SEP	4	1.00	1.00	100.00
1/30/2013	SEP	5	1.00	0.98	98.00
2/1/2013	SEP	6	1.00	1.01	101.00
2/1/2013	SEP	7	1.00	1.00	100.00
			Standard Deviation	**0.009511897**	
	Relative Standard Deviation (RSD)			0.9539152	(Needs to be ≤ 20%)
			MDL	**0.0298674**	

Laboratory Reagent Blank

- LRB
- Also known as Method Blank
- Standard Methods 1020.B.5
  - A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure (distillation, incubation, etc.)
- What tests does this apply to?
  - Chlorine, TSS
- How often?
  - Depends on method QA/QC

Laboratory Fortified Blank

- LFB
- Standard Methods 1020.B.6
  - A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added
  - Sample batch = 5% basis = 1 every 20 samples **(or day of for monthly reporting purposes)**
  - Use an added concentration of at least 10 times the MDL, or less than or equal to the midpoint of the calibration curve

Laboratory Fortified Blank

- Standard Methods 2020.B.2.e – TSS
  - Using stock solutions, prepare fortified concentrations so they are within the calibration curve
- Standard Methods 4020.B.2.e – Chlorine
  - Calculate percent recovery, plot control charts and determine control limits
- What tests does this apply to?
  - Chlorine, TSS

Laboratory Fortified Blank

- How often?
- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a LFB to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would suggest twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Duplicate

- Dup
- Not a part of the 12 Steps of QA, an addition from the State of TN
- Standard Methods 1020.B.8
  - As a minimum, include one duplicate sample with each sample set or on a 5% basis
- Standard Methods 1020.B.12
  - Calculate the RPD (relative percent difference)
  - Equal to or less than 20% RPD

Duplicate – Cl_2 and pH

- Standard Methods 4020.B.2.f
  - Randomly select routine samples to be analyzed twice
  - Process duplicate sample independently through the entire sample preparation and analysis
  - Include at least one duplicate for each matrix type daily or with each batch of 20

Duplicate

- What tests does this apply to?
  - Chlorine, pH, TSS and Settleable Solids
- How often?
- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria: (10% would be once every 10 samples for TSS)
  - If a permit stated that 3 analyses per week, we would allow for a dup to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would suggest twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Initial Calibration Verification & Continuing Calibration Verification

- ICV
  - Standard Methods 1020.B.11.b
    - Perform initial calibration using at least three concentrations of standards for linear curves
  - Calibrate pH meter or verify scale, thermometer and colorimeter/spectrophotometer

Initial Calibration Verification & Continuing Calibration Verification

- CCV
  - Standard Methods 1020.B.11.c
    - Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
  - Verify the calibration (especially if preset by manufacturer) at beginning of day, after every 10 readings and at the end of the batch
  - **Daily (or day of for monthly reporting purposes)**

Corrective Action

- Standard Methods 1020 B.15
  - QC data that are outside the acceptance limits or exhibit a trend are evidence of unacceptable error in the analytical process.
  - Take corrective action promptly to determine and eliminate the source of error.
  - Do not report data until the cause of the problem is identified and either corrected or qualified (see Table 1020:II)

Corrective Action

- The corrective action plan needs to be in your SOP for each method on what to do if your QC tests fail or are out of range
- If you have a "boo boo", write down how you fixed it
- Any issues should be recorded and a sentence on how it can be prevented, if possible, in the future
- Common problems and their corrections should be covered in your Standard Operating Procedures (SOP)
  - If you see things frequently, you can give them qualifiers that are noted in your SOP

QC Acceptance

- Have in SOP for each method the acceptance ranges for standards, duplicates, etc. and make sure they match the method requirements.
- If not mentioned in method, these are the accepted criteria for QC:
  - Blank < reporting limit
  - LFB ± 15%
  - ICV/CCV ± 10%
  - RPD ± 20%

Batch Size

- Each "Batch" could be daily (day of testing), every 10 samples or every 20 samples.
- Check method
- If you sample only once a month, need to run QC each time.

QC Frequency

- Usually lumped in with the definition of a "batch" and should be in the SOP of some kind

Standard Operating Procedure

- Here's that "13th Step", your SOP
- All procedures must be documented in some type of SOP
- It can be very simple but must provide the information necessary for someone who is not familiar with the test to perform it
  - Step by step instructions on how and where to collect the samples and then how to run the test.
- It must include the QC Acceptance Criteria, the definition of a "Batch" and the minimum frequency of QC checks

Standard Operating Procedure

- Common documents in an SOP:
  - Copy of method from manufacturer on how to calibrate instrument, run samples, etc.
  - QA/QC information from TDEC
  - Step-by-step instruction for you plant on the 12 Steps that apply to that test.
  - Where you grab your samples

TDEC - Fleming Training Center 67

Daily Laboratory Record

Month and Day _____

Operators on Duty														
Analysis		Units	00:00	02:00	04:00	06:00	08:00	10:00	12:00	14:00	16:00	18:00	20:00	22:00
Temperature	Raw	Celcius												
	Finished	Celcius												
Turbidity	Raw	NTU												
	Jar	NTU												
	Settled	NTU												
	Finished	NTU												
Chlorine, Residual	Top of Filter	mg/L												
	Lowest Plant Eff.	mg/L												
Alkalinity	Raw	mg/L												
	Jar	mg/L												
	Settled	mg/L												
	Finished	mg/L												
pH	Raw													
	Jar													
	Pre-Sed													
	Flash Mix													
	Settled													
	Clearwell													
	Finished													
Hardness	Raw	mg/L												
	Finished	mg/L												
Iron	Raw	mg/L												
	Finished	mg/L												
Manganese	Raw	mg/L												
	Finished	mg/L												
Fluoride	Raw	mg/L												
	Finished	mg/L												
Phosphate	Finished	mg/L												
TDS	Finished	mg/L												
Color	Finished	CU												
UV-254	Raw													
Odor	Finished	TON												
Carbon Dioxide	Raw	mg/L												
	Flash Mix	mg/L												
	Settled	mg/L												
	Finished	mg/L												
Langelier's	Finished													

12 Steps of Lab Quality Assurance

Parameter	Method	DOC	MDL	LRB	LFB	LFM / LFMD	Dup	ICAL / CCV	Control Charts	Corrective Action	QC Acceptance	Batch Size	*QC Frequency
Ammonia	SM4500-NH3 D - 1997	X	X	X	X	X		X, Calibrate meter daily	X	X	X	20	1/2 weeks
BOD_5 / $CBOD_5$	SM5210 B - 2001	X		X	X		X	X, Calibrate meter daily	X	X	X	20	1/2 weeks
Chlorine, TR	SM4500-Cl G - 2000	X	X	X	X		X	X, verify meter daily w Secondary Gel Standards	X	X	X	20	1/2 weeks
pH	SM4500-H+ B - 2000	X					X	X, Calibrate meter daily		X	X	20	1/2 weeks
Oxygen, dissolved	SM4500-O G - 2001	X					X	X, Calibrate meter daily & verify with air-saturated water		X	X	20	1/8 hours
	Hach Method 10360 Luminescence Oct. 2011	X					X	X, Calibrate meter daily & verify with air-saturated water		X	X	20	1/8 hours
Phosphorus, total	SM4500-P B and E - 1999	X	X	X	X	X		X, verify meter	X	X	X	20	1/2 weeks
TSS	SM2540 D - 1997	X		X	X		X	X, verify scale daily		X	X	10	1/2 weeks
Sett. Solids	SM2540 F - 1997						X			X		20	1/month
Temperature	SM2550 B - 2000							X, verify against NIST thermometer		X			Annually

DOC – Demonstration of Capability

- Each analyst should have a file kept from where they have calibrated and analyzed 4 standards to demonstrate they can accurately run this test
- DMRQA's could qualify for these
- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods
- Recommend backup analyst do this once a year

MDL – Method Detection Limit

- Annually run at least 7 samples at low levels

LRB – Laboratory Reagent Blank

- Analyze distilled/deionized water as a sample

LFB – Laboratory Fortified Blank

- Analyze a known standard

LFM/LFMD – Laboratory Fortified Matrix/Laboratory Fortified Matrix Duplicate

- Analyze a sample with a known amount of standard added (spike)

Dup – Duplicate

- Analyze a sample twice

ICAL/CCV – Initial Calibration/Continuing Calibration Verification

- Calibrate meter (DO, pH, ISE) or verify scale, thermometer and colorimeter/spectrophotometer
- Verify the calibration (especially if preset by manufacturer) at beginning of day and/or after every 10 readings, whichever comes first.

Corrective Action

- Have corrective action plan in SOP for each method on what to do if QC tests fail or are out of range.
- For example, if standards fail, re-calibrate and run test again.

QC Acceptance

- Have in SOP for each method the acceptance ranges for standards, duplicates, spikes, etc. and make sure they match the method requirements.

Batch Size

- Each batch could be daily, every 10 samples or every 20 samples. Check method.

*QC Frequency (depends on permit)

- For samples that need to be analyzed on a 5% basis or once for every 20 samples, follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would suggest twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - **Please note that influent and effluent samples count as two separate samples. For example, if you are supposed to run 3 BODs a week, that should be counted as running 6 samples for that week.**
- For samples that need to be analyzed on a 10% basis or once for 10 samples, follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would suggest twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - **Please note that influent and effluent samples count as two separate samples. For example, if you are supposed to run 5 TSSs a week, that should be counted as running 10 samples for that week and you should run your QC once a week.**

Standard Operating Procedure

- Here's that "13th Step", your SOP
- All procedures must be documented in some type of SOP
- It can be very simple but must provide the information necessary for someone who is not familiar with the test to perform it
  - Step by step instructions on how and where to collect the samples and then how to run the test.
- It must include the QC Acceptance Criteria, the definition of a "Batch" and the minimum frequency of QC checks

Section 3
pH

pH

pH

- One of the most important and frequently used tests in water chemistry
- A measure of the intensity of the acidic or alkaline character of a solution
- Logarithmic scale of ionic activity
  0 to 14 s.u. (standard units)
- pH values cannot be averaged

pH Measurement

- pH is typically measured with a meter and probe
- This is an electrochemical method of analysis

pH Theory

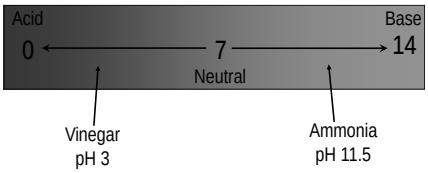
- Acid
  - increases the hydrogen ion (H+) concentration in a solution
- Base
  - increases the hydroxide ion (OH-) concentration in a solution

pH Theory

- pH is defined as the negative log of the molar hydrogen ion concentration in aqueous solution

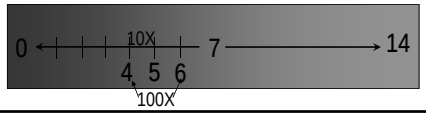
$$pH = -\log [H^+]$$

pH Scale



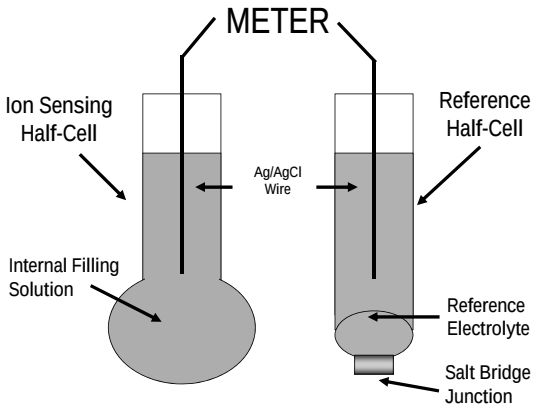
pH Scale

- pH is a negative logarithmic function
- Each decrease in pH unit = 10X increase in acidity
  - Solution at pH 4 is 10X more acidic than solution at pH 5
  - Solution at pH 4 is 100X more acidic than pH 6 solution



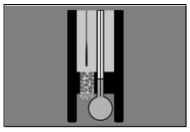
How Does a pH Probe Work?

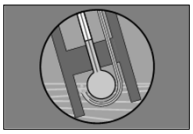
- Probe measures hydrogen ion concentration
  - Two electrodes in probe:
    a) sensing half-cell,
    b) reference half-cell



Reference Half-Cell

- Dispenses reference solution which completes circuit for meter



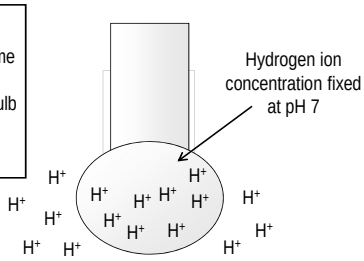


Sensing Half-Cell

pH 7 Solution

H^+ conc the same both inside and outside glass bulb

*No potential develops



Sensing Half-Cell

pH 7 Solution

H^+ conc the same both inside and outside glass bulb

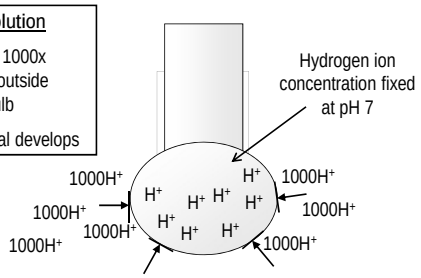
*No potential develops

Sensing Half-Cell

pH 4 Solution

H^+ conc 1000x greater outside glass bulb

*Potential develops



Sensing Half-Cell

pH 4 Solution

H^+ conc 1000x greater outside glass bulb

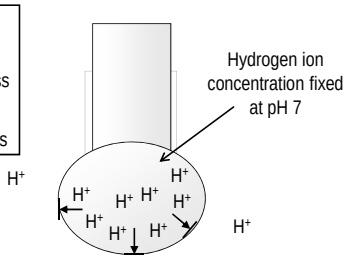
*Potential develops

Sensing Half-Cell

pH 10 Solution

H^+ conc 1000x greater inside glass bulb

*Potential develops



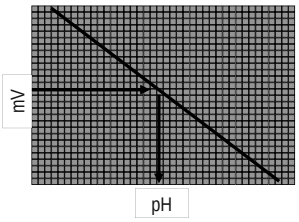
Sensing Half-Cell

pH 10 Solution

H^+ conc. 1000x greater inside glass bulb

*Potential develops

Calibration



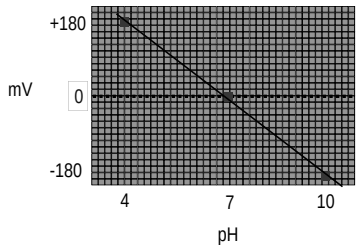
- A calibration curve allows the meter to convert a measured millivolt potential into a pH reading.

Calibration

- The optimal slope for pH is -58±3 mV/decade.

What does this mean?

Calibration

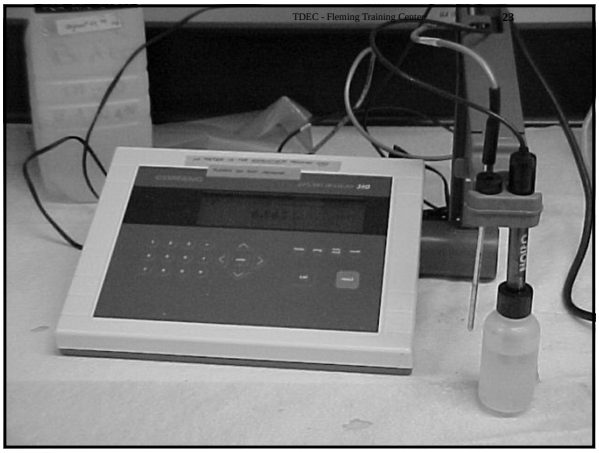


Calibration

- -180 mV difference measured between pH 4 and pH 7
- pH 4 to pH 7 (3 pH units) is 1000x concentration change
- Decade = 10-fold concentration change = 1 pH unit
- -180/3 = -60 ≈ -58 mV/decade

Importance of pH control

- Ammonia toxicity is influenced by pH
- pH plays an important role in the solubility of metal salts
- pH affects the rate at which chlorine reacts to form chloramines (which are less effective disinfectants)



pH Sampling

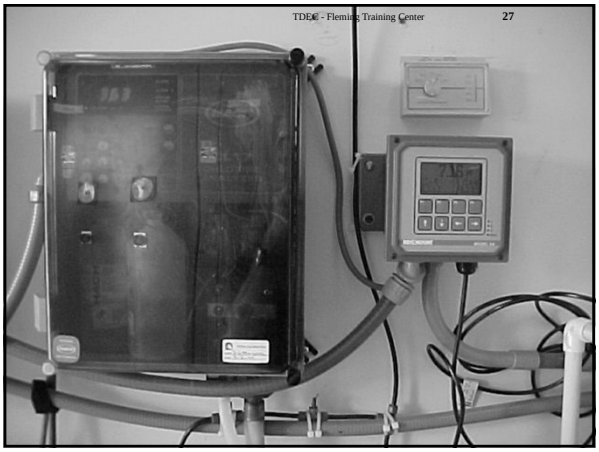
- Holding time = 15 minutes
- Preservation = none
- Sample container = glass or plastic
- Grab sample
- Continuous monitoring possible

pH Meter Calibration

- Follow manufacturers instructions
- Use fresh buffers (4, 7, & 10 s.u.)
- Stir buffers and samples at the same speed without a vortex
- Rinse and blot dry electrodes between samples and buffers
- Accurate and reproducible to within 0.1 s.u.

pH Meter Calibration (cont.)

- Start with pH = 7.0 buffer (usually)
- Second buffer 3 s.u. different than brackets expected sample pH (4 or 10)
- Immerse in a third buffer - reading should be within 0.1 s.u.
- If response is accurate - read and record previous buffers as samples (pH and temperature)



Continuous pH Monitoring EPA Method 150.2

- Immersion type electrodes easily removed from mounting:
  - Should be calibrated with two buffers that bracket expected pH and are at least 3 pH units apart
  - Adjustments made until readings are within ±0.1 s.u. of buffer value
  - Calibration must be made at least daily

Continuous pH Monitoring EPA Method 150.2

- Immersion type electrodes <u>not</u> easily removed from mounting :
  - Indirect procedure - System must agree within 0.1 s.u. of a calibrated lab meter on an effluent sample
  - Indirect calibration once per day
  - Recalibration - System should be calibrated against two fresh buffers at least every 30 days and more often if needed

COMMON DEFICIENCIES

- The pH meter was calibrated using one buffer or expired buffers
- The continuous pH meter was not calibrated on a regular basis
- Buffers were left open and being reused for a week

Maintenance

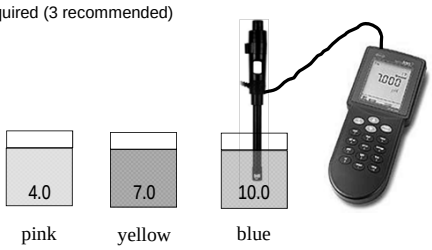
- New probe
- Calibration
- Measurement/Storage
- Troubleshooting
- Cleaning

New Probe

- Condition new pH probe in pH 7 buffer for approximately 30 minutes before initial use
- Probes must also be conditioned after cleaning or if it had been stored dry as long term storage

Calibrate

- Calibrate pH meters daily using two or three buffer solutions
  - 2 required (3 recommended)



Measurement

- Place probe into sample, stir, and wait for readings to stabilize
- Rinse and dry between measurements
- Storage between measurements
  - Sample *or* solution of similar ionic strength to sample
  - pH 7 buffer
  - pH electrode storage solution *(best)*

Measurement - Special Considerations

- Low ionic strength solutions
  - Very clean samples with low TDS
  - Absorption of atmospheric carbon dioxide is a major source of drift
    - Low ionic strength sample chamber
    - Condition electrode in a solution of comparable ionic strength before use

Troubleshooting

- mV reading in pH 7 buffer
  - Should read 0 ± 30 mV in pH 7 buffer
- Response time
  - May require cleaning if slow in buffered solution
- Slope
  - Optimal slope is -58 ± 3 mV/decade

Cleaning

- Slow response may indicate need for cleaning
  - Alternate soaking in dilute hydrochloric acid and dilute sodium hydroxide
  - Rinse with deionized water
  - Condition in pH 7 buffer before use
- Read probe manual for cleaning method recommended by manufacturer

40CFR136

Method Update Rule
For Backwash Lagoons that have Discharge Permits
May 10, 2013
Fleming Training Center

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC/ Other
Hydrogen Ion (pH), pH units	**Electronic Measurement**	……	**4500---H^+ B-2000**	D1293-99 (A or B)	973.41, [3] I-1586-85.[2]
	Automated Electrode	150.2 (Dec. 1982)[1]	……	……	See Footnote, [21] I-2587-85[2]

12 Quality Control Elements

1. DOC – demonstration of capability
2. MDL – method detection level
3. LRB/MB – method blank
4. LFB – laboratory fortified blank (standard)
5. LFM/LFMD – laboratory fortified matrix/duplicate (spike)
6. Internal standards, surrogate standards or tracer – ***only applies to organic analysis and radiochemistry***
7. Calibration- initial and continuing
8. Control charts or other trend analysis
9. Corrective action – root cause analysis
10. QC acceptance criteria
11. Definition of a batch (preparation and analytical)
12. Minimum frequency for conducting all QC elements
13. Unwritten 13th Step – SOP – Standard Operating Procedures need to be written and followed for all lab sampling and analyses

Not all of these items apply to all tests, there are many exceptions!

pH SM4500-H^+ B – 2000 Electrometric Method

- DOC
- Dup
- ICAL/CCV
- Corrective Action
- QC Acceptance
- Batch Size
- QC Frequency

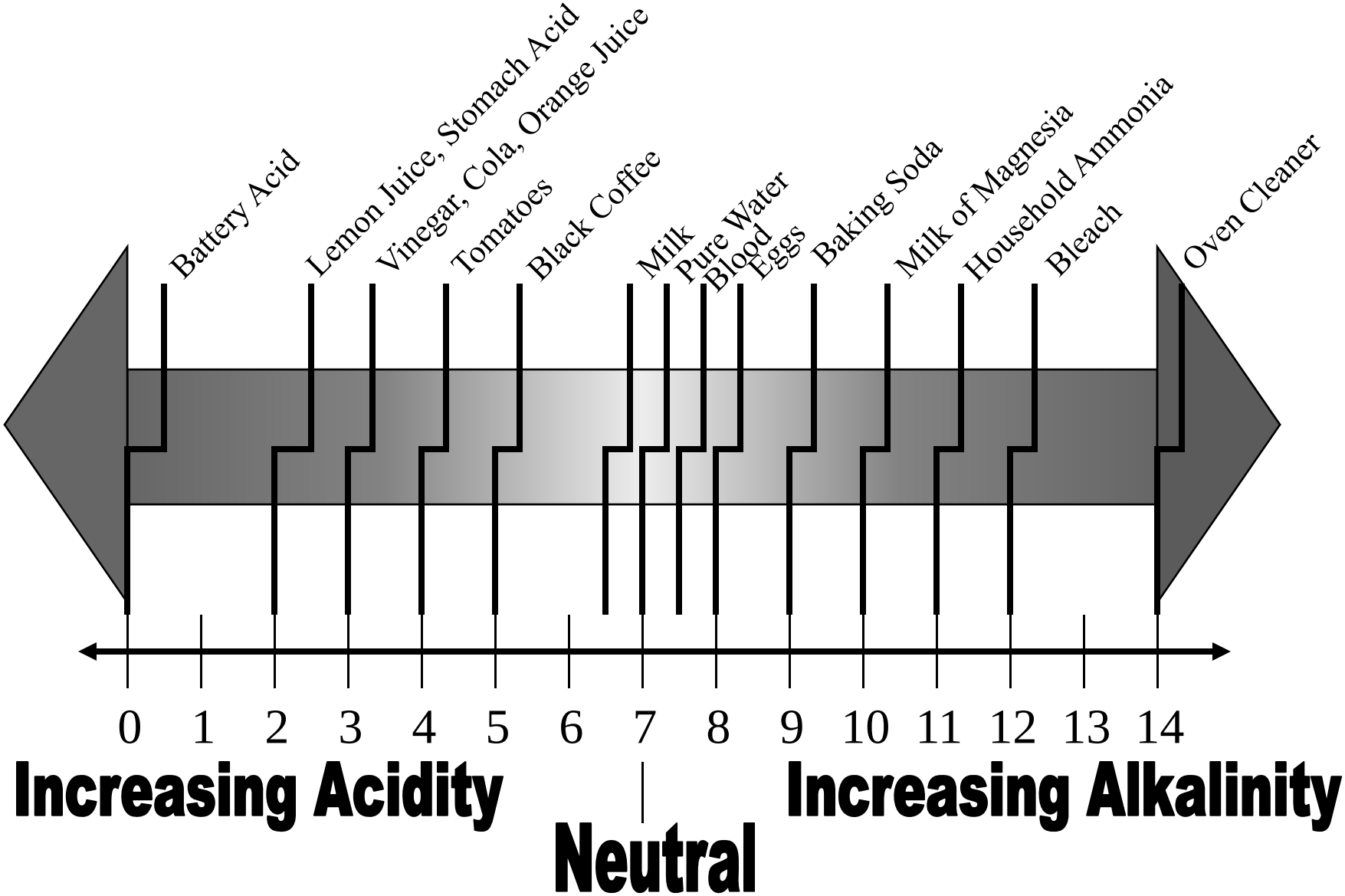
pH SM4500-H^+ B – 2000 Electrometric Measurement

- Read to 1/10th units only, 0.0 s.u.
- Demonstration of Capability (DOC)
  - Run buffer at least four times and compare to the limits listed in the method
  - Real people language: each operator running this test need to calibrate and analyze 4 buffers at a pH of 7
  - Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.
  - Recommend backup analyst do this once a year.

pH SM4500-H^+ B – 2000 Electrometric Measurement

- Initial Calibration
  - Calibrate per manufactures instructions with fresh buffers **daily**
- Calibration Verification
  - Read 7 buffer after analyzing samples **daily (or day of for monthly reporting purposes)**
- Duplicates of the sample
  - Run on a 5% basis, one for every 20 samples
  - Within ± 0.2 s.u.

TDEC - Fleming Training Center 43


Battery Acid
Lemon Juice, Stomach Acid
Vinegar, Cola, Orange Juice
Tomatoes
Black Coffee
Milk
Pure Water
Blood
Eggs
Baking Soda
Milk of Magnesia
Household Ammonia
Bleach
Oven Cleaner
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Increasing Acidity
Increasing Alkalinity
Neutral

pH

pH for Water

The pH stands for pouvoir hydrogène, which is French for power of hydrogen. The pH of a water sample indicates the intensity of its acidity or basicity. Its scale runs from 0 to 14, with 7 being neutral. The pH is a measure of the hydrogen ion concentration. Each decrease in pH unit equals a 10x increase in acid. For example, solution at pH of 4 is 10x more acidic than a solution at a pH of 5 and a solution at pH of 4 is 100x more acidic than a solution at a pH of 6.

pH is very important in water treatment. The coagulation process is most effective when water is in the proper pH range. The pH is used in determining if the water will be corrosive or scale forming. The effectiveness of the chlorination process is also affected by the pH of the water. Finished water must be in the pH range of 6.5 – 8.5.

The pH meter works by the use of a glass electrode and a silver – silver chloride (Ag – AgCl) electrode. A voltage is generated between them and is converted to a pH reading by the meter. Temperature affects the voltage generated. To get an accurate pH reading, you would need a temperature probe as well. Some meters have a combination electrode that serves the purpose for both probes and adjusts the pH if needed according to the temperature.

At least two buffers must be used to calibrate the pH meter. A pH 7 buffer must be used, in addition to either a pH 4 or pH 10 buffer, depending on the pH range expected for your samples. Some pH meters may be calibrated using three or more buffers. Follow the manufacturer's instructions. The meter should be ***calibrated daily*** and each calibration should use ***fresh buffer solutions***.

- **Procedure for calibrating pH meter:**
  - Press calibrate. The time and date of the last calibration will be displayed.
  - ENTER NO. BUFFERS is displayed. Press 2 or 3, depending on how many buffers will be used.
  - When the prompt appears, place the electrode in the 7.00 buffer and wait until the meter reading stabilizes.
  - When the prompt READY CAL AS 7.00 appears, press yes.
  - Repeat the two previous steps for each buffer, rinsing electrode with distilled water between buffers.
  - When calibration is completed, the meter will display the slope and proceed to the MEASURE mode. It is ready to measure the first sample. Re-read the buffers used to calibrate to check your calibration.

- **Procedure for measuring pH of samples:**
  - Remove electrode from storage solution and rinse with distilled water**.**
  - Place electrode in sample and wait for reading to stabilize.
  - If meter goes into "sleep" mode, press any key.

Fleming Training Center

pH Calibration Record

Date	Time	Temp of Buffers	Slope % 95% - 105%	mV of Buffers Used			Tech	Remarks
				4	7	10		
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					
			0.00					

Slope = **I** mV pH buffer 7 – mV pH buffer 4 **I** X 100/177 OR
Slope = [the absolute value of mV (pH buffer 7 – mV pH buffer 4)] X 100/177

Month_____ **pH Meter** _____

Fleming Training Center

pH Sample Record

Date	Time	Location	Temp. of Solution	Date of Last Calibration	Measured pH	Technician

Month_____ **pH Meter** _____

Initial Demonstration of Capability (DOC)

- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs calibrate and analyze 4 buffers at a pH of 7**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**
    - **Only good for that type of instrument you are using at that plant. If you have a backup instrument made by a different manufacturer or you work at another plant with a different make/model, you would need another DOC.**
        - **DOCs demonstrate you are proficient with that one instrument.**

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- **Real people language – calibrate daily with fresh buffers by following manufacturer's instructions.**

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 4020 B.2.f. – Randomly select routine samples to be analyzed twice.
    - Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – on a 5% basis (1 for every 20 samples) analyze 2 samples for pH, after reading one, pour out sample and start with a fresh sample**
    - **Example, grab sample in bucket and dip pH probe in twice to get a duplicate reading**
    - **Target value is to get close to the first value and have a small RPD (within ± 0.2 s.u.)**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
    - For the calibration verification to be valid, check standards must be within +/- 0.2 pH units of its true value, and calibration blank results must not be greater than one-half the reporting level
- **Real people language – read 7 Buffer after analyzing samples daily.**

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Duplicates within ± 0.2 s.u.

Batch Size

- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would suggest twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations

- NONE

Section 4
Specific Gravity

Density and Specific Gravity

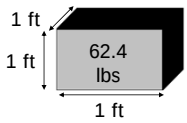
• TDEC - Fleming Training Center •1

Density

- Weight per unit volume
  - solids and gases expressed in lb/ft^3
  - liquids measured in lb/gal or lb/ft^3
- Density of water varies slightly with temperature and pressure
- Density of gases changes significantly with changes in temperature and pressure

• TDEC - Fleming Training Center •2

Density of Water



1 gal

The density of water is
62.4 lbs/ft^3
or
8.34 lbs/gal

• TDEC - Fleming Training Center •3

Specific Gravity

- Compares density of a substance to a standard density
- Does not have units
- For solids and liquids
  - compare to standard density of water
    - 62.4 lb/ft^3
    - 8.34 lb/gal

• TDEC - Fleming Training Center •4

Example #1

- The density of SAE 30 motor oil is 56 lb/ft^3. Find its specific gravity.

$$\text{Specific gravity} = \frac{\text{density of motor oil}}{\text{density of water}}$$

$$\text{Specific gravity} = \frac{56 \text{ lb/ft}^3}{62.4 \text{ lb/ft}^3} = 0.90$$

• TDEC - Fleming Training Center •5

Example #2

A sample of liquid alum has a density of 11.2 lb/gal. What is its specific gravity?

$$\text{Specific gravity} = \frac{\text{density of alum}}{\text{density of water}} = \frac{11.2 \text{ lb/gal}}{8.34 \text{ lb/gal}} = 1.34$$

• TDEC - Fleming Training Center •6

Specific Gravity of Gases

Compare to standard density of air:
0.075 lb/ft^3

Specific Gravity of Chlorine Gas

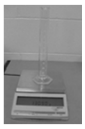
S.G. of Cl_2 gas= $\frac{\text{density of } Cl_2 \text{ gas}}{\text{density of air}}$

= $\frac{0.187 \text{ lb/ft}^3}{0.075 \text{ lb/ft}^3}$

= 2.49

Verification

- Place 100 mL graduated cylinder on a scale



130.90 g

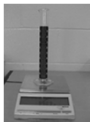
Verification

- Tare the scale so it reads zero with the cylinder on it.

0.00 g

Verification

- Weigh 100 mL of your sample or chemical.



99.09 g

Verification

Specific Gravity = $\frac{\text{Wt of 100 mL of solution, g}}{100 \text{ g}}$

Specific Gravity = $\frac{99.09 \text{ g}}{100 \text{ g}}$

Specific Gravity = 0.99

DENSITY & SPECIFIC GRAVITY

Density: Weight per unit volume.

2 ways to express density: _____

_____

Specific gravity: Density of any substance compared to a "standard density."

Standard density of water: _____ lb/gal

_____ lb/ft^3

1. Find the specific gravity for rock granite if the density is 162 lbs/ft^3.

2. Find the specific gravity for SAE 30 motor oil if the density is 56 lbs/ft^3.

3. Find the specific gravity of dry alum if the density is 65 lbs/ft^3.

4. Find the specific gravity for liquid alum that weighs 11.07 lbs/gal.

5. Find the specific gravity for fluorosilicic acid that weighs 10.5 lbs/gal.

6. Find the specific gravity for ferric sulfate that weighs 12.34 lbs/gal.

7. Find the density (lbs/ft^3) of a certain oil that has a S.G. of 0.92.

8. Find the density (lbs/gal) of ferric chloride that has a S.G. of 1.140.

9. Find the density (lbs/gal) of caustic soda that has a S.G. of 1.530.

10. Find the density (lbs/ft^3) of potassium permanganate that has a S.G. of 1.522.

11. A tank holds 1,240 gallons of a certain liquid. The specific gravity is 0.93. How many pounds of liquid are in the tank?

12. Pump rate desired: 25 gpm
Liquid weight: 74.9 lbs/ft^3
How many pounds of liquid can be pumped per day?

13. A certain pump delivers 23 gallons per minute.
    A. How many lbs of water does the pump deliver in 1 minute?
    B. How many lbs/min will the pump deliver if the liquid weighs 71.9 lbs/ft^3?

14. A certain pump delivers 14 gallons per minute.
    A. How many lbs of water does the pump deliver in 24 hours?
    B. How many lbs/day will the pump deliver if the liquid weighs 8.1 lbs/gal?

15. Compare the density of chlorine gas with the density of air. Chlorine gas weighs 0.187 lbs/ft^3. (Standard density of air = 0.075 lb/ft^3)

ANSWERS:

1. 2.6
2. 0.9
3. 1.04
4. 1.33
5. 1.26
6. 1.48
7. 57.4 lbs/ft^3
8. 9.5 lbs/gal
9. 12.76 lbs/gal
10. 95 lbs/ft^3
11. 9,617.7 lbs
12. 360,481 lbs/day
13. a. 191.8 lbs/min
    b. 221 lbs/min
14. a. 168,134 lbs/day
    b. 163,296 lbs/day
15. 2.49

Specific Gravity

Sample	Sample Size	Sample Weight	Specific Gravity

$$\text{Specific Gravity} = \frac{\text{weight of 100 mL of solution, g}}{100\text{ g}}$$

Section 5
Potassium Permanganate Residual

Potassium Permanganate

Water Treatment Lab

1 TDEC - Fleming Training Center

Potassium Permanganate

- $KMnO_4$
- Used in water treatment for the oxidation of iron, manganese and substances causing taste and odor
- Also can be used to treat Zebra mussels

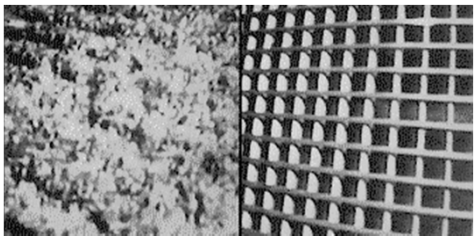
2 TDEC - Fleming Training Center

Zebra Mussels

Zebra mussels (*Dreissena polymorpha*) fouling an intake pipe.
Photo courtesy of Peter Yates.

3 TDEC - Fleming Training Center

Zebra Mussels



4 TDEC - Fleming Training Center

Oxidizer

- As permanganate oxidizes compounds in the water, it changes from purple to brown
- Final product is manganese dioxide (MnO_2)
  - An insoluble precipitate that can be removed by sedimentation or filtration
- All $KMnO_4$ needs to be converted to MnO_2 before filtration
  - Otherwise the pink color may pass through the filters and into the clearwell

5 TDEC - Fleming Training Center

Oxidizer

- If too little permanganate is added, dissolved iron and manganese may pass through the treatment process into the clearwell
- Once chlorine is added, these minerals may precipitate out
  - Causing color problems in the distribution system

6 TDEC - Fleming Training Center

CAIROX®
Potassium Permanganate
CAS No. 7722-64-7

Determination of CAIROX® Potassium Permanganate Residual for Drinking Water Applications: DPD Spectrophotometric Method

Analytical Method 103

Objective

This method can be used to determine the residual CAIROX® Potassium Permanganate in water. It uses standard DPD reagents and is based on the Hach spectrophotometric method for the determination of free chlorine.

Equipment/Reagents Required

1. Spectrophotometer or equivalent
2. DPD free chlorine powder packet
3. 1.0 g/L $CaCl_2$ stock solution (if the source water is soft water)
4. 0.22 micron, oxidant resistant, glass fiber filters

Procedure

1. Obtain a representative sample of the plant's water that has been treated with CAIROX® Potassium Permanganate.

2. Filter the sample through a 0.22 µm filter. This will remove any MnO_2 that would interfere with the analysis. If the water is soft (i.e. <40 mg/L hardness as $CaCO_3$), add 1 mL of a 1 g/L $CaCL_2$ stock solution per liter of sample and wait approximately 5 minutes before filtering.

3. Pour 25 mL of the filtered sample into a Hach Cell and use this sample to zero the spectrophotometer.

4. Pour 25 mL of the filtered sample into another Hach Cell and add the contents of 1 DPD free chlorine powder packet. Swirl to mix and make sure no bubbles remain in or on the cell.

5. Place the reactant cell into the spectrophotometer and read the free chlorine value. Record the reading as "A".

6. The amount of permanganate in the original filtered sample is calculated using the following equation:

$$\text{mg/L } KMnO_4 = (\text{reading "A"} \times 0.893)$$

Additional Drinking Water Methods

Additional analytical methods are available from Carus Chemical Company. Those methods include;

Method 102: Determination of CAIROX® Potassium Permanganate Residual for Drinking Water Applications-Spectrophotometric Method

Method 104: Determination of CAIROX® Potassium Permanganate Value (PV_t) for Drinking Water Applications- DPD Spectrophotometric Method

Method 106: Determination of CAIROX® Potassium Permanganate with Free Chlorine in Drinking Water Applications-DPD Spectrophotometric Method

Method 110: The CAIROX® Potassium Permanganate Jar Test (Treatability Study) for Water Treatment

Standard Methods, 4500-$KMnO_4$, *From Standard Methods for the Examination of Water and Wastewater, 20th Edition ©1998.*

Carus Chemical Company
315 Fifth Street
P. O. Box 599
Peru, IL 61354
Tel. (815) 223-1500
Fax (815) 224-6697
Web:www.caruschem.com
E-Mail:salesmkt@caruschem.com

The information contained herein is accurate to the best of our knowledge. However, data, safety standards and government regulations are subject to change; and the conditions of handling, use or misuse of the product are beyond our control. Carus Chemical Company makes no warranty, either express or implied, including any warranties of merchantability and fitness for a particular purpose. Carus also disclaims all liability for reliance on the completeness or confirming accuracy of any information included herein. Users should satisfy themselves that they are aware of all current data relevant to their particular uses.

 Copyright© 2001

(Carus and Design) is a registered service mark of Carus Corporation. CAIROX® is a registered trademark of Carus Corporation. rev. 1/2004
Responsible Care® is a registered service mark of the American Chemistry Council.

JAR TESTING FOR POTASSIUM PERMANGANATE DEMAND

Stock Solutions
(Strong Stock Solution)
5 grams potassium permanganate dissolved in 500 mL distilled water.

(Test Stock Solution)
1 mL strong stock solution thoroughly mixed in 100 mL distilled water.

Each 10 mL of the test stock solution added to a 1000 mL sample equals 1 ppm.

If you have a six position stirrer:

Using a graduated cylinder, measure 1000 ml . of the sample to be tested into each of the six beakers. Dose each beaker to simulate plant practices in pre-treatment, pH adjustment, coagulant, etc. Do not add carbon or chlorine. Using a graduated pipet, dose each beaker with the test stock solution in the following manner.

Jar #	$KMnO_4$ mL	$KMnO_4$ ppm	Color
1	1.0	0.10	no pink
2	1.5	0.15	no pink
3	2.0	0.20	no pink
4	2.5	0.25	no pink
5	3.0	0.30	pink
6	3.5	0.35	pink

Stir the beakers to simulate the turbulence where the $KMnO_4$ is to be added and observe the color change.

As the iron and manganese begin to oxidize, the sample will turn varying shades of brown, indicating the presence of oxidized iron and or manganese. Samples which retain a brown or yellow color indicate that the oxidation process is incomplete and will require a higher dosage of $KMnO_4$. The end point has been reached when a pink color is observed and remains for at least 10 minutes. In the preceding table a pink color first developed in beaker #5 which had been dosed with 3 mL/0.3 ppm. If the first jar test does not produce the correct color change, continue with increased dosages.

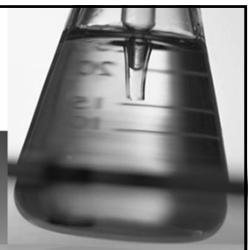
When applying potassium permanganate to raw water, care must be taken not to bring pink water to the filter unless you have "green sand". Also, permanganate generally reacts more quickly at pH levels above 7.0.

A quick way to check the success of a $KMnO_4$ application is by adding 5 mL of the test stock solution to 1000 mL finished water. If the sample turns brown there is iron or manganese remaining in the finished water. If the sample remains pink, oxidation is complete.

With proper application, potassium permanganate is an extremely useful chemical treatment. As well as being a strong oxidizer for iron and manganese, $KMnO_4$ used as a disinfectant in pre-treatment could help control the formation of trihalomethanes by allowing chlorine to be added later in the treatment process or after filtration. Its usefulness also extends to algae control as well as many taste odor problems.

Request Further Information

Section 6
Chlorine, Free Residual and Total



Chlorine Residual

Water Treatment Lab

Chlorination

- Chlorination is the process of adding chlorine to water for the destruction or inactivation of pathogenic (disease-causing) organisms

Chemistry of Chlorination

$$Cl_2 + H_2O \rightarrow \underset{\text{hypochlorous acid}}{HOCl} + \underset{\text{hydrochloric acid}}{HCl}$$

- Hypochlorous acid
  - Most effective disinfectant
  - Prevalent at pH less than 7

    Dissociates at higher pH:

    $$HOCl \rightarrow H^+ + \underset{\text{hypochlorite ion}}{OCl^-}$$
  - Hypochlorite ion is only 1% as effective as hypochlorous acid.

Chemistry of Hypochlorination

$$NaOCl + H_2O \rightarrow \underset{\text{hypochlorous acid}}{HOCl} + NaOH$$

- Sodium hypochlorite will slightly raise the pH because of the sodium hydroxide (NaOH)

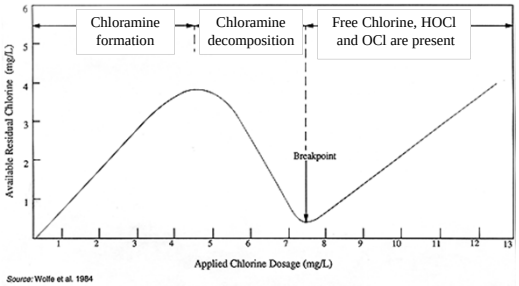
Chemistry of Chlorination

- Chlorine reacts with reducing agents in the water
  - organic matter
  - iron and manganese
  - nitrites
- No free residual will be formed until all reducing agents are destroyed
- Chlorine also reacts with ammonia and organics to form combined residuals
- These are not as effective as free residual

Residual Formation

- The breakpoint is the point at which the chlorine dosage has met the demand
- Any additional chlorine will result in a free residual

Breakpoint



Source: Wolfe et al. 1984

Figure 3.6 Theoretical breakpoint chlorination scheme (1.0 mg/L ammonia-nitrogen; pH 7; temperature 25°C; contact time 2 hours)

Chlorine Demand

- Chlorine Demand
  - The difference between the chlorine added to the water and the amount of residual chlorine remaining after a given time
    - Dose = Demand + Residual

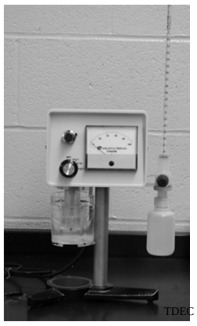
Chlorine Demand

- Chlorine demand can be measured by using separate samples (same source, divided up into separate samples) each dosed with a series of increasing doses of chlorine
- After appropriate contact time, measure free chlorine residual
- Demand is determined by the difference between the original dose and the final free residual concentration

Disinfection Control Tests

- Chlorine Residual
  - Presence of residual
  - Free or combined
  - Concentration
  - By amperometric titration (most accurate, not affected by color or turbidity) or DPD method
- Bacteriological Test
  - Indicates fecal contamination
  - Coliforms are more resistant to chlorine than other fecal bacteria, if coliforms are not present, other fecals will not be present either

Amperometric Titration



- Accurate and unaffected by sample color or turbidity
- Takes greater skill to use than DPD method with colorimetric devices

Amperometric Titration Procedure

- Fill burette with 0.0056N phenylarsine oxide (PAO)
- Measure 200 mL samples into cell and place in the holder on the titrator
- Unless sample pH is known to be between 6.5 and 7.5, add 1 mL of pH 7 phosphate buffer to produce pH of 6.5 – 7.5
- Turn on stirrer and adjust control knob until meter reads max on scale

Amperometric Titration Procedure

- Add PAO in 0.1 mL increments
  - This should cause the meter reading to deflect downward
- Adjust the control knob as needed to keep the pointer on the scale
- End-point is reached when the addition of titrant no longer results in a downward deflection

Amperometric Titration Procedure

- Read the burette
  - Subtracting the last amount added (that did not cause a downward deflection)
  - The burette reading in mL equals the free chlorine residual in mg/L

DPD Colorimetric Method

- Easiest method
- Detection of chlorine residual at 0.02 – 2.00 mg/L (depending on instrument and DPD)
- Zero instrument on sample before adding DPD
- Swirl to mix the DPD for 20 seconds
- Within one minute, read sample

DPD Colorimetric Method

- Pocket Colorimeter can read low and high range
  - Low range is 0 – 2.00
  - High range is
    - Pocket Colorimeter = 0 – 4.5
    - Pocket Colorimeter II = 0.1 – 8.0

Pocket Colorimeter

Pocket Colorimeter II

0.02 – 2.00 mg/L Cl_2

1. Fill a 10-mL cell with sample (the blank). Cap.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

2. Press the **POWER** key to turn the meter on.

The arrow should indicate the low range channel (LR).

Note: *See page 2–4 for information on selecting the correct range channel.*

3. Remove the meter cap. Place the blank in the cell holder with the diamond mark facing the keypad. Fit the meter cap over the cell compartment to cover the cell.

Note: *Wipe excess liquid and finger prints off sample cells.*

0.02 – 2.00 mg/L Cl_2

4. Press **ZERO/SCROLL**.

The display will show "- - - -" then "0.00".

Remove the blank from the cell holder.

5. Fill a second 10-mL cell to the 10-mL line with sample.

Note: *Do not use the same sample cells for free and total chlorine analysis without thoroughly rinsing the cells with sample between free and total tests.*

6. Add the contents of one DPD **Free** Chlorine Powder Pillow or one DPD **Total** Chlorine Powder Pillow to the sample cell (the prepared sample).

Note: *SwifTest™ Dispensers for Free or Total Chlorine can be used in place of powder pillows.*

0.02 – 2.00 mg/L Cl_2

7. Cap and shake gently for 20 seconds.

Note: *Shaking dissipates bubbles that may form in samples with dissolved gases.*

Note: *A pink color will develop if chlorine is present.*

8. For **free** chlorine, place the prepared sample cell in the cell holder. Cover with the instrument cap and proceed to step 10 within **one** minute after adding the DPD Free Pillow.

Note: *Accuracy is not affected by undissolved powder.*

Note: *Wipe off sample cells.*

9. For **total** chlorine, place the prepared sample in the cell holder and cover the cell with the instrument cap. Wait **three to six** minutes after adding the DPD Total Pillow.

Proceed to step 10.

0.02 – 2.00 mg/L Cl_2

10. Press **READ/ENTER**.

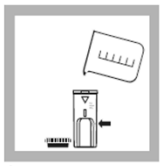
The instrument will show "- - - -" followed by the results in mg/L chlorine.

Note: *If the sample temporarily turns yellow after reagent addition, or if the display shows overrange (page 2–12) dilute a fresh sample and repeat the test. A slight loss of chlorine may occur because of the dilution. Multiply the result by the appropriate dilution factor.*

0.1 – 8.0 mg/L Cl_2

- Press the MENU key.
- The display will show "SEL".
- A flashing arrow indicates the current range.
- Press the READ/ENTER key to toggle between ranges.
- Press MENU again to accept and exit back to the measurement screen.

0.1 – 8.0 mg/L Cl_2



1. Fill a 1-cm/10-mL cell with sample (the blank). Cap.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

2. Press the **POWER** key to turn the meter on.

The arrow should indicate the high range channel (HR).

Note: *See page 2–4 for information on selecting the correct range channel.*

3. Remove the meter cap. Place the blank into the cell holder, with the diamond mark facing the back of the cell holder. Cover the cell with the cap.

Note: *Wipe liquid off sample cells.*

0.1 – 8.0 mg/L Cl_2

4. Press: **ZERO/SCROLL**
The display will show "- - - -" followed by "0.0".
Remove the blank.

5. Fill another 1-cm/10-mL sample cell to the 5-mL line with sample. Cap.
Note: *Do not use the same sample cells for free and total chlorine without thoroughly rinsing the cells between the free and total tests.*

6. Add the contents of two DPD **Free** Chlorine or two DPD **Total** Chlorine Powder Pillows to the sample cell (the prepared sample). Cap the cell and shake gently for 20 seconds.
Note: *Gentle shaking dissipates bubbles which may form in samples containing dissolved gases.*

0.1 – 8.0 mg/L Cl_2

7. For **free** chlorine, place the prepared sample cell in the cell holder and cover with the instrument cap within **one** minute after adding the DPD Free Pillow.
Proceed immediately to step 9.
Note: *The SwifTest™ Dispenser can be used in place of the powder pillow (see page 1—38).*

8. For **total** chlorine, place the prepared sample in the cell holder and cover with the instrument cap. Wait **three to six** minutes after adding the DPD Total Pillows. Proceed to step 9.
Note: *Wipe off sample cells.*

9. Press **READ/ENTER**.
The instrument will show "- - - -" followed by the results in mg/L chlorine (Cl_2).

10 – 200 mg/L Cl_2

High Range Chlorine Test Kit 10–200 mg/L

WARNING: Handling chemical samples, standards, and reagents can be dangerous. Review the Material Safety Data Sheets before handling any chemicals.

Note: *Very high organic matter content may make the endpoint difficult to detect.*

English

1. Fill the plastic measuring tube to the top with sample.
Pour the sample from the measuring tube into the square mixing bottle.

2. Add the contents of one Potassium Iodide Powder Pillow to the bottle. Swirl to mix.

3. Add the contents of one Sulfamic Acid Powder Pillow to the bottle.
Swirl gently to mix. A yellow color will develop if chlorine is present.

4. Add the Sodium Thiosulfate Solution drop by drop while swirling the mixing bottle. When the color changes from yellow to colorless, record the number of drops added.

5. Multiply the number of drops added by 10 to obtain the chlorine concentration in mg/L.

DPD Accuracy Check

- Pre-made Gelex Standards
  - Similar to turbidity secondary standards
  - Make sure to check expiration dates

DPD Accuracy Check

- Potassium permanganate solutions
  - Weigh out 0.891g of reagent grade $KMnO_4$
  - Transfer to 1000 mL volumetric flask, fill with distilled water and mix
  - Transfer 10 mL of this solution to 100 mL flask, fill with distilled water and mix

40CFR136

Method Update Rule
For Backwash Lagoons that have Discharge Permits
May 10, 2013
Fleming Training Center

40 CFR 136 05-21-2012 Table 1B

Parameter	Methodology	EPA	Standard Methods	ASTM	USGS/AOAC/ Other
Chlorine-Total Residual, mg/L	Amperometric Direct	……	4500-Cl D-2000	D1253-08	
	Amperometric Direct (Low Level)	……	4500-Cl E-2000		
	Iodometric Direct	……	4500-Cl B-2000		
	Back Titration Ether End-Point[15]	……	4500-Cl C-2000		
	DPD-FAS	……	4500-Cl F-2000		
	Spectrophotometric, DPD	……	**4500-Cl G-2000**		
	Electrode	……	……	……	See Footnote [16]

12 Quality Control Elements

1. DOC – demonstration of capability
2. MDL – method detection level
3. LRB/MB – method blank
4. LFB – laboratory fortified blank (standard)
5. LFM/LFMD – laboratory fortified matrix/duplicate (spike)
6. Internal standards, surrogate standards or tracer – ***only applies to organic analysis and radiochemistry***
7. Calibration- initial and continuing
8. Control charts or other trend analysis
9. Corrective action – root cause analysis
10. QC acceptance criteria
11. Definition of a batch (preparation and analytical)
12. Minimum frequency for conducting all QC elements
13. Unwritten 13th Step – SOP – Standard Operating Procedures need to be written and followed for all lab sampling and analyses

Not all of these items apply to all tests, there are many exceptions!

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- DOC
- MDL
- LRB
- LFB
- Dup
- ICAL/CCV
- Control Charts
- Corrective Action
- QC Acceptance
- Batch Size
- QC Frequency

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Demonstration of Capability (DOC)
  - Run a laboratory-fortified blank (LFB) at least four times and compare to the limits listed in the method
    - No limits listed for chlorine
  - Real people language: each operator running this test need to analyze 4 samples of a Chlorine Standard or Potassium Permanganate ($KMnO_4$) at a concentration around 0.5 mg/L.
  - Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.
  - Recommend backup analyst do this once a year.

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Method Detection level
  - HACH- Estimated Detection Level=0.02mg/L
  - From SM 1030 C.
    - 0.02mg/L * 5= 0.10 mg/L~ MDL
    - **Make a 0.10 mg/L standard**
    - **Analyze 7 portions over ≥ 3 days**
    - Calculate standard deviation (s)
    - n1 Σ+ n2 Σ+ n3 Σ+…….n7 Σ+ 2nd σxn= s
    - s* 3.14= MDL

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Laboratory Reagent Blank
  - Real people language: analyze distilled water as a sample by adding DPD powder pillow and waiting the 3-6 minutes before reading
    - Target value is less than MDL
    - Run **Daily (or day of for monthly reporting purposes)**
- Laboratory Fortified Blank
  - Real people language: analyze a chlorine standard or potassium permanganate ($KMnO_4$) at a concentration around 0.5 mg/L
    - Run on a 5% basis, one for every 20 samples **(or day of for monthly reporting purposes)**
- Duplicates of the sample
  - Run on a 5% basis, one for every 20 samples **(or day of for monthly reporting purposes)**
  - Calculate %RPD, ≤ 20%

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Initial Calibration
  - Prepare a set of chlorine standard or potassium permanganate ($KMnO_4$) in accordance with the Guidance for Secondary Standards Use in Calibration **monthly**.
    - Once per month at minimum, before the use of new DPD reagents, or the use of new gel standards

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Stock Standard Solution
  - 0.891 grams of reagent grade $KMnO_4$ in 1000 mL vol. flask made to mark with deionized water.
  - Deionized water must never be stored in plastic containers or exposed to airborne contamination.
  - Store the stock solution in amber bottle in a cool area.
  - The typical shelf life of the stock solution is six (6) months.
  - If solids appear in the solution, **do not use.**

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Intermediate (Working) Standard Solution
  - 10 mL of STOCK made in 1000 mL vol. flask made to mark with deionized water.
  - The flask should be labeled with the name, $KMnO_4$, date of preparation, initials of who made it.
  - This information should also be entered into a logbook.
- **The intermediate stock solution should be stable for approximately 5 days if kept cool and away from light.**

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Potassium Permanganate Standard Solution
  - Care should be taken that the pipette and glassware are clean and thoroughly rinsed with deionized water to avoid contamination.
  - Store only in glass container (preferably amber glass) never in plastic containers.
  - The working solution should be remade if solids appear in the bottom of the container.

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Calibration Standard Solutions
  - Four to five calibration standard solutions should be made according to the table below to create a calibration curve once per month at a minimum.
  - The linear regression of the curve should correlate to 0.995 or better.
  - This curve is then used to check or calibrate the instrument.
  - Gel standards are run against the curve and must agree to within + 10%.
- **The working solution should be stable for approximately 2 hours and will fade rapidly (within 15 minutes) if chlorine demand-free water is not used.**

Total Residual Chlorine SM4500-Cl G - 2000, DPD

- Calibration Standard Solutions
  - A target value (e.g. permit value for a facility) should be known and three gel standards, 0.00 mg/L, blank, and two other standards (a low and a high standard) that bracket the target value should be chosen.
  - Gel standards are run against the curve and must agree to within + 10%.

Total Residual Chlorine
SM4500-Cl G - 2000, DPD

mL Working Standard Diluted w/Deionized water	Chlorine Equivalent mg/L
20 mL (vol. Pipette) to 100 mL (vol. flask)	2.0 mg/L
10 mL (vol. Pipette) to 100 mL (vol. flask)	1.0 mg/L
5 mL (vol. Pipette) to 100 mL (vol. flask)	0.5 mg/L
1 mL (vol. Pipette) to 100 mL (vol. flask)	0.1 mg/L
1 mL (vol. Pipette) to 200 mL (vol. flask)	0.05 mg/L
1 mL (vol. Pipette) to 500 mL (vol. flask)	0.02 mg/L
100 mL of deionized water	0.00 mg/L

Don't forget to use DPD on Potassium Permanganate standards

Total Residual Chlorine
SM4500-Cl G - 2000, DPD

- Calibration Verification **daily (or day of for monthly reporting purposes)**
- Verify meter with secondary gel standards using a minimum of one blank and two gel standards that bracket the expected sample concentration
- OR verify meter after running samples with a standard of chlorine or potassium permanganate

Chlorine Lab Math

1. A water system has a chlorine demand of 4.1 mg/L and wants to have a 1.1 mg/L residual. What would be the dose?

2. A system just had a main break. The chlorine level of 3.3 mg/L has dropped to 0.3 mg/L. What is the chlorine demand?

3. A water plant treats 7.5 MGD. If the chlorine dose needs to be 3 mg/L, what is the chlorine requirement in pounds per day?

4. Determine the chlorine dose in mg/L if 13 pounds of chlorine are fed while treating 968,000 gallons of water.

5. How many pounds of 65% available chlorine HTH is needed to make 1 gallon of 10% solution?

6. How many gallons of bleach (15% available chlorine) will it take to make a 4% solution when added to enough water to make 50 gallons of hypochlorite?

Answers:

1. 5.2 mg/L
2. 3.0 mg/L
3. 188 lbs/day
4. 1.62 mg/L
5. 1.28 lbs
6. 13 gallons

Chlorine

Calibration Curve & Method Detection Limit (MDL)

The Use of Secondary Standards for Spectrophotometer/Colorimeter Calibration

- Secondary standards (gel standards) are specifically designed to verify the instrument's calibration and to check the instrument's performance.
- They are not intended to be used to create calibration curves or to calibrate the instrument.
- Because the DPD reagent cannot be mixed with the gel standards, the quality and the reaction time of the reagent cannot be assessed.
- For these reasons gel standards cannot take the place of primary standards.

TDEC TENNESSEE DEPARTMENT OF ENVIRONMENT AND CONSERVATION

The Use of Secondary Standards for Spectrophotometer/Colorimeter Calibration

- The analyst is responsible for the following:
  - Preparing the calibration curve for each instrument once per month at a minimum with chlorine standards or potassium permanganate (see instructions below for $KMnO_4$), before the use of new DPD reagents, or the use of new gel standards
  - Recording reagent lot #'s for reagents and standards
  - Recording calibration concentrations
  - Verifying the calibration curve using a minimum of one blank and two gel standards that bracket the expected sample concentration
  - Recording all verification data

Potassium permanganate ($KMnO_4$) stock standard solution

- 0.891 grams of reagent grade $KMnO_4$ in 1000 mL vol. flask made to mark with deionized water.
- Deionized water must never be stored in plastic containers or exposed to airborne contamination. Store the stock solution in an amber bottle in a cool area.
- The typical shelf life of the stock solution is six (6) months. If solids appear in the solution, do not use
- ***Avoid leaving the cap off for extended periods of time and avoid contamination.***

Intermediate (working) standard solution (10 mg/L)

- 10 mL of STOCK made in 1000 mL vol. flask made to mark with deionized water.
- The flask should be labeled with the name, $KMnO_4$, date of preparation, and initials of who made it.
- This information should also be entered into a logbook
- **The intermediate stock solution should be stable for approximately 5 days if kept cool and away from light.*
- Care should be taken that the pipette and glassware are clean and thoroughly rinsed with deionized water to avoid contamination.
- Store only in a glass container (preferably amber glass) never in plastic containers. The working solution should be remade if solids appear in the bottom of the container

Calibration Standard Solutions

- If using $KMnO_4$, four to five calibration standard solutions should be made according to the table on the next slide with the addition of DPD to create a calibration curve ***once per month*** at a minimum.
- The correlation coefficient of the curve should correlate to 0.995 or better.
- This curve is then used to check instrument calibration.
- Gel standards are run against the curve and must agree to within $\pm$ 10%
- **The working solution should be stable for approximately 2 hours and will fade rapidly (within 15 minutes) if chlorine demand-free water is not used.**

ICV/CCV –Chlorine

mL Working Standard Diluted w/Deionized water	Chlorine Equivalent mg/L
20 mL (vol. Pipette) to 100 mL (vol. flask)	2.0 mg/L
10 mL (vol. Pipette) to 100 mL (vol. flask)	1.0 mg/L
5 mL (vol. Pipette) to 100 mL (vol. flask)	0.5 mg/L
1 mL (vol. Pipette) to 100 mL (vol. flask)	0.1 mg/L
½ mL (vol. Pipette) to 100 mL (vol. flask)	0.05 mg/L
1 mL (vol. Pipette) to 500 mL (vol. flask)	0.02 mg/L
100 mL of deionized water	0.00 mg/L

Don't forget to use DPD on Potassium Permanganate standards

Calibration Standard Solutions

Dilutions for Today's Example – Pick 4

mL Working Standard Diluted w/Deionized water	Chlorine Equivalent mg/L
20 mL (vol. Pipette) to 100 mL (vol. flask)	2.0 mg/L
10 mL (vol. Pipette) to 100 mL (vol. flask)	1.0 mg/L
5 mL (vol. Pipette) to 100 mL (vol. flask)	0.5 mg/L
1 mL (vol. Pipette) to 100 mL (vol. flask)	0.1 mg/L
½ mL (vol. Pipette) to 100 mL (vol. flask)	0.05 mg/L
1 mL (vol. Pipette) to 500 mL (vol. flask)	0.02 mg/L

Don't forget to use DPD on Potassium Permanganate standards

Subject	true value (x)	value read (y)
1	0.02	0.02
2	0.05	0.03
3	0.10	0.05
4	0.50	0.42
5	1.00	0.91
R^2 =	**0.997567397**	

Although, still greater than 0.995

Not a good recovery, tried a second dilution

Calibration Standard Solutions

Subject	true value (x)	value read (y)
1	0.02	0.02
2	0.05	0.03
3	0.10	0.09
4	0.50	0.42
5	1.00	0.91
R^2 =	**0.99833**	

Better than previous calibration curve

Better recovery with second dilution

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, use an estimate of five times the estimated true detection level (5 x 0.010 mg/L = 0.050 mg/L).
  - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
  - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.
- 4020 B.1.b. – Verify MDL at least annually.
  - Ideally use pooled data from several analysts rather than data from one analyst.

Method Detection Limit (MDL)

- Real people language – have several operators, who run this test, analyze chlorine or Potassium Permanganate ($KMnO_4$) standards at a concentration of 0.05 mg/L over several days with a total of at least 7 samples
  - Joe analyzes 3 samples on Monday
  - Bob analyzes 3 samples on Tuesday
  - Mary analyzes 3 samples on Wednesday
- Run this once a year

Method Detection Limit (MDL)

Dilutions for Today's Example for MDL

mL Working Standard Diluted w/Deionized water	Chlorine Equivalent mg/L
½ mL (vol. Pipette) to 100 mL (vol. flask)	0.05 mg/L

Don't forget to use DPD on Potassium Permanganate standards

Date	Analyst	Number	True Value	Value Read	% Recovery (50-150%)
12/27/13	SEP	1	0.05	0.06	120.00
12/27/13	SEP	2	0.05	0.05	100.00
12/27/13	SEP	3	0.05	0.05	100.00
12/27/13	SEP	4	0.05	0.08	160.00
12/27/13	SEP	5	0.05	0.04	80.00
12/27/13	SEP	6	0.05	0.05	100.00
12/27/13	SEP	7	0.05	0.06	120.00
			Standard Deviation	0.012724	
			Relative Standard Deviation (RSD)	22.83827	(Needs to be ≤ 20%)
			MDL	0.03995	

Chlorine, Free

DOC316.53.01023

USEPA DPD Method[1] **Method 8021**

(0.02 to 2.00 mg/L) **Powder Pillows or AccuVac® Ampuls**

Scope and Application: For testing free chlorine (hypochlorous acid and hypochlorite ion) in water, treated waters, estuary and seawater. USEPA accepted for reporting for drinking water analyses.[2]

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater.*

[2] Procedure is equivalent to USEPA and Standard Method 4500-Cl G for drinking water.

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

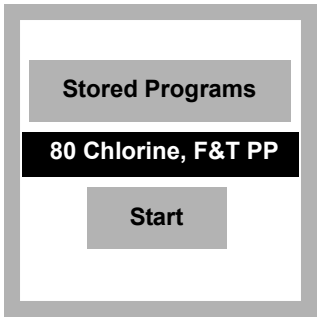
If the test over-ranges, dilute the sample with a known volume of high quality, chlorine demand-free water and repeat the test. Some loss of chlorine may occur due to the dilution. Multiply the result by the dilution factor. Alternatively, samples with high chlorine concentrations may be analyzed directly without dilution by using Method 10069, Chlorine, Free HR, or Method 10245, Chlorine Free MR .
The SwifTest Dispenser for Free Chlorine can be used in place of the powder pillow in step 4.
Analyze samples immediately. Do not preserve for later analysis.
The sample cell shown is a generic representation. Refer to *Instrument-specific information* for the correct sample cell and adapter configuration.
An empty AccuVac ampule can be used as a blank in place of the sample cell in Step 2.
Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

Collect the following items:

Description	Quantity
Powder Pillow Test:	
DPD Free Chlorine Reagent Powder Pillows, 10-mL	1
Sample Cells (see *Instrument-specific information*)	2
AccuVac Test:	
DPD Free Chlorine Reagent AccuVac® Ampuls	1
Beaker, 50-mL	1
Sample Cell (see *Instrument-specific information*)	1

See *Consumables and replacement items* for reorder information.

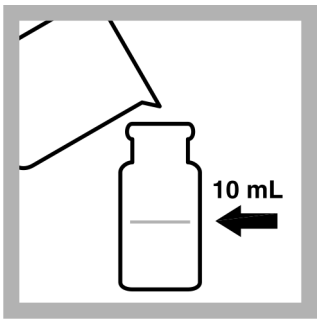
Powder pillow procedure



1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



2. Blank Preparation: Fill a sample cell with 10 mL of sample.

3. Wipe the blank and insert it into the cell holder.

ZERO the instrument.

The display will show:

0.00 mg/L Cl_2

4. Prepared Sample: Fill a second cell with 10 mL of sample.

Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell.

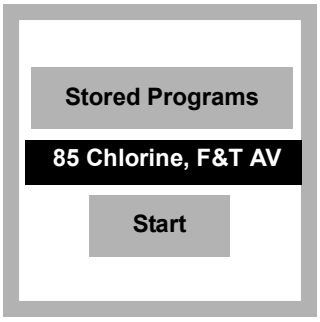
5. Swirl the sample cell for 20 seconds to mix.

A pink color will develop if chlorine is present. Proceed to step 6 immediately.

6. Within one minute of adding the reagent, insert the prepared sample into the cell holder.

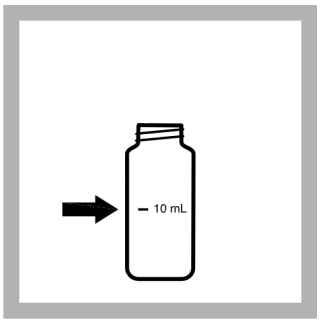
Results are in mg/L Cl_2.

AccuVac Ampuls procedure



1. Select the test.

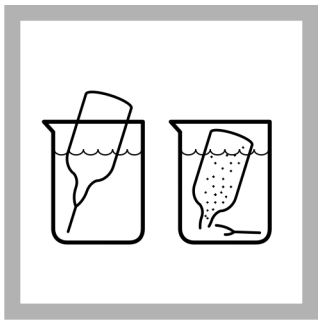
Insert an adapter if required (see *Instrument-specific information*).



2. Blank Preparation: Fill a sample cell with 10-mL of sample.

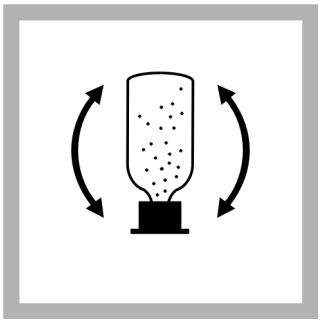
3. Wipe the blank and insert it into the cell holder.

ZERO the instrument. The display will show: 0.00 mg/L Cl_2

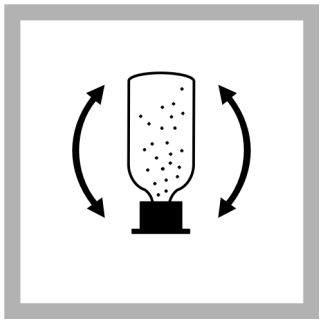


4. Prepared Sample: Collect at least 40 mL of sample in a 50-mL beaker.

Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



5. Quickly invert the Ampul several times to mix. Wipe off any liquid or fingerprints.



6. Within one minute after sample addition, wipe the AccuVac Ampul and insert it into the cell holder.

READ the results in mg/L Cl_2

Interferences

Table 2 Interfering substances and levels

Interfering substance	Interference levels and treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N Sodium Hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition.
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N Sulfuric Acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition.
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1000 mg/L as $CaCO_3$
Iodine, I_2	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6–7. **2.** Add 3 drops Potassium Iodide (30-g/L) to a 10-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops Sodium Arsenite [1] (5-g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L increase in the reading.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH or highly buffered samples	Adjust to pH 6–7 using acid (Sulfuric Acid, 1.000 N) or base (Sodium Hydroxide, 1.00 N).

[1] Samples treated with sodium arsenite for interferences will be hazardous waste as regulated by Federal RCRA for arsenic (D004). See the current MSDS for proper disposal of hazardous material.

Sample collection, preservation and storage

- Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of free chlorine in water.
- Avoid plastic containers since these may have a large chlorine demand.
- Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

- A common error in testing for chlorine is not obtaining a representative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine analysis immediately.

Accuracy check

Standard additions method (Sample spike)
Required for accuracy check:

- Chlorine Standard Solution, 2-mL PourRite® Ampule, 25–30 mg/L
- Breaker, PourRite Ampules
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select Options>More>Standard Additions from the instrument menu.
3. Enter the average chlorine concentration shown on the label of the ampule container.
4. A summary of the standard additions procedure will be displayed. Press **OK** to accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row.
5. Open one Voluette ampule standard.
6. Prepare spiked samples: add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 10-mL portions of fresh sample.

   Note: *For AccuVac® Ampuls, add 0.4 mL, 0.8 mL and 1.2 mL of standard to three 50-mL portions of fresh sample.*

7. Follow the test procedure for each of the spiked samples using the powder pillows or AccuVac ampules, starting with the smallest sample spike. Measure each of the spiked samples in the instrument.
8. Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Note: *If results are not within acceptable limits (± 10%), be sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If all procedures are followed correctly but the standard additions results are not within acceptable limits, the sample may contain an interference.*

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
80	1.25 mg/L Cl_2	1.23–1.27 mg/L Cl_2	0.02 mg/L Cl_2
85	1.25 mg/L Cl_2	1.21–1.29 mg/L Cl_2	0.02 mg/L Cl_2

Summary of method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color, the intensity of which is proportional to the chlorine concentration. Test results are measured at 530 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
DPD Free Chlorine Reagent Powder Pillows, 10-mL	1	100/pkg	2105569
OR			
DPD Free Chlorine Reagent AccuVac® Ampuls	1	1	2502025

Required apparatus

Description	Quantity	Unit	Catalog number
Beaker, 50-mL	1	each	50041H
AccuVac Snapper	1	each	2405200
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402

Recommended standards

Description	Unit	Catalog number
Chlorine Standard Solution, 2-mL PourRite® Ampule, 25–30 mg/L	20/pkg	2630020
PourRite Ampule breaker, 2-mL	each	2484600

Optional reagents and apparatus

Description	Unit	Catalog number
Chlorine-demand Free Water	500 mL	2641549
Cylinder, mixing, 25 mL	each	2088640
Cylinder, mixing, 50 mL	each	189641
Sodium Hydroxide, 1 N	100 mL	104532
Sulfuric Acid, 1 N	100 mL	127032
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
SwifTest Dispenser for Free Chlorine[1]	each	2802300
Pipet, TenSette®, Pipet, 0.1 - 1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
pH Paper, 0 - 14 pH range	100/pkg	2601300
Voluette Ampule breaker, 10 mL	each	2196800
AccuVac, vials for sample blanks	25/pkg	2677925
Chlorine Standard Solution, 2-mL PourRite® Ampule, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
DPD Free Chlorine Reagent Powder Pillows, 10-mL	1000/pkg	2105528
DPD Free Chlorine Reagent Powder Pillows, 10-mL	300/pkg	2105503
DPD Free Chlorine Reagent, 10 mL, SwifTest Dispenser refill vial	250 tests	2105560
SpecCheck Secondary Standard Kit, Chlorine DPD, 0–2.0 mg/L Set	each	2635300

[1] Includes one vial of 2105560 for 250 tests

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company, 2007, 2010. All rights reserved. Printed in the U.S.A.

Edition 6

Chlorine, Free and Total, High Range

DOC316.53.01449

USEPA DPD Method[1] **Method DPD**

0.1 to 8.0 mg/L Cl_2 **Powder Pillows**

Scope and application: For testing higher levels of free chlorine (hypochlorous acid and hypochlorite ion) in water and treated waters. For testing higher levels of total chlorine in water, treated waters and wastewater.[2] This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] USEPA accepted for reporting wastewater and drinking water analyses.
[2] Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water.

Test preparation

Before starting

If the chlorine concentration is typically less than 2 mg/L, use the low range (LR) procedure.
Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Always do tests in sample cells. Do not put the instrument in the sample or pour the sample into the cell holder.
Make sure that the sample cells are clean and there are no scratches where the light passes through them.
Rinse the sample cell and cap with the sample three times before the sample cell is filled.
Make sure that there are no fingerprints or liquid on the external surface of the sample cells. Wipe with a lint-free cloth before measurement.
Cold waters can cause condensation on the sample cell or bubbles in the sample cell during color development. Examine the sample cell for condensation or bubbles. Remove condensation with a lint-free cloth. Invert the sample cell to remove bubbles.
High range (HR) free chlorine determinations are subject to variable levels of interferences from monochloramine. Refer to Interferences on page 4.
Install the instrument cap over the cell holder before ZERO or READ is pushed.
Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.
If the test result is over-range, or if the sample temporarily turns yellow after the reagent addition, dilute the sample with a known volume of high quality, chlorine demand-free water and do the test again. Some loss of chlorine may occur due to the dilution. Multiply the result by the dilution factor. Additional methods are available to measure chlorine without dilution.
After the test, immediately empty and rinse the sample cell. Rinse the sample cell and cap three times with deionized water.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
The SwifTest Dispenser for Free Chlorine or Total Chlorine can be used in place of the powder pillow in the test procedures. One dispensation is equal to one powder pillow for 10-mL samples.

Items to collect

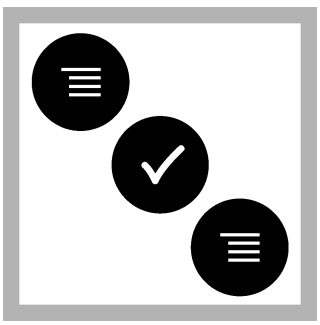
Description	Quantity
Chlorine, Free: DPD Free Chlorine Reagent Powder Pillows, 10-mL	2
Chlorine, Total: DPD Total Chlorine Reagent Powder Pillows, 10-mL	2
Sample cells, 1-cm/10-mL	2

Refer to Consumables and replacement items on page 6 for order information.

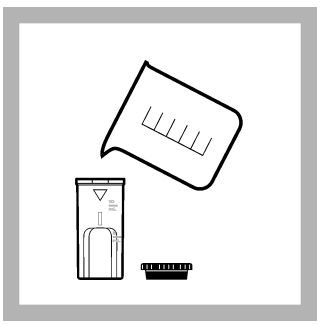
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

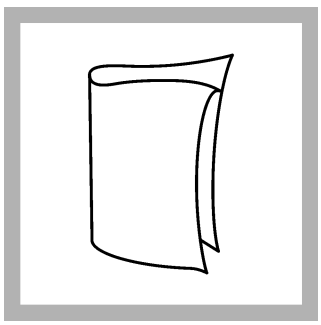
Powder pillow procedure



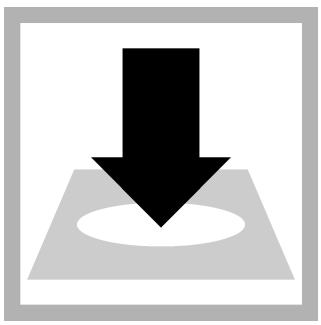
1. Set the instrument to high range (HR). Refer to the instrument documentation.



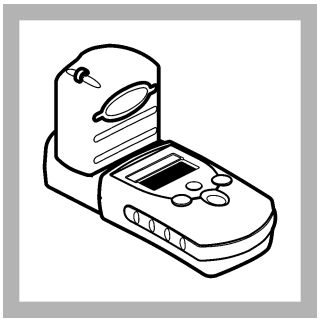
2. Prepare the blank: Fill a 1-cm/10-mL sample cell to the 5-mL mark with sample. Close the sample cell.



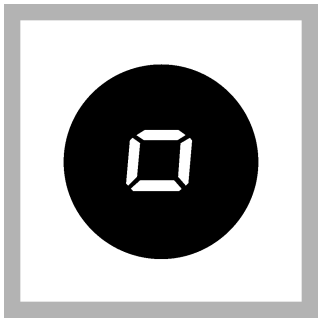
3. Clean the blank sample cell.



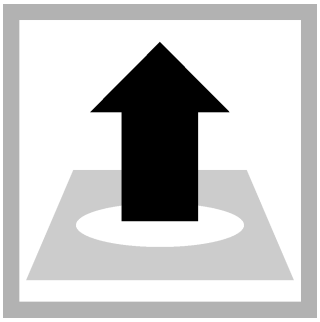
4. Insert the blank into the cell holder. Point the triangle mark on the sample cell away from the keypad.



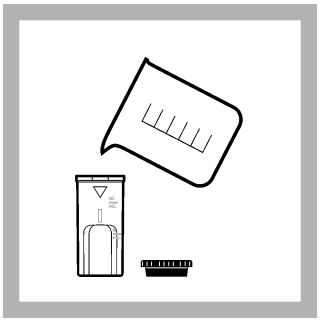
5. Install the instrument cap over the cell holder.



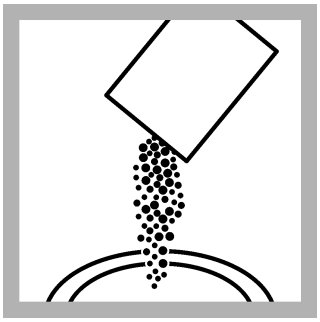
6. Push **ZERO**. The display shows “0.0”.



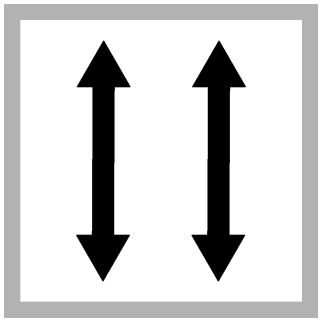
7. Remove the sample cell from the cell holder.



8. Prepare the sample: Fill a second 1-cm/10-mL sample cell to the 5-mL mark with sample.

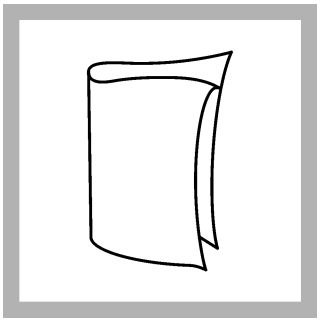


9. Add two 10-mL DPD Free Chlorine Reagent Powder Pillows or two 10-mL DPD Total Chlorine Reagent Powder Pillows to the second sample cell.

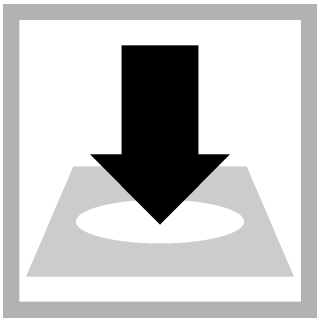


10. Close the sample cell. Shake the sample cell for about **20 seconds** to dissolve the reagent. Undissolved power will not affect accuracy.

A pink color will show if chlorine is in the sample.



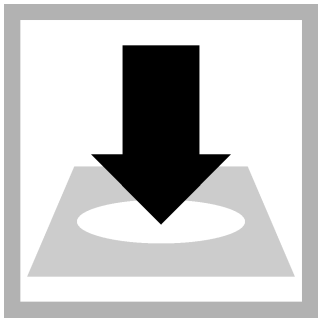
11. Clean the prepared sample cell.



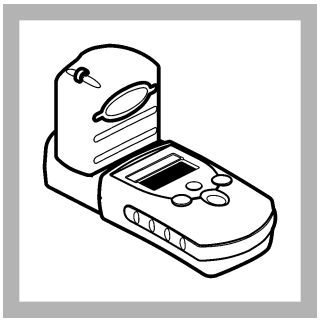
12. Free chlorine measurement: Within 1 minute of the reagent addition, insert the prepared sample into the cell holder. Point the triangle mark on the sample cell away from the keypad.

Go to step 15.

13. Set and start a timer for 3 minutes. A 3-minute reaction time starts.



14. Total chlorine measurement: After 3 minutes and within 6 minutes of the reagent addition, insert the prepared sample into the cell holder. Point the triangle mark on the sample cell away from the keypad.



15. Install the instrument cap over the cell holder.

16. Push READ. Results show in mg/L chlorine (Cl_2).

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to be added on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Alkalinity	More than 250 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Bromine, Br_2	Positive interference at all levels
Chlorine Dioxide, ClO_2	Positive interference at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1000 mg/L as $CaCO_3$
Iodine, I_2	Positive interference at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	Pre-treat the sample as follows: **1.** Adjust the sample pH to 6–7. **2.** Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops of Sodium Arsenite (5-g/L) and mix. **5.** Use the test procedure to measure the concentration of the treated sample. **6.** Subtract this result from the result without the treatment to obtain the correct chlorine concentration.
Monochloramine	For conventional free chlorine disinfection (beyond the breakpoint), monochloramine concentrations are very low. If monochloramine is in the sample, its interference in the free chlorine test changes with the temperature, the relative amount of monochloramine to free ammonia and the time necessary to do the analysis. Table 1 gives the approximate interference levels of monochloramine in the free chlorine test as mg/L Cl_2.
Ozone	Positive interference at all levels
Peroxides	May interfere
Adjust to pH 6–7 with acid (Sulfuric Acid, 1 N) or base (Sodium Hydroxide, 1 N). Correct the test result for the dilution caused by the volume additions.	Can prevent the correct pH adjustment of the sample by the reagents. Sample pre-treatment may be necessary.

Table 1 Monochloramine level versus temperature

NH_2Cl	Sample temperature			
(as Cl_2)	5 °C (40 °F)	10 °C (50 °F)	20 °C (68 °F)	30 °C (83 °F)
1.2	0.2	0.2	0.3	0.3
2.5	0.4	0.5	0.6	0.6
3.5	0.5	0.6	0.7	0.8

Pollution prevention and waste management

If sodium arsenite was added to the sample for manganese or chromium interferences, the reacted samples will contain arsenic and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations. must be

disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Accuracy check

Standard additions method

Use the standard additions method to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Chlorine Standard Solution, 2-mL PourRite® Ampule, 50–75 mg/L (use mg/L on label)
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 5-mL portions of fresh sample. Mix well.
2. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
3. Compare the expected result to the actual result. The expected increase in the chlorine concentration is the Cl_2 mg/L concentration from the label of the standard solution multiplied by 0.1 mL for every 5 mL of standard solution added.

Standard solution method

If the Standard Calibration Adjust feature is used to adjust the calibration curve of the Pocket Colorimeter II, the concentration of the chlorine standard must be between 4.5 and 7.0 mg/L chlorine for the HR procedure.

Verification of on-line analyzers

This procedure can be used to meet the requirements of USEPA Method 334.0 - Determination of Residual Chlorine in Drinking Water Using an On-line Chlorine Analyzer. The procedure and requirements for compliance with EPA Method 334.0 can be downloaded directly from http://www.hach.com/method334.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a Pocket Colorimeter II during ideal test conditions. Users can get different results under different test conditions.

Precision (95% confidence interval)
5.0 ± 0.2 mg/L Cl_2

Summary of method

Chlorine can be in water as free chlorine and as combined chlorine. Both forms can be in the same solution and can be determined together as total chlorine. Free chlorine is in a solution as hypochlorous acid or hypochlorite ion. Combined chlorine represents a combination of chlorine-containing compounds, including monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives. The combined chlorine oxidizes iodide (I^-) to iodine (I_2). The iodine and free chlorine reacts with DPD (N,N-diethyl-p-phenylenediamine) to form a red solution. The color intensity is proportional to the chlorine concentration. To determine the concentration of combined chlorine, complete a free chlorine test and a total chlorine test. Subtract the results of the free chlorine test from the total chlorine test to get the combined chlorine concentration.

To increase the range of analysis, more indicator is added in proportion to the sample volume in the high range procedure. For example, in this high range (HR) procedure two powder pillows made for a 25-mL sample are added to a 5-mL sample to increase the test range.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 10-mL	2	100/pkg	2105569
DPD Total Chlorine Reagent Powder Pillow, 10-mL	2	100/pkg	2105669

Required apparatus

Description	Quantity/test	Unit	Item no.
Sample cells, 1-cm/10-mL	2	2/pkg	4864302

Recommended standards and apparatus

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
PourRite® Ampule Breaker, 2-mL	each	2484600

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25-mL	each	2088640
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Paper, pH, 0–14 pH range	100/pkg	2601300
DPD Free Chlorine Reagent Powder Pillows, 25-mL	1000/pkg	1407028
DPD Total Chlorine Reagent Powder Pillows, 25-mL	1000/pkg	1406428
SwifTest™ dispenser for free chlorine[1]	each	2802300
SwifTest™ dispenser for total chlorine [2]	each	2802400
DPD Free Chlorine Reagent, 10-mL, SwifTest™ Dispenser refill vial	250 tests	2105560
DPD Total Chlorine Reagent, 10-mL, SwifTest™ Dispenser refill vial	250 tests	2105660
SpecCheck™ Gel Secondary Standard Kit, Chlorine DPD, 0–10 mg/L	4/pkg	2893300
Water, organic-free	500 mL	2641549

[1] Includes one vial of 2105560 for 250 tests
[2] Includes one vial of 2105660 for 250 tests

HACH®

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company/Hach Lange GmbH, 2014. All rights reserved. Printed in U.S.A.

04/2014, Edition 1

Chlorine, Total

DOC316.53.01027

USEPA DPD Method[1] **Method 8167**

0.02 to 2.00 mg/L Cl_2 **Powder Pillows or AccuVac® Ampuls**

Scope and application: For testing residual chlorine and chloramines in water, wastewater, estuary water and seawater; USEPA-accepted for reporting for drinking and wastewater analyses.[2] This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] Adapted from Standard Methods for the Examination of Water and Wastewater.
[2] Procedure is equivalent to USEPA and Standard Method 4500-Cl G for drinking water and wastewater analysis.

Test preparation

Instrument-specific information

The tables in this section show all of the instruments that have the program for this test. Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests. Table 2 shows sample cell and adapter requirements for AccuVac Ampul tests.

To use either table, select an instrument, then read across to find the corresponding information for this test.

Table 1 Instrument-specific information for powder pillows

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter	Sample cell
DR 6000 DR 5000 DR 900	—	2427606
DR 3900	LZV846 (A)	
DR 3800 DR 2800 DR 2700	LZV584 (C)	2122800

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
If the test result is over-range, or if the sample temporarily turns yellow after the reagent addition, dilute the sample with a known volume of high quality, chlorine demand-free water and repeat the test. Some loss of chlorine may occur due to the dilution. Multiply the result by the dilution factor. Additional methods are available to measure chlorine without dilution.
For chloramination disinfection control, use one of the available Chloramine (Mono) methods.
For best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to get the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used and use any recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Use the Safety Data Sheets for disposal information for unused reagents. Consult the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
The SwifTest Dispenser for Total Chlorine can be used in place of the powder pillow in the test procedure.
An AccuVac Ampule for Blanks can be used to zero the instrument in the AccuVac test procedure.

Items to collect

Powder pillows

Description	Quantity
DPD Total Chlorine Reagent Powder Pillow, 10-mL	1
Sample cells. (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 7 for reorder information.

AccuVac Ampuls

Description	Quantity
DPD Total Chlorine Reagent AccuVac® Ampul	1
Beaker, 50-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1
Stopper for 18-mm tubes and AccuVac Ampuls	1

Refer to Consumables and replacement items on page 7 for reorder information.

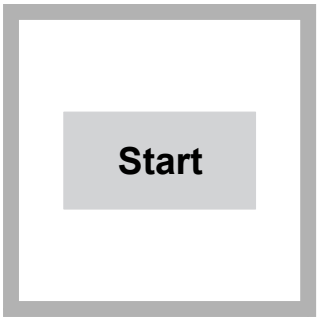
Sample collection

- Samples must be analyzed immediately and cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and it is unstable in natural waters. It reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Avoid plastic containers since these may have a large chlorine demand.
- Pre-treat glass sample containers to remove any chlorine demand. Soak the containers in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample

containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

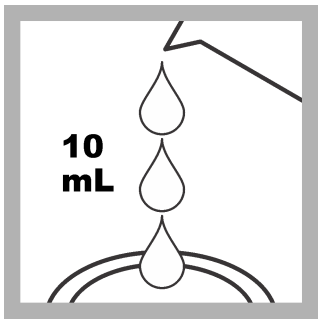
- Be sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Then let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample. If a sample cell is used, rinse the cell several times with the sample, then carefully fill to the 10-mL mark.

Powder pillow procedure



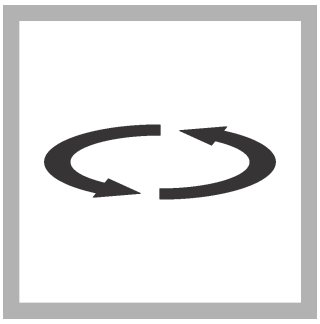
1. Start program **80 Chlorine F&T PP**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

Note: *Although the program name may vary between instruments, the program number does not change.*



2. Fill a sample cell with 10 mL of sample.

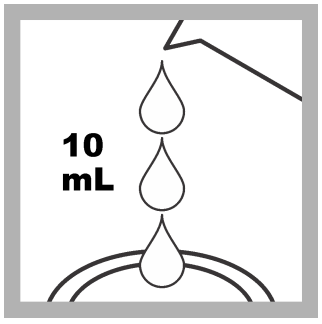
3. Prepare the sample: Add the contents of one powder pillow to the sample cell.



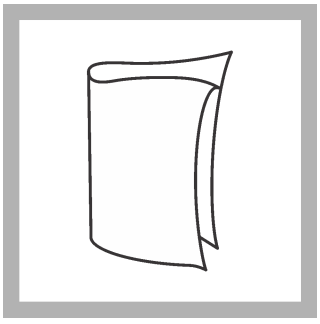
4. Swirl the sample cell for 20 seconds to mix.
A pink color shows if chlorine is present in the sample.

5. Start the instrument timer. A 3-minute reaction time starts.

Prepare the sample blank and set the instrument to zero during the reaction time.

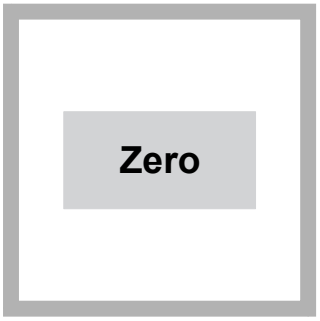


6. Prepare the blank: Fill a second sample cell with 10 mL of sample.

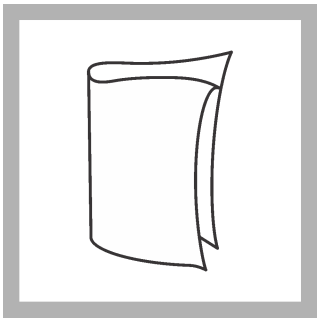


7. Clean the blank.

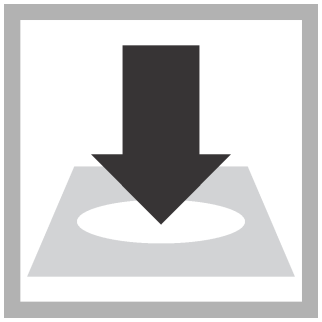
8. Insert the blank into the cell holder.



9. Push **ZERO**. The display shows 0.00 mg/L Cl_2.



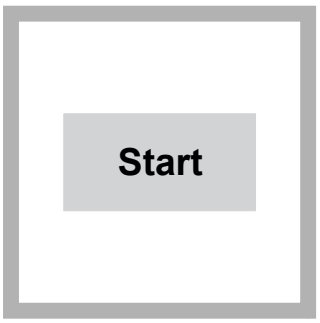
10. Clean the prepared sample.



11. Within 3 minutes after the timer expires, insert the prepared sample into the cell holder.

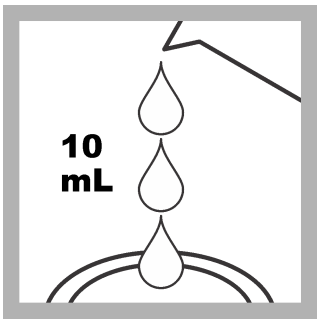
12. Push **READ**. Results show in mg/L Cl_2.

AccuVac Ampul procedure

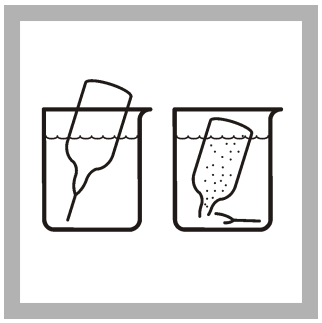


1. Start program **85 Chlorine F&T AV**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

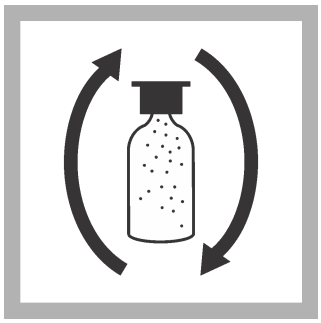
Note: *Although the program name may vary between instruments, the program number does not change.*



2. Prepare the blank: Fill the sample cell with 10 mL of sample.



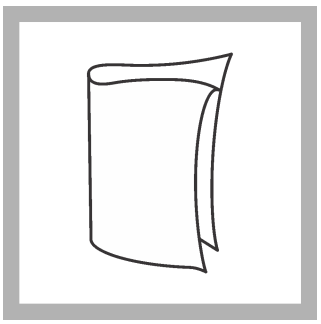
3. Prepare the sample: Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



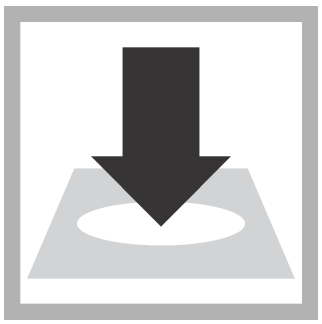
4. Quickly invert the Ampul several times to mix.

5. Start the instrument timer. A 3-minute reaction time starts.

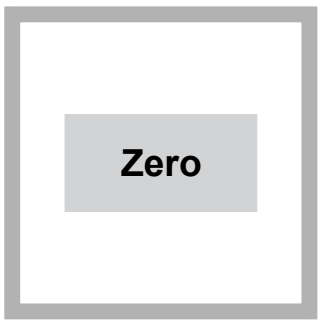
Prepare the sample blank and set the instrument to zero during the reaction time.



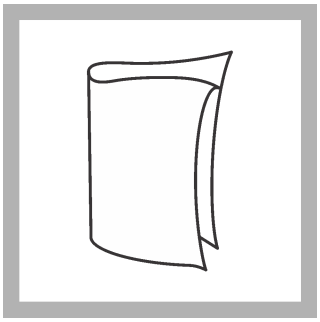
6. Clean the blank.



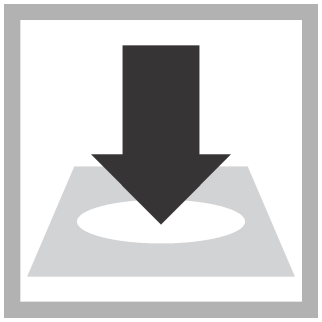
7. Insert the blank into the cell holder.



8. Push **ZERO**. The display shows 0.00 mg/L Cl_2.



9. Clean the AccuVac Ampul.



10. Within 3 minutes after the timer expires, insert the prepared sample AccuVac Ampul into the cell holder.

11. Push **READ**. Results show in mg/L Cl_2.

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to be added on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Alkalinity	More than 250 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1000 mg/L as $CaCO_3$
Iodine, I_2	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	Pre-treat the sample as follows: **1.** Adjust the sample pH to 6–7. **2.** Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops of Sodium Arsenite (5-g/L) and mix. **5.** Use the test procedure to measure the concentration of the treated sample. **6.** Subtract this result from the result without the treatment to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment of the sample by the reagents. Sample pretreatment may be necessary. Adjust to pH 6–7 with acid (Sulfuric Acid, 1.000 N) or base (Sodium Hydroxide, 1.00 N).

Pollution prevention and waste management

If sodium arsenite was added to the sample for manganese or chromium interferences, the reacted samples will contain arsenic and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Chlorine Standard Solution, 2-mL PourRite® Ampule, 25–30 mg/L (use mg/L on label)
- Breaker, PourRite Ampules
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.

   Note: *For AccuVac® Ampuls, add 0.4 mL, 0.8 mL and 1.2 mL of the standard solution to three 50-mL portions of fresh sample.*
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users may get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
80	1.25 mg/L Cl_2	1.23–1.27 mg/L Cl_2	0.02 mg/L Cl_2
85	1.25 mg/L Cl_2	1.21–1.29 mg/L Cl_2	0.02 mg/L Cl_2

Summary of method

Chlorine can be present in water as free chlorine and as combined chlorine. Both forms can exist in the same water and be determined together as total chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine and free chlorine react with DPD (N,N-diethyl-p-phenylenediamine) to form a pink color which is proportional to the total chlorine concentration.

To find the concentration of combined chlorine, run a free chlorine test and a total chlorine test. Subtract the results of the free chlorine test from the total chlorine test to obtain the combined chlorine concentration. The measurement wavelength is 530 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
DPD Total Chlorine Reagent Powder Pillow, 10-mL	1	100/pkg	2105669
OR			
DPD Total Chlorine Reagent AccuVac® Ampul	1	25/pkg	2503025

Required apparatus

Description	Quantity/Test	Unit	Item no.
AccuVac Snapper	1	each	2405200
Beaker, 50-mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 2-mL PourRite® Ampules, 25–30 mg/L	20/pkg	2630020

Optional reagents and apparatus

Description	Unit	Item no.
AccuVac® vials for sample blanks	25/pkg	2677925
Ampule Breaker, PourRite® ampules	each	2484600
Ampule Breaker, Voluette® ampules	each	2196800
Water, Chlorine-demand Free	500 mL	2641549
Cylinder, mixing, 25-mL	each	2088640
Cylinder, mixing, 50-mL	each	189641
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
DPD Total Chlorine Reagent Powder Pillows, 10-mL	1000/pkg	2105628
DPD Total Chlorine Reagent Powder Pillows, 10-mL	300/pkg	2105603
DPD Total Chlorine Reagent, 10 mL, SwifTest™ Dispenser refill vial	250 tests	2105660
Paper, pH, 0–14 pH range	100/pkg	2601300
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet 1970001	50/pkg	2185696
Pipet tips for TenSette Pipet 1970001	1000/pkg	2185628
Potassium Iodide, 30 g/L	100 mL	34332
Sodium Arsenite, 5 g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
SpecCheck™ Secondary Standard Kit, Chlorine DPD, 0-2.0 mg/L Set	each	2635300

Consumables and replacement items (continued)

Description	Unit	Item no.
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Water, deionized	4 L	27256

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company/Hach Lange GmbH, 1989–2013. All rights reserved.

04/2013, Edition 8

Chlorine, Free

DOC316.53.01155

USEPA[1] Amperometric Buret Titration Method[2]

Method 8334

0.5 mg/L and above

Buret Titration

Scope and Application: For water and wastewater.

[1] USEPA accepted; 40 CFR Part 141, Section 141.74.

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater* (4500 Cl^-D).

Test preparation

Before starting the test:

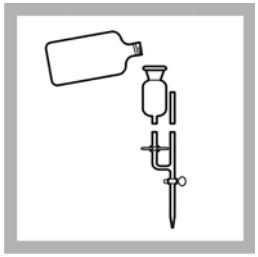
Chlorine can be lost from the sample during sample collection. Review the precautions in *Sample collection, preservation and storage* before the test is started.
Use only a 50-mm stir bar. The wrong size can cause the loss of chlorine, unstable readings and loss of method sensitivity, especially when measuring low level chlorine concentrations.
For added convenience when stirring, use the TitraStir® apparatus.
When a new probe is placed in service or when the probe has not been used recently, prepare it according to the Probe Stabilization instructions in the Amperometric Titrator Instruction Manual.

Collect the following items:

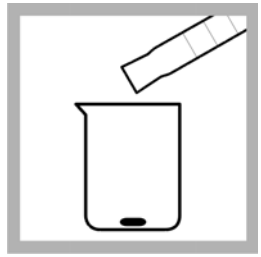
Description	Quantity
Phenylarsine Oxide Solution, 0.00564 N	1 bottle
Phosphate Buffer Solution, pH 7	1 mL
Amperometric Buret Titrator System	1
Beaker, 250-mL	1
Graduated cylinder, 250-mL	1

See *Consumables and replacement items* for reorder information.

Buret titration

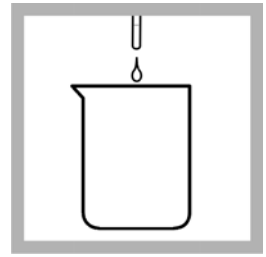


1. Fill the 5-mL automatic buret to the zero mark with 0.00564 N Phenylarsine Oxide (PAO) Solution.

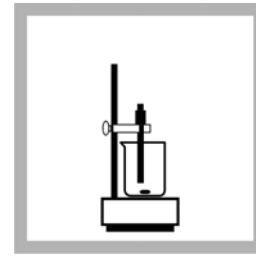


2. Put a 50-mm stir bar into a 250-mL beaker.

Use a graduated cylinder to measure 200 mL of sample. Add the sample to the beaker.

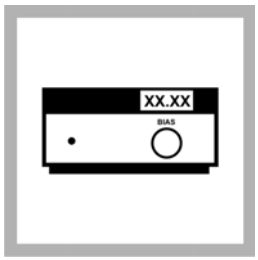


3. If the pH is less than 6 or greater than 7.5, add 1.0 mL of pH 7 Phosphate Buffer Solution to make the prepared sample.



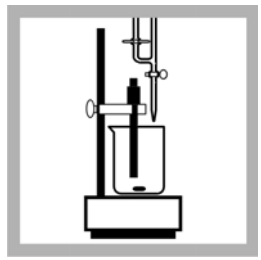
4. Place the beaker of prepared sample on the TitraStir titration stand and turn on the stirring motor. Put the tip of the probe fully into the prepared sample. The platinum wires must be submerged.

If a stir plate other than the TitraStir® is used, set the speed for moderate mixing. Do not adjust the speed after this point.

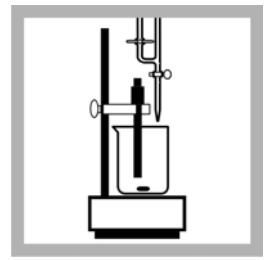


5. Turn the BIAS control knob to adjust the value on the display to approximately 1.00.

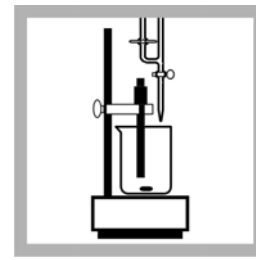
The BIAS adjustment controls the slope of the titration curve. The actual value is not important. Only the relative value as the titration continues is important. A precise adjustment is not necessary.



6. Dispense the titrant into the beaker in small increments while monitoring the values on the Amperometric Titrator. The values will decrease.

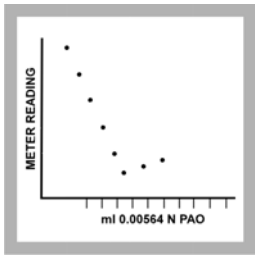


7. Continue dispensing slowly. Near the end point of the titration, write down the value on the display and the corresponding total volume of titrant that was added. Read the volume to the nearest 0.01 mL. Add a small amount of titrant and wait several seconds for a stable value. Write down the value.

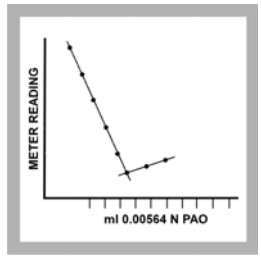


8. Continue the titration by recording at least three points on the downward sloping curve and at least three points after the end point has been reached. The value on the display will not change significantly after the end point.

Buret titration (continued)



9. Make a graph of the titration. Plot the values from the amperometric titrator on the vertical axis and the corresponding volume of titrant on the horizontal axis.



10. Draw the two best intersecting lines through the points as shown above. Find the volume of titrant to the nearest 0.01 mL at the intersection of the two lines. This is the mL titrant end point. This volume is equivalent to the free chlorine concentration in mg/L.

mL titrant =
mg/L free chlorine as Cl_2

Interferences

Refer to the Amperometric Titrator Instruction Manual for a discussion of sources of errors and interferences using the amperometric methods.

Sample collection, preservation and storage

Start the chlorine analysis immediately after the samples are collected. Chlorine is a strong oxidizing agent and is not stable in natural waters. Chlorine reacts quickly with various inorganic compounds and slowly oxidizes organic compounds. Many factors such as sample composition, sunlight, pH, temperature and salinity can cause the decomposition of chlorine in water.

Do not use plastic containers because plastic can react with and consume chlorine. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of demineralized water) for at least 1 hour. Rinse thoroughly with demineralized or distilled water. If sample containers are rinsed thoroughly with demineralized or distilled water after use, only occasional pre-treatment is necessary.

Do not use the same sample containers for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample containers for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes before sample collection. Let the sample container overflow with the sample several times, then cap the container so that there is no headspace (air) above the sample. Start the chlorine analysis immediately.

Summary of method

Free chlorine is measured by a titration at pH 7 with PAO solution to the amperometric end point. The amperometric titration method has greater sensitivity and accuracy when compared to colorimetric methods. Refer to the Amperometric Titrator Instruction Manual for more information.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Phenylarsine Oxide Solution, 0.00564 N	varies	1 L	199953
Phosphate Buffer Solution, pH 7	1 mL	100 mL MDB	2155332

Required apparatus

Description	Unit	Catalog number
Amperometric Buret Titrator System, 115 VAC	each	1930010
Beaker, 250-mL	each	50046H
Graduated Cylinder, 250-mL	each	50846
Stir bar, 50 mm	each	2095355
TitraStir® apparatus, 115 VAC	each	1940000
TitraStir apparatus, 230 VAC	each	1940010
pH Paper, 0–14 pH range	100/pkg)	2601300

Optional reagents and apparatus

Description	Unit	Catalog number
Chlorine Standard Solution, 10-mL Voluette® Ampules, 50–75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite® Ampule, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 2-mL PourRite Ampule, 25–30 mg/L	20/pkg	2630020
Voluette Ampule breaker 10-mL	each	2196800
PourRite Ampule breaker 2-mL	each	2484600
Water, deionized	500 mL	27249

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company, 2007, 2010, 2012. All rights reserved. Printed in the U.S.A.

Total Residual Chlorine, SM 4500-Cl G, 22nd edition (2000) – DPD Colorimetric Method

Minimum Detectable Concentration – 4500-Cl G.1.c. – approximately 10 μg/L (0.010 mg/L)

Initial Demonstration of Capability (DOC)

- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to analyze 4 samples of a chlorine standard or potassium permanganate ($KMnO_4$) at a concentration of 0.5 mg/L**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**
    - **Only good for that type of instrument you are using at that plant. If you have a backup instrument made by a different manufacturer or you work at another plant with a different make/model, you would need another DOC.**
        - **DOCs demonstrate you are proficient with that one instrument.**

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, use an estimate of five times the estimated true detection level (5 x 0.010 mg/L = 0.050 mg/L).
    - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
    - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.
- 4020 B.1.b. – Verify MDL at least ***annually***.
    - Ideally use pooled data from several analysts rather than data from one analyst.
- **Real people language – have several operators, who run this test, analyze chlorine standards or Potassium Permanganate ($KMnO_4$) at a concentration of 0.05 mg/L over several days with a total of at least 7 samples**
    - **Joe analyzes 3 samples on Monday**
    - **Bob analyzes 3 samples on Tuesday**
    - **Mary analyzes 3 samples on Wednesday**
- **Run this once a year**

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- 4020.B.2.a. – Calibrate initially with at least one blank and three calibration standards.
    - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
    - The back-calculated and true concentrations should agree within ± 10%.

- **Real people language – prepare a set of chlorine standards or potassium permanganate ($KMnO_4$) in accordance with Guidance for Secondary Stds use in Calibration 10-19-2012 monthly.**

Method Blank

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 4020 B.2.d. – Include at least one method blank ***daily*** or with each batch of 20 or fewer samples, whichever is more frequent.
    - If any method blanks measurements are at or above the reporting level, take immediate corrective action.
- **Real people language – analyze distilled water as a sample by adding a DPD powder pillow and waiting the 3-6 minutes before reading**
    - **Target value is less than detection level**
    - **Do this every day you analyze total residual chlorine**

Laboratory Fortified Blank (LFB)

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis = 1 every 20 samples
    - Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.
- 4020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits
- **Real people language – analyze chlorine standard or potassium permanganate sample at a concentration of 0.5 mg/L**
    - **Run on a 5% basis, see batch size for more information**

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 4020 B.2.f. – Randomly select routine samples to be analyzed twice.
    - Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – on a 5% basis (1 for every 20 samples) analyze 2 samples for chlorine, after reading one, pour out sample and start with a fresh sample**
    - **First sample is result, second sample is duplicate**
    - **Target value is to get close to the first value and have a small RPD**

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.

Chlorine QA/QC Bench sheet

mL Working Standard Diluted with Deionized Water	Chlorine Equivalent	Actual Reading
20 mL (vol. pipet) to 100 mL (vol. flask)	2.0 mg/L	
10 mL (vol. pipet) to 100 mL (vol. flask)	1.0 mg/L	
5 mL (vol. pipet) to 100 mL (vol. flask)	0.5 mg/L	
1 mL (vol. pipet) to 100 mL (vol. flask)	0.1 mg/L	
0.5 mL (vol. pipet) to 100 mL (vol. flask)	0.05 mg/L	
1 mL (vol. pipet) to 500 mL (vol. flask)	0.02 mg/L	

- For the calibration verification to be valid, check standards must not exceed 10% of its true value, and calibration blank results must not be greater than one-half the reporting level

- **Real people language**
  - **Read Secondary Standards in accordance with Guidance for Secondary Stds use in Calibration 10-19-2012 daily.**
  - **OR run a chlorine or potassium permanganate standard daily.**

Control Charts – 1020 B.13.

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Blanks < reporting limits
- LFB ± 15%
- ICV/CCV ± 10%
- RPD± 20%

Batch Size

- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would suggest twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - If sampling only once a month, need to run QC once a month.

Calculations

- % Recovery for LFB
  - $= \frac{\text{LFB concentration}}{\text{Expected concentration}} \times 100\%$
- RPD – relative percent differences for duplicates and LFM/LFMD
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

Section 7
Bacteriological Testing

Microbiological Sampling

TDEC - Fleming Training Center 1

Objectives

- Importance of proper sampling and analysis
- Selecting sampling points
- Collection, preservation, and storage of samples
- Preparation of samples for testing
- Methods for bacteriological analysis

TDEC - Fleming Training Center 2

Importance of Proper Sampling

- Representative sample - contains basically the same constituents as the body of water from which it was taken
- Test results are worthless unless they indicate actual water quality

TDEC - Fleming Training Center 3

Selecting Sampling Points

- Total Coliform Rule (1990) requires written sampling plan to be approved by the State.
- Points should be representative of system:
  - Dead ends
  - Pressure zones
  - Storage facilities

TDEC - Fleming Training Center 4

Collection of Samples

- Only approved containers should be used
  - 125 mL volume
  - Pre-sterilized bottles recommended
  - Other bottles sterilized at 121ºC for 15 minutes
  - Should contain sodium thiosulfate

TDEC - Fleming Training Center 5

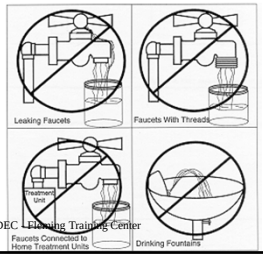
Collection of Samples

- Check sample bottle for flaws before use
- Leave adequate space at top for mixing
- Use *aseptic* technique to avoid contamination

TDEC - Fleming Training Center 6

Collection of Samples

- Collect samples from approved faucets only



Sample Sites cont.

- Avoid sampling from hydrants, taps from water softeners and leaking faucets
  - Very good chance for contamination
- Collect sample from a non-swivel faucet

Sample Sites cont.

- Mixing faucets should not be used because water passing through the "hot" waterside may not be representative of the water in the distribution system
  - Water in the hot water tank is more likely to grow bacteria because the warm water may promote growth

Sample Sites cont.

- Threaded taps should be avoided
  - Bacteria can grow in the grooves of the threads
  - Never take samples from taps that are clearly contaminated with scum or build up around faucet

Sample Sites cont.

- Avoid faucets close to the ground or sink bottom
  - Close to the ground can be contaminated with dirt
  - Close to the sink bottom may not allow room for bottle to be put under flow without touching the inside of the bottle

Sample Sites cont.

- Good sample sites:
  - Water tank
  - Dead end with sampling tap
  - Fire halls
  - Public buildings

Sampling Procedure cont.

- If a faucet has a strainer, aerator or any other attachment, remove before sampling

- Let the water run for several minutes (3-5 min) to insure fresh water from the main

TDEC - Fleming Training Center 13

Sampling Procedure cont.

- Take Free Chlorine Residual using DPD method and record

- Disinfect faucet with either a dilute bleach spray (~200 mg/L), rubbing alcohol (~25%) or flame it with a propane or butane torch

TDEC - Fleming Training Center 14

Sampling Procedure cont.

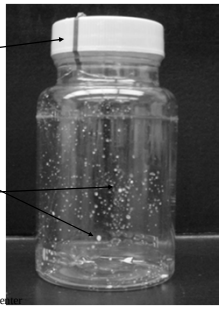
- Reopen the faucet and let the water run in a stream about the size of a pencil to prevent splashing during sampling
  - Remember the bottles are sterile
  - DO NOT rinse the bottle
  - If you feel you have contaminated the bottle, dispose & start with a new one
  - Use fresh bottles, old bottles left out in the sun may not eliminate chlorine as well

TDEC - Fleming Training Center 15

Sampling Procedure cont.

Sterile bottle, never been opened

Sodium Thiosulfate (white crystals)



TDEC - Fleming Training Center

Sampling Procedure cont.

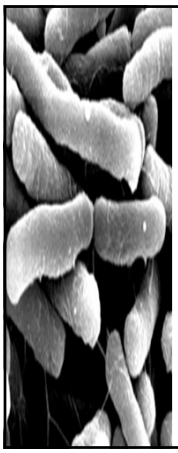
- Hold the bottle in one hand near the bottom and with the other hand remove the top
  - Care should be taken in removing the lid so as not to touch the inside of the bottle or lid

TDEC - Fleming Training Center 17

Sampling Procedure cont.

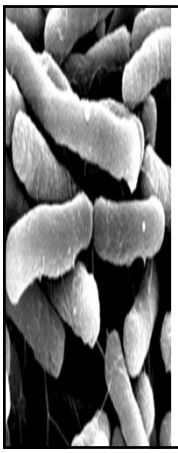
- Hold the bottle under the faucet, allowing only a small, steady stream to flow from the faucet
  - When filling the bottle, hold the bottle so as to avoid water contacting the hand and running into the bottle
  - Collect 100 mL ± 2%
    - Meniscus needs to touch the 100 mL mark
  - Immediately remove bottle from underneath the faucet and replace the lid

TDEC - Fleming Training Center 18



Sampling Procedure cont.

- Document the required information from the sample site
  - Time and date collected
  - Location or address
  - Free chlorine residual
  - Collector's name
  - Sample type
    - Routine DS sample
    - Check sample
    - Raw or finished water sample
    - Repeat or confirmation sample
    - Other special purpose sample



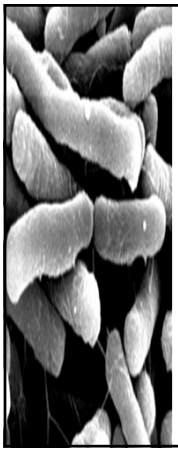
Sample Label

Site *196 E. Main Street Billieville, TN*

Date / Time *August 15, 2005 8:15 AM*

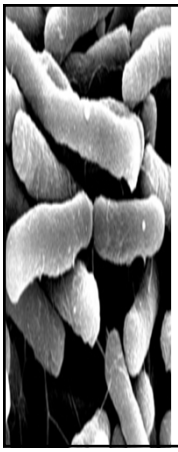
Sampled by *Billy Joe Smith*

Comments *grab sample, monthly Bac't*
Residual chlorine = 2.1 mg/L



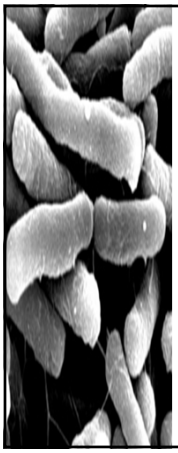
Sampling Procedure cont.

- Replace all attachments after sampling is completed
- All samples must be tested within 30 hours of collection



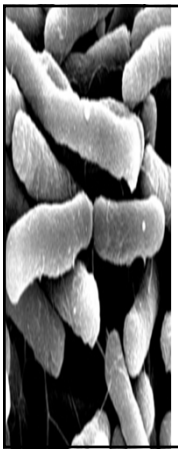
Positive Samples

- Repeat samples shall be collected within 24 hours of positive results.
  - One repeat sample at original site of total coliform-positive sample
  - At least one at a tap within 5 service connections upstream
  - At least one at a tap within 5 service connections downstream



Approved Methods

- Four methods are approved by EPA for determination of total coliforms:
  - Membrane Filter Method
  - Multiple-Tube Fermentation
  - Presence-Absence Test
  - MMO-MUG Technique



Indicator Organism

- Always present in contaminated water
- Always absent when contamination is absent
- Survives longer in water than other pathogens
- Is easily identified

Coliform group

Bacteriological Samples

- The MCL for coliform bacteria is based on presence or absence.
- Finished and distributed water should be 0 (absent)
- Must keep results for 5 years.

TDEC - Fleming Training Center 25

Membrane Filter Technique

- Minimum sample size that can be filtered is 20 - 30 mL
- For samples smaller than 10 mL:
  - Pour 30mL dilution water into funnel, pipet sample into funnel; swirl to mix
  - Pipet sample into dilution water

TDEC - Fleming Training Center 26

Membrane Filter Technique

- 100 mL sample is filtered through a membrane filter under a vacuum
- Filter is placed on a sterile petri-dish containing M-Endo broth (food source for bacteria) for Total Coliforms
- Petri-dish is labeled, turned upside down, placed in incubator at 35º ± 0.5º C for 24 hours

TDEC - Fleming Training Center 27

Membrane Filter Technique

- A coliform bacteria colony will grow at each point on filter where a viable bacterium was left during filtering
- The colonies will appear red with a green-gold metallic sheen

TDEC - Fleming Training Center 28

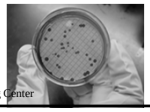
Fecal Coliform Determination

- Membrane filtration test
- More reliably indicates the potential presence of pathogenic organisms
- Same procedure as Total Coliform, 100 ml sample is filtered through a membrane filter under a vacuum

TDEC - Fleming Training Center 29

Fecal Coliform Determination

- Filter placed on steril petri-dish containing mFC broth
- Incubation at 44.5º ± 0.2º C for 24 hours
- Bacterial colonies appear blue
  - Looks for heat tolerant bacteria



TDEC - Fleming Training Center 30

Enzyme Substrate Tests

- Colilert (P/A)
- Colilert Quanti-Tray
- Colilert-18 (P/A)
- Colilert-18 Quanti-Tray
- E*Colite
- Colisure
- Readycult Coliforms 100 (P/A) and Fluorocult LMX Broth
- Colitag

TDEC - Fleming Training Center 31

All incubation temperatures are 35 ± 0.5° C

Name	Time in hours	Total Coliform Positive	E. coli positive
Colilert IDEXX	24 (no more than 28 hrs)	Clear → Yellow	Fluoresces
Colilert-18 IDEXX	18 (up to 22 hrs)	Clear → Yellow	Fluoresces
Colisure IDEXX	24 hours (up to 48 hrs)	Yellow → Magenta	Fluoresces
Colitag™ Colitag	24 ± 2 hrs	Clear → Yellow	Fluoresces
E*Colite™ Charm Sciences	28	Yellow → Blue	Fluoresces
Readycult® EMD Chemicals	24 ± 1 hr	Yellow → Blue	Fluoresces Confirmation by Indole test

TDEC - Fleming Training Center 32

Colilert / Colilert 18 for P/A

- Equipment needed
  - Incubator
  - UV lamp
  - Comparator
  - pH meter to check tryptic soy broth
- Sample bottle is used in the testing procedure
- Tests for total coliforms and E. coli in one step
  - Sample turns yellow if positive for total coliforms
  - Sample fluoresces if positive for E. coli

TDEC - Fleming Training Center 33

Colilert / Colilert 18 for P/A

- Colilert Video Demonstration
- Quanti-Tray/2000: Video Demonstration

TDEC - Fleming Training Center 34

Colilert's "Blue Flash"

- Samples containing excessive amounts of free chlorine can cause this reaction.
- A 700 mg/l level of chlorine will produce this transient blue color when Colilert is added.
- Sometimes gas production can be seen immediately after the Colilert is added along with the blue reaction.

TDEC - Fleming Training Center 35

Colilert's "Blue Flash"

- The sample should be considered invalid and it is recommended to resample and retest.
- The source and/or amount of chlorine in the sample should also be investigated for 700 mg/l is not a typical chlorine level in a water sample.

TDEC - Fleming Training Center 36

Colilert's "Blue Flash"

- This can be done if someone has poured bleach into a well or even "dosed" a bac't bottle with as little as 1.3 mL of fresh bleach.
- To catch lower doses of chlorine for outside samples, send two bottles, one with sodium thiosulfate for your bac't analysis and one without to check for chlorine
  - There should not be any chlorine present in a well sample

Colilert / Colilert 18 for P/A

- Detects a single viable coliform per sample
- For Colilert 18, samples need to be pre-warmed to 35°C before incubation period starts
- Colilert 18 can lift boil water notices 6 hours earlier than other methods
- Shelf life is 12 months for media packet

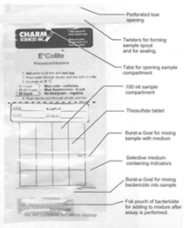
Colisure

- Step 1
  - Add reagent (shelf life is 12 months) to sample
  - Incubate for 24 hours
    - If samples are not room temperature, they need to be pre-warmed before incubating
- Step 2
  - Read results
    - Yellow = negative
    - Magenta = total coliform positive
    - Magenta/fluorescent = E. coli positive

Colitag

- Detects 1 CFU of total coliform or *E. coli* bacteria per 100 mL sample
- Acid-resucitation technology
  - With self adjusting pH level
  - Detects chlorine-injured cells

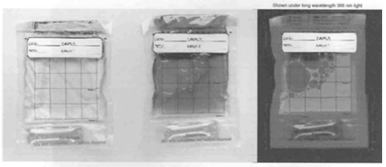
E*Colite™



- Add water sample to bag
- Push water into the medium compartment
- Incubate for 28 hours at 35° C
- Info at: www.charm.com

E*Colite™

- Interpretation
  - If a blue sample does not fluoresce, continue incubating an



Readycult® 100

Negative

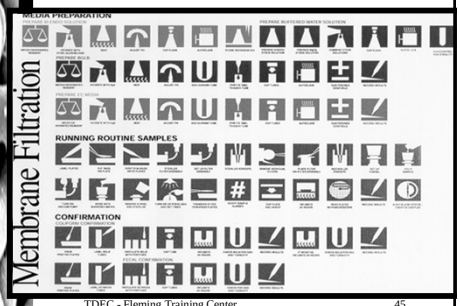
Positive Coliforms

- Add Readycult® snap packet (3 year shelf life) to 100 mL sample, incubate for 24 hours at 35.5 °C
- Any color change to blue-green (even if only at the upper section of sample) confirms the presence of total coliforms; don't need a color comparator

Readycult® 100

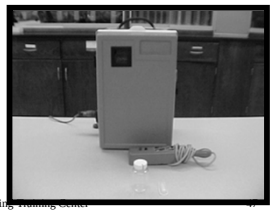
- A light blue fluorescence indicates the presence of *E. coli* (94-96% *E. coli* specific)
- If confirmation of *E. coli* is desired, the indole test can be performed directly in the same broth by adding Kovac's reagent (or Bactident® Indole)
  - If a red ring appears immediately, you have positive confirmation

Membrane Filter Pictorial



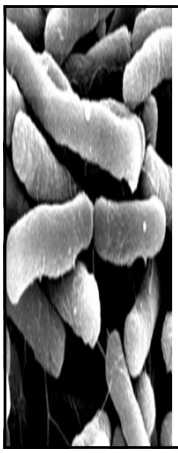
Colilert Method Pictorial

Equipment Comparison



Expected Reactions of Various Microorganisms

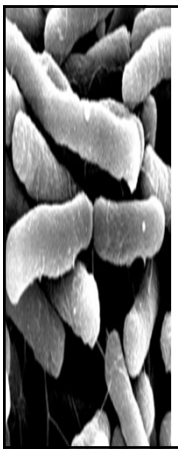
- Total coliforms will produce a red colony
  - *Enterobacter species*
    - *E. cloacae*
    - *E. aerogenes*
  - *Klebsiella species*
    - *K. pneumoniae*
  - *Citrobacter species*
    - *C. freundii*



Expected Reactions of Various Microorganisms

- *Escherichia coli* will produce a blue colony
  - *E. coli* O157:H7 will not produce a blue colony, but will grow as a red colony

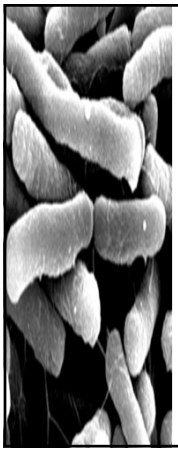
TDEC - Fleming Training Center 49



Expected Reactions of Various Microorganisms

- Known negative reaction (no growth) after 24-25 hours
  - *Pseudomonas aeruginosa*
    - Variable reaction may be positive for total coliform when incubated longer than 25 hours
  - *Proteus vulgaris*
  - *Aeromonas hydrophila*

TDEC - Fleming Training Center 50



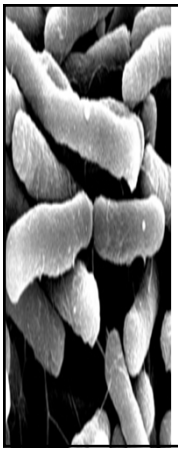
M-ColiBlue24® Trouble-Shooting Guide, Hach Company, www.Hach.com

Expected Reactions of Various Microorganisms

- Some strains of the following microorganisms are known to produce a false-positive total coliform reaction (a red colony, but not a true total coliform)

•*Serratia species*
•*Hafnia alvei*
•*Vibrio fluvialis*
•*Aeromonas species*
•*Proteus vulgaris*
•*Providencia stuartii*
•*Yersinia enterocolitica*
•*Leclercia adecarboxylata*
•*Ewingella americana*
•*Staphylococcus species*
•*Proteus mirabilis*

51 TDEC - Fleming Training Center



E. coli Information

- For Colilert®: IDEXX Laboratories, www.idexx.com
- For mTEC Agar and mColiBlue-24® media: Hach Company, www.Hach.com
- EPA Method 1603: E.coli In Water By Membrane Filtration Using Modified-Thermotolerant Escherichia coli Agar (Modified mTEC), September 2002, EPA-821-R-02-023

52 TDEC - Fleming Training Center

Glossary of Microbiological Terms

Aseptic – free from germs, fermentation, or putrefaction; sterile.

Aseptic technique – procedure in which no microbiological contamination occurs.

Autoclave – device used for sterilizing laboratory equipment by using pressurized steam.

Coliform bacteria – a group of bacteria including all the aerobic and facultative anaerobic gram-negative, non-spore forming, rod shaped bacteria that ferment lactose with gas and acid production within 48 hours at 35°C. The presence of coliform bacteria in drinking water indicates fecal contamination.

Colilert Method – a presence/absence test for total coliforms that will also confirm the presence or absence of *E. coli* within 24 hours.

Composite sample – series of samples taken at different times and mixed together to determine average concentration of a substance in the water.

Desiccator – heavy glass container that allows substances to be cooled in a dry environment. It is used to store substances that readily absorb moisture from the air. It contains a chemical in the bottom that absorbs moisture and keeps the relative humidity near zero.

Dilution water – reagent grade water that is buffered with potassium dihydrogen phosphate and magnesium chloride and sterilized in an autoclave. It is used for rinsing the funnel used in the membrane filter method, and for diluting samples.

Escherichia coli (*E. coli*) – a bacteria of the fecal coliform group. Its presence may be tested for in lieu of fecal coliforms following a total coliform positive sample in the distribution system. This organism is used for quality control of m-Endo broth for bacteriological testing.

Fecal coliform – a bacteria of the coliform group that indicates fecal contamination. The presence of fecal coliforms in a water sample is a violation of the Total Coliform Rule.

Grab sample – a sample of water collected at a specific time and place that represents water quality at that time and place.

Graduated cylinder – glass or plastic container used for making measurements of volume. They are less accurate than pipets and volumetric flasks, but are more accurate than beakers and Erlenmeyer flasks.

Heterotrophic Plate Count (HPC) – laboratory procedure used for estimating the total bacterial count in a water sample. Also called standard plate count.

Incubator – heated container that maintains a constant temperature for the proper development of microbiological cultures.

Indicator organism – an organism that is always present in contaminated water, is not present in uncontaminated water, survives longer in water than other pathogens, and is easily identified. The indicator organism for bacteriological quality of drinking water is the total coliform group.

Klebsiella – a member of the coliform group, used for quality control of media for bacteriological testing.

m-Endo broth – nutritive media used in the membrane filter method for total coliform analysis.

Maximum Contaminant Level (MCL) – the maximum permissible level of a contaminant in drinking water as specified by the Safe Drinking Water Act.

Membrane Filter Method – test for coliform bacteria that uses a 0.45μ filter to trap coliform bacteria from a 100 mL sample, then incubates the bacteria in a petri dish with nutritive broth at 35°C for 24 hours. The presence of total coliforms is indicated by dark colonies with a green-gold metallic sheen.

MPN – Most Probable Number of coliform bacteria in a 100 mL sample. Used in the Multiple Tube Fermentation Method and other methods

Pathogen – an organism capable of causing disease in a host.

Petri dish – a round, shallow glass or plastic dish with a loose-fitting lid used for bacterial cultures.

Pipet – glass tube used for accurately measuring small volumes. Includes volumetric, Mohr, and serological.

Potable water – water that does not contain objectionable pollution, contamination, minerals, or infective agents, and is considered satisfactory for drinking

Representative sample – sample that contains basically the same constituents as the body of water from which it was taken.

Sodium thiosulfate – chemical in a bacteriological sample bottle that neutralizes the chlorine residual in a water sample.

Sterilization – destruction or inactivation of all microorganisms.

Total Coliform Rule – a regulation that became effective December 31, 1990. It changed the MCL for total coliforms from a quantitative density to presence/absence.

Volumetric flask – glassware used for mixing accurate solutions. Each flask is calibrated for a single volume.

Waterborne disease – an illness that is caused a pathogenic organism carried by water.

Long Term 2 Enhanced Surface Water Treatment Rule

Overview

Contents

LT2ESWTR Purpose
Rule Overview
Source Water Monitoring
Bin Classification
Microbial Toolbox
Implementing Option(s)
Follow-up Monitoring
Profiling and Benchmarking
Other Issues

LT2ESWTR

The Long Term 2 Enhanced Surface Water

- Treatment Rule (LT2ESWTR) requires Public Water Systems (PWS) that use surface water or ground water under the direct influence of surface water to monitor their source water for Cryptosporidium, E. coli, or turbidity for a limited period.
- Based on the results additional treatment techniques may be required for some systems.

Purposes of the LT2ESWTR

Improve public health protection

- Reduce illness caused by *Crypto* and other microorganisms
- Tailor requirements based on:
  - Level of treatment
  - Source water quality
  - System size
- Provide systems and states with flexibility

Supplement and fill data gaps

- Most systems will only need to monitor

Balance disinfection with control of DBPs

Cryptosporidium (Crypto)

- Protozoan parasite
- Common in surface water
- Resistant to traditional disinfectants
- Can pass through filters
- Causes cryptosporidiosis
- Filtration and alternative disinfectants can remove and/or inactivate

Cryptosporidiosis

- Diarrheal disease caused by Cryptosporidium
- The parasite is protected by an outer shell that allows it to survive outside the body for long periods of time and makes it very resistant to chlorine- based disinfectants
- The infective stage of the organism, the oocyst is 3 um in diameter or about half the size of a red blood cell

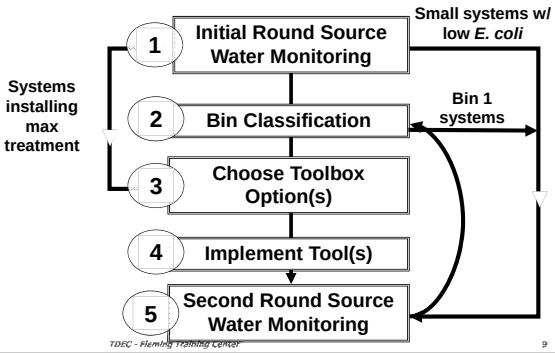
Cryptosporidiosis

- In March and April 1993 in Milwaukee there was an outbreak where approximately 403,000 people experienced diarrheal illness
  - At least 104 deaths attributed to this outbreak
- The chlorine CT of 9600 needed to kill Cryptosporidium oocysts is approximately 640 times greater than required for Giardia cysts

LT2ESWTR Overview

- Source water monitoring
- Screening procedure for small systems
- Target treatment for highest-risk systems
- *Crypto* inactivation at all unfiltered systems
- Cover or treat uncovered storage facilities

LT2ESWTR Process



Applicability

- All Subpart H systems
  - Use surface water or GWUDI sources
  - CWSs, NTNCWSs, TNCWSs
  - Wholesale systems
- Compliance deadlines and options based on people served
  - Divided into four schedules
  - Wholesale systems with own Subpart H source(s) comply based on requirements for largest system in their CDS
- Filtered and unfiltered systems

Initial Monitoring: Filtered Systems

Monitor:

- *Crypto*
- *E. coli*
- Turbidity

} **Indicators**

Frequency:

- Monthly for 24 months

Schedule	Largest System	Start Monitoring...
1	100,000 +	October 2006
2	50,000 - 99,999	April 2007
3	10,000 - 49,999	April 2008

Initial Monitoring: 5-day Window

Systems must sample within a 5-day period

- 2 days before or 2 days after date indicated in the sample schedule

Example: Sample schedule has system sampling on the 15th of every month

February 2007						
S	M	T	W	Th	F	S
11	12	13	14	15	16	17

Initial Monitoring: System Flexibilities

- Can avoid monitoring or stop monitoring by committing to meet *Crypto* treatment goals
  - Filtered: 5.5-log removal/inactivation
  - Unfiltered: 3-log inactivation
- Systems can sample more frequently
- Small systems have additional options

Initial Monitoring: System Flexibilities (cont.)

- Bin classification calculations differ according to how many *Crypto* samples were taken
  - 24 – 47 samples: highest average of 12 consecutive months
  - 48+ samples: overall average
- May be advantageous to sample at least 48 times

Analytical Methods: Indicators

Crypto
- Methods 1623 or 1622
- 10L in bulk or filtered
- Matrix spike samples

E. coli
- Enumeration, not presence/absence
- Sample volume = 100 mL

Turbidity

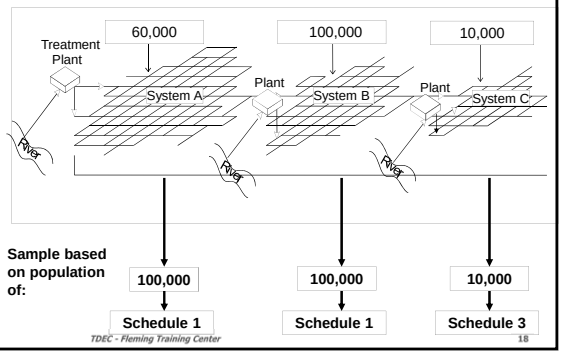
Combined Distribution Systems (CDSs)

- CDS requirements apply to wholesale system only
- Compliance date for wholesaler in CDS is compliance date for largest system in CDS
- Largest system is not necessarily the wholesaler
- Not all requirements apply to purchased systems without a Subpart H source

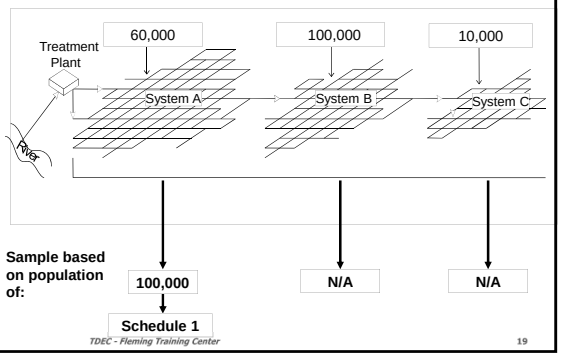
CDS (Cont.)

If a wholesale system is placed on the schedule of a larger system in its CDS
- System must monitor on larger system's schedule
- System must meet monitoring requirements that apply to larger system
- System has same monitoring options as larger system

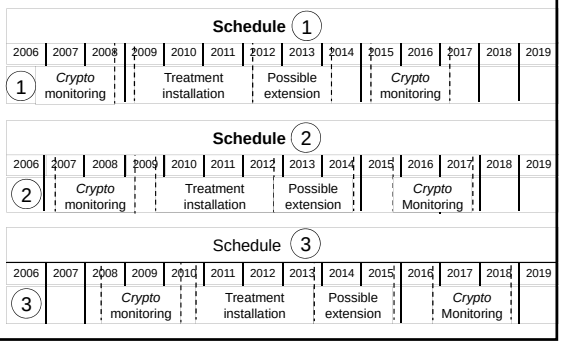
CDS (Cont.)



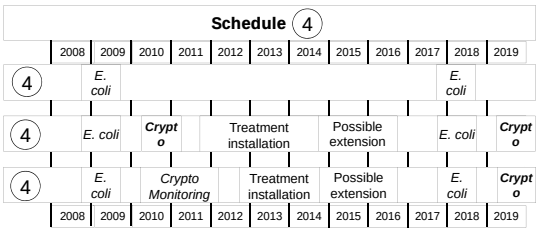
CDS (Cont.)



Implementation Timeline



Implementation Timeline



PWS 100,000 & above

Submit sampling schedule and sampling location or intent to grandfather no later than July 1, 2006

Begin Crypto monitoring no later than October 1, 2006

Submit grandfathered data no later than December 1, 2006

Report bin classification no later than April 1, 2009

PWS 50,000 – 100,000

Submit sampling schedule and sampling location or intent to grandfather no later than January 1, 2007

Begin Crypto monitoring no later than April 1, 2007

Submit grandfathered data no later than June 1, 2007

Report bin classification no later than October 1, 2009

PWS 10,000 – 50,000

Submit sampling schedule and sampling location or intent to grandfather no later than January 1, 2008

Begin Crypto monitoring no later than April 1, 2008

Submit grandfathered data no later than June 1, 2008

Report bin classification no later than October 1, 2010

PWS < 10,000

Filtered WTP

- Submit sampling schedule and sampling location no later than July 1, 2008
- Begin *E. coli* monitoring no later than October 1, 2008

E. coli Trigger Levels

If *E. coli* trigger levels are exceeded

- Annual mean of 10 *E. coli*/100 ml for lakes/reservoirs
- Annual mean of 50 *E. coli*/100 ml for flowing streams
  - Submit sampling schedule for *Crypto* within 45 months of rule
  - Begin 1 year of semi-monthly source water monitoring within 48 months of rule

PWS < 10,000

Filtered WTP that exceed *E. coli* trigger levels

- Submit sampling schedule and location no later than January 1, 2010
- Begin *Crypto* monitoring no later than April 1, 2010
- Submit bin classification no later than October 1, 2011

PWS < 10,000

Unfiltered WTP

- Submit sampling schedule and sampling location no later than January 1, 2010
- Begin *Crypto* monitoring no later than April 1, 2010
- Submit bin classification no later than October 1, 2012

LT2 Rule

A second round of monitoring will begin 6.5 years after initial bin classification.

PWS are not required to conduct monitoring if they submit a notice of intent to provide maximum Cryptosporidium treatment level 5.5 log for filtered plants and 3.0 log for unfiltered plants.

Sample Collection Methods

Bulk grab samples for shipment a minimum of 10L cubitainer $$$

In-the-field filtration

- Pall Gelman Envirochek or Envirochek HV
- IDEXX Filta-Max

Sample Collection Location

Plant intake prior to any treatment

- Plants that do not have a tap prior to treatment
  - Manually collect sample as close to intake as possible at a similar depth and distance from shore
  - Establish a sampling location prior to treatment
- Plants that use presedimentation
  - After presedimentation basin but before any other treatment

Sample Collection Location

Plants that use different water sources at the same time

- Sample where sources are combined before treatment
- Manually collect sample at each source and composite into one proportional sample
- Manually collect separate samples and have analyzed independently

Plants that use raw water off-stream storage

- Collect sample after the off-stream storage reservoir

Sample Collection Location

Plants that use bank filtration

- If subsequent filtration is used, collect sample in the well after bank filtration but before any other treatment
- If no subsequent filtration is used, collect sample in surface water source

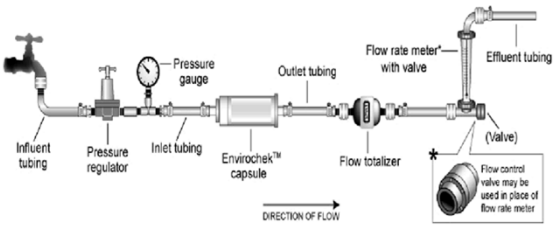
Sample Collection

Procedure from a pressurized source

- Flush tap for 2 – 3 minutes
- Connect sampling system without filter
- Flush with 20 L of source water and adjust flow rate to 2 L/min
- Install filter and monitor flow totalizer for a minimum of 10 L to maximum of 50 L or a volume that will generate a 2 mL packed pellet

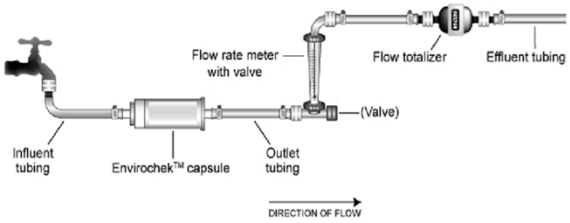
Sample Collection

Pressurized Sample System Setup > 20 psig



Sample Collection

Sample System Setup for 1 – 20 psiq



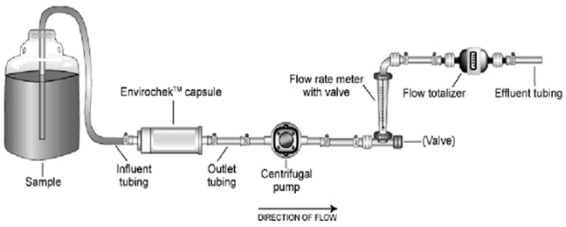
Sample Collection

Procedure from an unpressurized source

- Flush sampling system with 20 L of source water
- Adjust flow rate to 2 L/min
- Install filter and monitor flow totalizer for a minimum of 10 L to a maximum of 50 L or a volume that will generate a 2 ml packed pellet

Sample Collection

Unpressurized Sample System Setup



Sample Collection

Matrix Spike

- MS samples are used to assess overall recovery and variability for source water samples.
- 1 MS sample for every 20 monitoring samples
  - Large PWSs monitoring monthly (1 sample/month for 2 years = 24 samples), 2 MS samples
  - Large PWSs monitoring semi-monthly (2 samples/month for 2 years = 48 samples), 3 MS samples
  - Small PWSs triggered into *Crypto* monitoring and collect semi-monthly (2 samples/month = 24 samples), 2 MS samples

Sample Collection

Matrix Spike

- Collection Procedure
  - Filter a LT2 sample as usual (ex. 50L)
  - Using a second filter for the MS, filter 10L less
  - Collect the remaining 10L in a cubitainer
  - Ship both filters and 10L cubitainer to lab

LT2 Rule

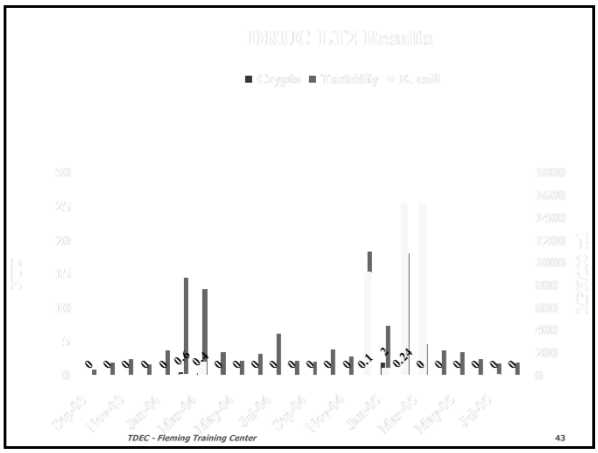
Description	Unit Price	Total
Method 1623 Field Samples	450.00 x 24	10,800
Matrix Spike Including Filter	500.00 x 2	1,000
Additional Slides	175.00	TBD
Additional Analysis	450.00	TBD
Consumable Supplies	10.00 x 24	240
Shipping Supplies	15.00 x 24	360
Sampling Apparatus	200.00 x 1	200
Total		$12,600

Budgetary Considerations for LT2 by Analytical Services Inc.

Additional Costs

Bacteriological Analysis

Overnight Shipping Charges



Bin Classification

Cryptosporidium Bin Classification	Bin Classification
Crypto < 0.075 oocysts/L	Bin 1
0.075 oocysts/L ≤ Crypto < 1.0 oocysts/L	Bin 2
1.0 oocysts/L ≤ Crypto < 3.0 oocysts/L	Bin 3
Crypto ≥ 3.0 oocysts/L	Bin 4

Bin Classifications

DRUC = .265 Bin 2

Shelbyville = .202 Bin 2

BCUD = .116 Bin 2

Lewisburg = .488 Bin 2

Columbia = .192 Bin 2

Toolbox Options

Toolbox option	Proposed *Cryptosporidium* credits
Source Toolbox Components	
Watershed control program	0.5 log credit. (Section 1.2.5.1)
Alternative source/intake management	No presumptive credit. (Section 1.2.5.2)
Pre-filtration Toolbox Components	
Presedimentation basin with coagulation	0.5 log credit for new basins with continuous operation and coagulant addition. No presumptive credit for basins existing when monitoring is required. (Section 1.2.6.1)
Two-stage lime softening	0.5 log credit for two-stage softening with coagulant addition. (Section 1.2.6.2)
Bank filtration	0.5 log credit for 25 foot setback; 1.0 log credit for 50 foot setback. No presumptive credit for bank filtration that serves as pretreatment when monitoring is required. (Section 1.2.6.3)

Toolbox Options

Treatment Performance Toolbox Components	
Combined filter performance	0.5 log credit for CFE turbidity ≤0.15 NTU in 95% of samples each month. (Section 1.2.7.1)
Individual filter performance	1.0 log credit for IFE ≤0.1 NTU in 95% of daily maximum samples each month and no filter >0.3 NTU in two consecutive measurements. (Section 1.2.7.2)
Demonstration of performance	Credit based on demonstration to the state. (Section 1.2.7.3)
Additional Filtration Toolbox Components	
Bag filters	1 log credit for demonstrating at least 2 log removal efficiency in challenge test. (Section 1.2.8.1)
Cartridge filters	2 log credit for demonstrating at least 3 log removal efficiency in challenge test. (Section 1.2.8.1)
Membrane filtration	Log removal credit up to the lower value of the removal efficiency demonstrated during the challenge test or verified by the direct integrity test applied to the system. (Section 1.2.8.2)
Second stage filtration	0.5 log credit for second separate filtration stage in treatment process following coagulation. (Section 1.2.8.3)

LT2ESWTR

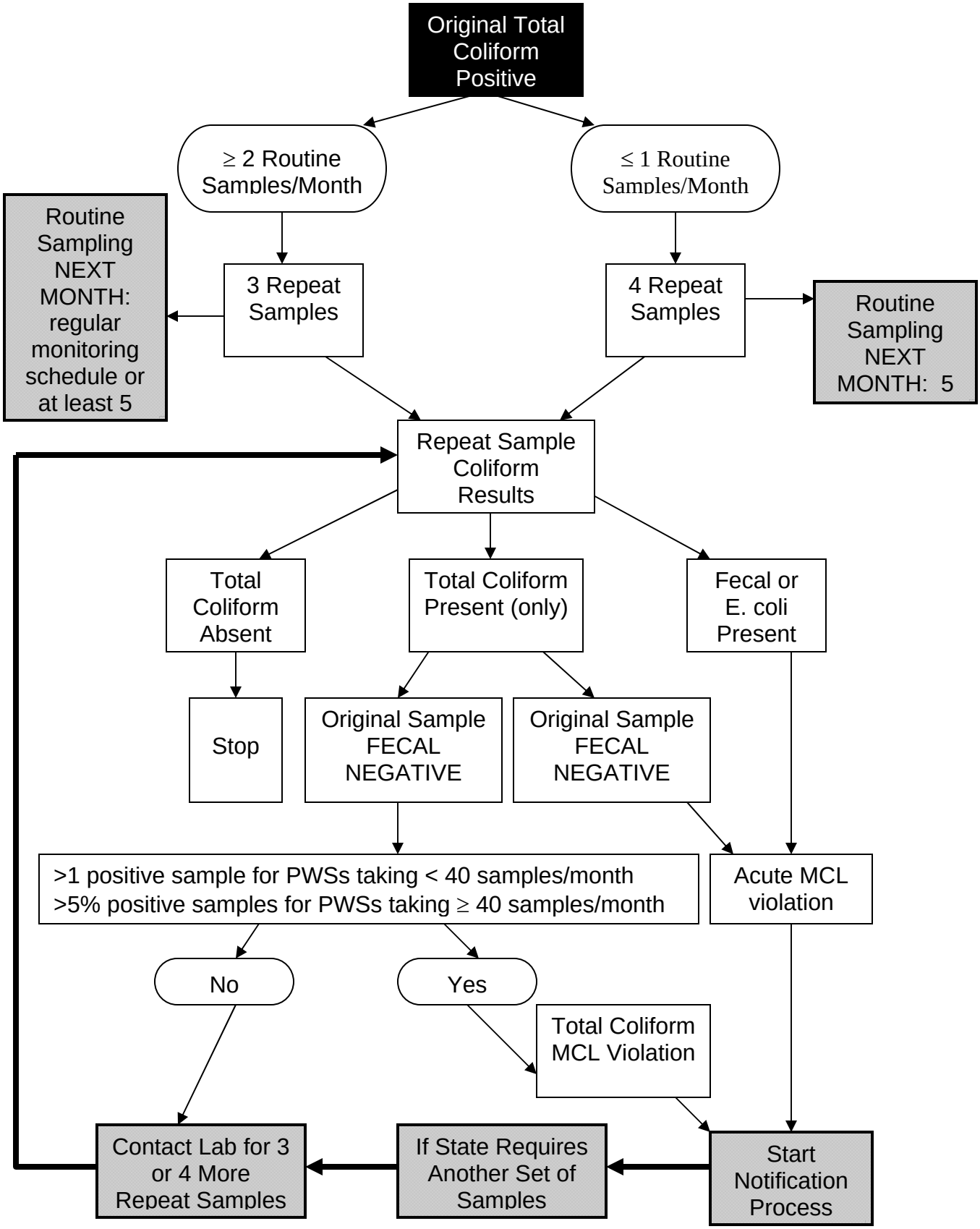
WTP's that are in Bin Classifications 3 or 4 are required to use Ozone, Chlorine Dioxide, UV, Bag Filtration, Cartridge Filtration or Bank Filtration to achieve a 1 log removal in addition to options in the Toolbox in order to reach the 2 to 3 log removal rule.

Toolbox Options

Toolbox option	Proposed *Cryptosporidium* credits
Slow sand filters	2.5 log credit for second separate filtration process and no residual may be present in influent to slow sand process. (Section 1.2.8.4)
Inactivation Toolbox Components	
Chlorine dioxide	Demonstrate compliance with contact time table. (Section 1.2.9.1)
Ozone	Log credit based on demonstration of compliance with CT table. (Section 1.2.9.2)
UV	Demonstrate compliance based on UV dose table. (Section 1.2.9.3)

TDEC - Fleming Training Center 49

Total Coliform Action Flow Chart



Coliforms—Total and *E. coli*

USEPA Membrane Filtration Method

Method 10029[1]

m-ColiBlue24®

Scope and Application: For potable water, nonpotable water, recreation water and wastewater.

[1] USEPA approved.

Test preparation

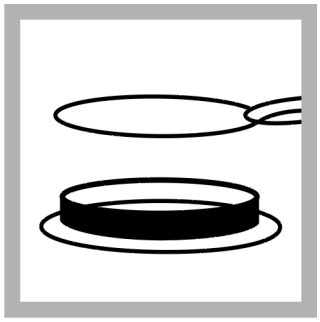
Before starting the test:

When the sample is less than 20 mL (diluted or undiluted), add 10 mL of sterile dilution water to the filter funnel before applying the vacuum. This aids in distributing the bacteria evenly across the entire filter surface.
The volume of sample to be filtered will vary with the sample type. Select a maximum sample size to give 20 to 200 colony-forming units (CFU) per filter. The ideal sample volume of nonpotable water or wastewater for coliform testing yields 20–80 coliform colonies per filter. Generally, for finished, potable water, the volume to be filtered will be 100 mL.
If using PourRite™ ampules, allow the media to warm to room temperature before opening.
Disinfect the work bench with a germicidal cloth, dilute bleach solution, bactericidal spray or dilute iodine solution. Wash hands thoroughly with soap and water.

m-ColiBlue24 Broth PourRite Ampules

The m-ColiBlue24 Broth can be used to analyze drinking water, bottled water, beverages; surface, well, and groundwater, waste water, recreational waters and process water for ultrapure, chemical processing and pharmaceutical applications.

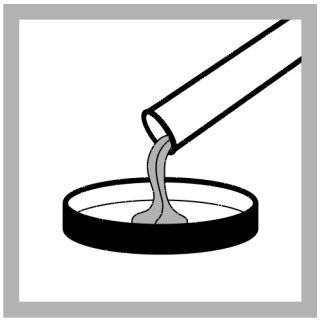
Simultaneous total coliform and *E. coli* screening, method 10029



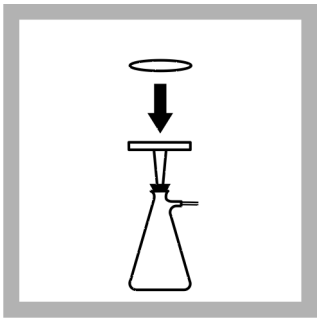
1. Use sterilized forceps to place a sterile, absorbent pad in a sterile petri dish. Replace the lid on the dish.

Do not touch the pad or the inside of the petri dish.

To sterilize the forceps, dip them in alcohol and flame in an alcohol or Bunsen burner. Let the forceps cool before use.

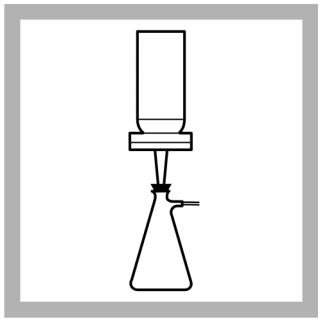


2. Invert ampules two or three times to mix broth. Break open an ampule of m-ColiBlue24 Broth using an ampule breaker. Pour the contents evenly over the absorbent pad. Replace the petri dish lid.



3. Set up the Membrane Filter Apparatus. With sterile forceps, place a membrane filter, grid side up, into the assembly.

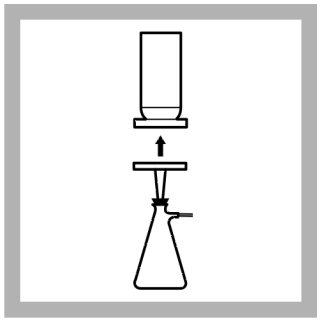
Alternatively, a sterile disposable filter unit may be used.



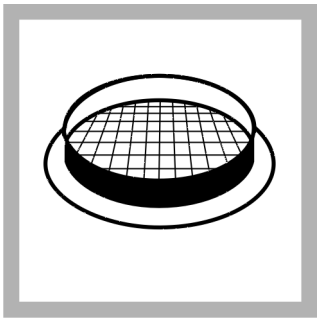
4. Invert the sample for 30 seconds to mix. Pour 100 mL of sample or diluted sample into the funnel. Apply vacuum and filter the sample. Rinse the funnel walls with 20 to 30 mL of sterile buffered dilution water. Apply vacuum. Rinse again two more times.

Release the vacuum when the filter is dry to prevent damage to the filter.

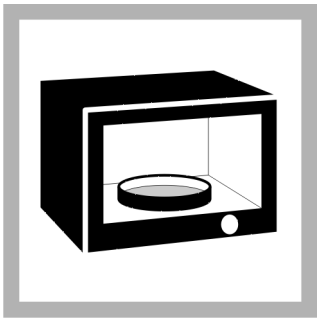
Simultaneous total coliform and *E. coli* screening, method 10029 (continued)



5. Turn off the vacuum and lift off the funnel top. Using sterile forceps, transfer the filter to the previously prepared petri dish.



6. With a slight rolling motion, place the filter, grid side up, on the absorbent pad. Check for trapped air under the filter and make sure the filter touches the entire pad. Replace the petri dish lid.



7. Invert the petri dish and incubate at 35 ± 0.5 °C for 24 hours.

8. Remove the petri dish from the incubator and examine the filters for colony growth. Colonies are typically readily visible; however, a microscope or other 10–15X magnifier may be useful. Red and blue colonies indicate total coliforms and blue colonies specifically indicate *E. coli*.

Sometimes only the center of a colony will show color. Therefore, a colony with any amount of red color should be counted as red and a colony with any amount of blue should be counted as a blue colony. Red colonies may vary in color intensity. Blue colonies may appear blue to purple. Count all the red and blue colonies as total coliforms. Count all the blue to purple colonies as *E. coli.*

Optional testing of red colonies

The m-ColiBlue24 Broth is formulated so that coliforms other than *E. coli* grow as red colonies. The percentage of red colonies that are false positives (non-coliforms) is comparable to the percentage of sheen colonies grown on m-Endo Broth that are false positives (non-coliforms); therefore, confirmation is not required.

A few varieties of the non-coliform bacteria *Pseudomonas, Vibrio,* and *Aeromonas* spp. may grow on m-ColiBlue24 Broth and form red colonies. Such bacteria can be readily distinguished from total coliforms by the oxidase test. *Pseudomonas, Vibrio*, and *Aeromonas* spp. are oxidase-positive. Total coliforms and *Escherichia coli* are oxidase-negative. If your sample contains high levels of interfering bacteria, you can perform an oxidase test to confirm which red colonies are total coliforms.

Two oxidase procedures are provided. Count the red and blue colonies on the m-ColiBlue24 Broth membrane filter before starting the oxidase test.

Oxidase method 1
This method enables you to conveniently and rapidly evaluate membrane filters that have numerous colonies. Use this method after 24 hours of incubation on m-ColiBlue24 Broth.

Research* shows that the oxidase test cannot be performed on media that undergoes acidification during bacterial growth. The m-ColiBlue24 Broth is formulated so that the medium does not undergo such acidification. Consequently, many colonies can be simultaneously tested for their oxidase reaction using the following procedure.

1. Remove the lid from the petri dish containing the m-ColiBlue24 Broth membrane filter, invert the lid, and place it on the bench top.

   Controls: Positive and negative controls are important. *Pseudomonas aeruginosa* is recommended for positive controls and *Escherichia coli* for negative controls. Use Aqua QC-Stiks™ for quality control procedures.

2. Drop approximately 0.5 mL of Difco SpotTest™ Oxidase Reagent into the center of the inverted lid.

3. Using sterile forceps, transfer the membrane filter from the pad and place the filter upright in the inverted lid.

4. Within 10 to 15 seconds, the oxidase reagent will soak into the filter and cause the oxidase-positive colonies to turn purple. This purple color may be visible in the colony itself or adjacent to the colony. Oxidase-negative colonies will retain the red color they developed when incubated on m-ColiBlue24 Broth.

5. After the initial 10 to 15 second reaction time, start counting the red colonies that turn purple. Count individual colonies by using a microscope with 10–15X magnification

   Note: *To simplify colony counting place a spare lid on the lid containing the oxidase reagent and membrane filter. Use a felt-tip pen to mark the lid as you identify the purple colonies. After 30 seconds, you can count marks that indicate purple (oxidase-positive) colonies.*

6. Stop counting 30 seconds after initial 10 to 15 second reaction time, because oxidase-negative colonies will start to develop a purple color.

   Note: *Bacteria are not killed with this procedure, so colonies may be selected for streaking and for additional testing.*

Colonies that are blue after the initial 24-hour incubation on m-ColiBlue24 Broth are almost always *E. coli* and do not need confirmation with the oxidase procedure.

Oxidase method 2
This method is the official oxidase test described in *Standard Methods for the Examination of Water and Wastewater,* 18th edition, 1992.

1. Select red colonies from an m-ColiBlue24 Broth membrane filter and streak onto Tryptic Soy Agar.

2. Incubate Tryptic Soy Agar plates at 35 °C (95 °F) for 18–24 hours or until isolated colonies are obtained.

---

* A.H. Havelaar et al. 1980. False-negative oxidase reaction as a result of medium acidification. *Antonie van Leeuwenhoek*. 46, 301-312. L.K. Hunt et al. 1981. Role of pH in oxidase variability of *Aeromonas hydrophila. Journal of Clinical Microbiology*. 13: 1054-1059.

Controls: Positive and negative controls are important. *Pseudomonas aeruginosa* is recommended for positive and *Escherichia coli* for negative controls. Use Aqua QC-Stiks™* for quality control procedures.

3. Saturate a piece of filter paper with Difco SpotTest Oxidase Reagent. (This reagent contains a stabilized solution of N,N,N',N'-tetramethyl-p-phenylenediamine dihydrochloride.)

   Note: *Alternatively, oxidase reagent can be dropped directly onto colonies growing on Tryptic Soy Agar. Oxidase-positive colonies will turn from pink to purple.*

4. Using a sterile nichrome inoculating needle, transfer cellular material from an isolated Tryptic Soy Agar colony to the moist filter paper.

   Note: *Do not use iron or other reactive needles for inoculation, because they will cause false-positive results. Wooden applicator sticks work well.*

5. Oxidase-negative colonies will not react with the reagent, but oxidase-positive colonies will cause the reagent to turn dark purple within 10 seconds.

6. Oxidase-negative colonies should be counted as total coliform bacteria.

Interpreting and reporting results

Report coliform density as the number of colonies per 100 mL of sample. For total coliforms, use samples that produce 20 to 80 coliform colonies, and not more than 200 colonies of all types, per membrane to compute coliform density. For fecal coliform testing, samples should produce 20 to 60 fecal coliform colonies.

Use ***Equation A*** to calculate coliform density. Note that "mL sample" refers to actual sample volume, and not volume of the dilution.

Equation A—Coliform density on a single membrane filter

$$\text{Coliform colonies per 100 mL} = \frac{\text{Coliform colonies counted}}{\text{mL of sample filtered}} \text{ ì } 100$$

- If growth covers the entire filtration area of the membrane, or a portion of it, and colonies are not discrete, report results as "Confluent Growth With or Without Coliforms."
- If the total number of colonies (coliforms plus non-coliforms) exceeds 200 per membrane or the colonies are too indistinct for accurate counting, report the results as "Too Numerous To Count" (TNTC).

In either case, run a new sample using a dilution that will give about 50 coliform colonies and not more than 200 colonies of all types.

When testing nonpotable water, if no filter meets the desired minimum colony count, calculate the average coliform density with Equation B.

Equation B—Average coliform density for 1) duplicates, 2) multiple dilutions, or 3) more than one filter/sample

$$\text{Coliform colonies per 100 mL} = \frac{\text{Sum of colonies in all samples}}{\text{Sum of volumes (in mL) of all samples}} \text{ ì } 100$$

Controls:
Positive and negative controls are important. *Pseudomonas aeruginosa* is recommended as a negative control and *Escherichia coli* as a positive control. Use the AQUA QC-STIK™ Device for quality control procedures. Instructions for use come with each AQUA QC-STIK Device.

Potable water samples from municipal treatment facilities should be negative for total coliforms and fecal coliforms.

* Aqua QC-Stiks is a trademark of MicroBiologics.

Consumables and replacement items

Required media and reagents

Description	Unit	Catalog number
m-ColiBlue24® Broth Ampules, glass	20/pkg	2608420
m-ColiBlue24® Broth Ampules, plastic	50/pkg	2608450
m-ColiBlue24® prepared agar plates	15/pkg	2805215

Required apparatus

Description	Unit	Catalog number
Ampule Breaker, PourRite™	each	2484600
Bags, Whirl-Pak®, with dechlorinating agent, 180 mL	100/pkg	2075333
Counter, hand tally	each	1469600
Dilution Water, buffered, sterile, 99 mL	25/pkg	1430598
Dish, Petri, with pad, 47-mm, sterile, disposable, Gelman	100/pkg	1471799
Dish, Petri, with pad, 47-mm, sterile, disposable, Millipore	150/pkg	2936300
Filter Holder, magnetic coupling (use with 24861-00)	each	1352900
Filter Funnel Manifold, aluminum, 3-place (use with 13529-00)	each	2486100
Filters, Membrane, 47-mm, 0.45-µm, gridded, sterile, Gelman	200/pkg	1353001
Filters, Membrane, 47-mm, 0.45-µm, gridded, sterile, Millipore	150/pkg	2936100
Filtering Flask, 1000-mL	each	54653
Forceps, stainless steel	each	2141100
Incubator, Culture, 120 VAC, 50/60 Hz	each	2619200
Incubator, Culture, 220 VAC, 50/60 Hz	each	2619202
Microscope, Compound	each	2942500
Pump, vacuum/pressure, portable, 115 VAC, 60 Hz	each	2824800
Pump, vacuum/pressure, portable, 220 VAC, 50 Hz	each	2824802
Stopper, rubber, one hole, No. 8	6/pkg	211908
Tubing, rubber, 0.8 cm (5/16 in.) ID	3.7 m (12 ft)	56019

Optional media, reagents and apparatus

Description	Unit	Catalog number
Adapter for rechargeable battery pack, 230 VAC (for 2580300)	each	2595902
Alcohol Burner	1	2087742
Aspirator, water	each	213102
Autoclave, 120 VAC, 50/60 Hz	each	2898600
Bag, for contaminated items	200/pkg	2463300
Bags, Whirl-Pak®, without dechlorinating agent, 207 mL	100/pkg	2233199
Bags, Whirl-Pak®, without dechlorinating agent, 720 mL	10/pkg	1437297
Battery eliminator	each	2580400
Battery pack, rechargeable, for portable incubator 12 VDC	each	2580300
Bottle, sample, sterilized, 100-mL, disposable with dechlorinating agent	12/pkg	2599112

Optional media, reagents and apparatus (continued)

Description	Unit	Catalog number
Bottle, sample, sterilized, 100-mL, disposable with dechlorinating agent	50/pkg	2599150
Bottle, sample, sterilized, 100-mL, disposable	12/pkg	2495012
Bottle, sample, sterilized, 100-mL, disposable	50/pkg	2495050
Bunsen burner with tubing	each	2162700
Dechlorinating Reagent Powder Pillows	100/pkg	1436369
Dish, Petri, 47-mm, sterile, disposable	100/pkg	1485299
Dish, Petri, 47-mm, sterile, disposable	500/pkg	1485200
Filter Funnel Manifold, aluminum, 3-place (use with 1352900)	each	2486100
Filter Unit, sterile, disposable with gridded membrane (use with 2656700)	12/pkg	2656600
Filtration Support (for field use), stainless steel	each	2586200
Funnels, Push-Fit and membrane filters (use with 2586200)	72/pkg	2586300
Germicidal Cloths	50/pkg	2463200
Incubator, portable, 12 VDC	each	2569900
Incubator, water bath, 120 VAC, 50/60 Hz	each	2616300
Isopropyl alcohol	500 mL	1445949
m-ColiBlue24® Broth, 100 mL glass bottle	1 each	2608442
Pad, absorbent, with dispenser	1000/pkg	1491800
Powder Pillows for buffered dilution water (25 of each)[1]	50/pkg	2143166
Pump, hand vacuum	each	1428300
Sterilization Indicator, Sterikon®	15/pkg	2811115
Sterilization Indicator, Sterikon®	100/pkg	2811199
Syringe, 140-mL, polypropylene (use with 2586200)	each	2586100
Wicks, replacement, for alcohol burner 2087742	—	2097810

[1] Add the contents of one potassium dihydrogen phosphate and one magnesium chloride powder pillow to one liter of distilled water and autoclave (sterilize) to prepare American Public Health Association buffered dilution water.

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company, 2007. All rights reserved. Printed in the U.S.A.

Bacteriological Testing

Test method	River Water	Sample 1	Sample 2	Control
Colilert Quanti-Tray				
Colisure Quanti-Tray				
Membrane Filter mEndo (coliform)				Neg = pseud Pos = E. coli
Membrane Filter M-ColiBlue (*e.coli*)				Neg = pseud Pos = E. coli
Membrane Filter Pseudomonas				

Section 8
Corrosion Control

Phosphorous Testing

Forms of Phosphates

- Orthophosphate: Produced by natural processes and are found in sewage
- Polyphosphate (or Metaphosphate): Used for treating boiler waters and are in detergents. In water they change into orthophosphate form
- Organic Bound Phosphate: Result from breakdown of organic pesticides

Environmental Impact

- Phosphate will stimulate the growth of aquatic plants
- High levels of phosphates entering waterways can stimulate algae and water plants to grow wildly which chokes up the waterways and uses up large amounts of dissolved oxygen

Environmental Impact

- Eutrophication or over-fertilization of receiving water from wastewater effluents
- Digestive problems can occur from extremely high levels of phosphate

Water Stabilization

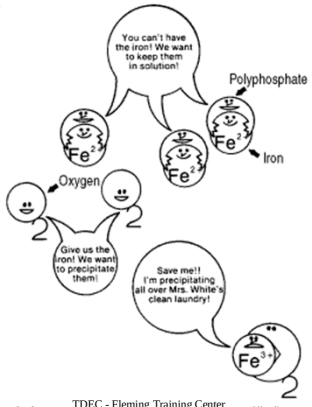
- The process for controlling corrosion and scale deposits on pipelines and plumbing fixtures.
- Corrosion and scale deposits in the distribution system can be very costly for utility.

Water Stabilization

- Problems range from excessive customer complaints to increased pumping costs, to replacement of mains due to leaks and breaks.
- Corrosion control is also important in protecting consumers from the dangers of excess lead and copper.

Polyphosphates

- Polyphoshates work as sequestering agents - tie up iron and manganese to prevent color and taste complaints
  - They also tie up calcium carbonate to prevent excess scale
  - Calcium (from alkalinity) is required as a catalyst
  - If low alkalinity, need a blend of polyphosphate and orthophosphate



Orthophosphates

- Orthophosphate coats pipe, polyphosphate sequesters
- Orthophosphates work well for lead and copper protection

Methods for Determining Phosphates

- Orthophosphate is the amount of inorganic phosphorus in a sample and is measured by direct colorimetric procedures
- Total phosphorus is the amount of all phosphorus present in the sample regardless of form and is measured by the persulfate digestion procedure followed by the colormetric analysis

Total Phosphates

- Acid persulfate digestion method EPA approved
- Measure 25 ml of sample into Erlenmeyer flask
- Add contents of Potassium Persulfate powder pillow and mix
- Add 2.0 ml of 5.25 N Sulfuric Acid Solution
- Place flask on hot plate and Boil gently for 30 minutes, concentrate to less than 20 ml
- Cool sample to room temperature

Total Phosphates

- Add 2.0 ml of 5.0 N Sodium Hydroxide and mix
- Pour sample into 25 ml graduated cylinder, bring back to original volume of 25 ml and pour into clean sample bottle
- Proceed with reactive (ortho) phosphorus test

- THE DIGESTIVE METHOD IS PERFORMED PRIOR TO TESING FOR TOTAL PHOSPHORUS

Ortho-Phosphates

- Phosphorous PhosVer (Ascorbic Acid) reactive method
- Fill a sample cell with sample and one PhosVer 3 Phosphate powder pillow or use AccuVac Ampuls
- Swirl to mix reagent
- Two minute reaction time before testing (10 for digested samples)

TDEC - Fleming Training Center 13

Ortho-Phosphates

- Fill another sample cell with water from sample
  - This is your blank.
- Place in the cell holder of the analytical machine
- When timer beeps, the display will show mg/L P PV, press zero and wait for display to show 0.00 mg/L $PO4^{3-}$

TDEC - Fleming Training Center 14

Ortho-Phosphates

- Place the sample into the machine and press read/enter (DR 4000 will do this automatically)
- If phosphate is present, the sample will turn BLUE in color.

TDEC - Fleming Training Center 15

Shortcut for Total Phosphorous

- If you feed a blend of ortho and poly phosphates and you know the % ortho:
  - Divide ortho mg/L by % to get approximate total concentration
  - Example: 0.32 mg/L ortho and the blend is 30% ortho
    - $0.32 \div 0.30 \approx 1.07$ mg/L total phosphate

TDEC - Fleming Training Center 16

Phosphorus, Reactive (Orthophosphate)

DOC316.53.01119

USEPA[1] PhosVer 3 (Ascorbic Acid) Method[2] **Method 8048**

0.02 to 2.50 mg/L PO_4^{3-} **Powder Pillows or AccuVac® Ampuls**

Scope and Application: For water, wastewater and seawater

[1] USEPA Accepted for reporting for wastewater analyses. Procedure is equivalent to USEPA and Standard Method 4500-P-E for wastewater.

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater.*

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

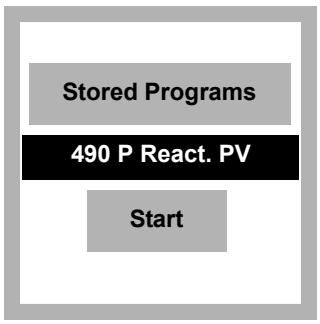
For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water instead of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust.

Collect the following items:

Description	Quantity
Powder Pillow Test:	
PhosVer® 3 Phosphate Reagent powder pillow	1
Sample Cells, 1-inch, 10-mL	2
Stopper for 18 mm Tube	1
AccuVac Test:	
PhosVer® 3 Phosphate Reagent AccuVac® Ampul	1
Beaker, 50-mL	1
Sample Cell, 10-mL round	1
Stopper for 18-mm Tube (supplied with PhosVer AccuVacs)	1

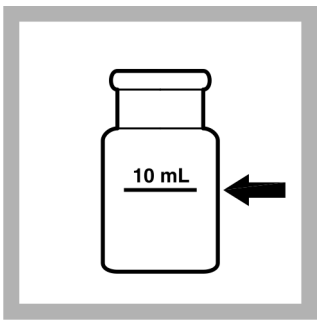
See *Consumables and replacement items* for reorder information.

PhosVer 3 (Ascorbic Acid) method for powder pillows

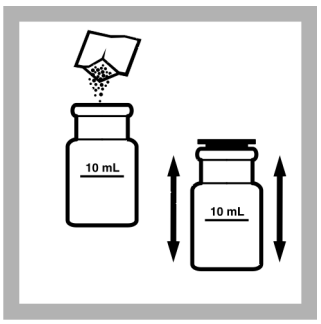


1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).



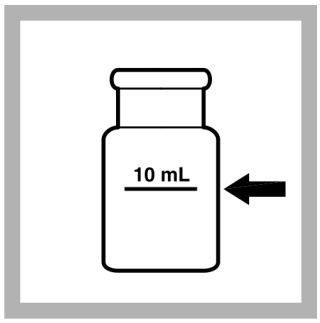
2. Fill a sample cell with 10-mL of sample.



3. Prepared Sample: Add the contents of one PhosVer 3 phosphate Powder Pillow to the cell. Immediately stopper and shake vigorously for 30 seconds.

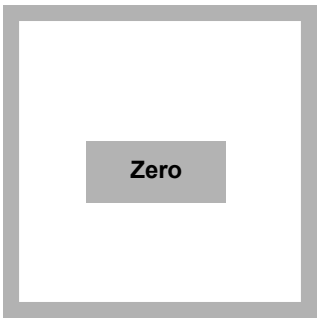
4. Start the instrument timer.

A two-minute reaction period will begin. If the sample was digested using the Acid Persulfate digestion, a ten-minute reaction period is required.



5. Blank Preparation: Fill a second sample cell with 10 mL of sample.

6. When the timer expires, wipe the blank and insert it into the cell holder.



7. ZERO the instrument.

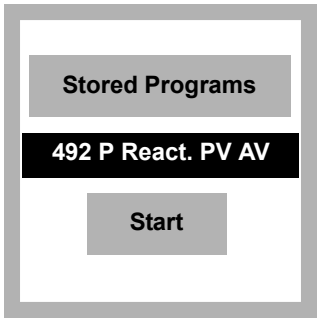
The display will show:

0.00 mg/L PO_4^{3-}

8. Wipe the prepared sample and insert it into the cell holder.

READ the results in mg/L PO_4^{3-}.

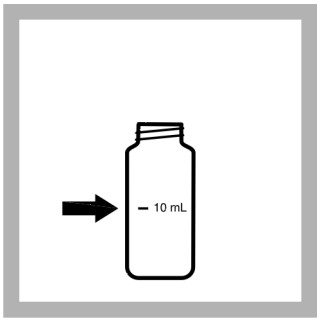
PhosVer 3 (Ascorbic Acid) method for AccuVac® Ampuls



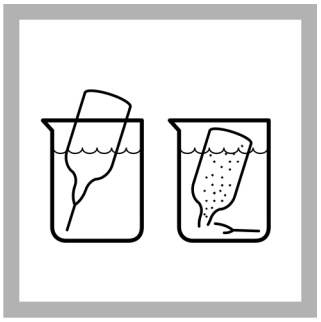
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

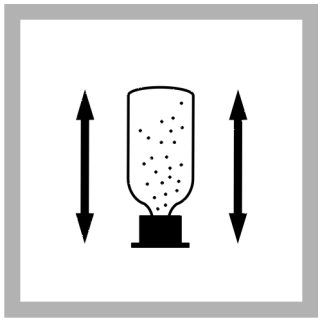
Refer to the user manual for orientation.



2. Blank Preparation: Fill a sample cell with 10-mL of sample.



3. Prepared Sample: Fill a PhosVer 3 Phosphate AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



4. Secure an Ampul cap over the tip of the Ampul. Shake the Ampul for approximately 30 seconds.

Accuracy is unaffected by undissolved powder.

5. Start the instrument timer.

A two-minute reaction period will begin. If the sample was digested using the Acid Persulfate digestion, a ten-minute reaction period is required.

6. When the timer expires, wipe the blank and insert it into the cell holder.

ZERO the instrument.

The display will show:

0.00 mg/L PO_4^{3-}

7. Wipe the prepared sample and insert it into the cell holder.

READ the results in mg/L PO_4^{3-}.

Interferences

Table 2 Interfering substances

Interfering substance	Interference level
Aluminum	Greater than 200 mg/L
Arsenate	Interferes at any level.
Chromium	Greater than 100 mg/L
Copper	Greater than 10 mg/L
Hydrogen Sulfide	Interferes at any level
Iron	Greater than 100 mg/L
Nickel	Greater than 300 mg/L
pH, excess buffering	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment. pH 2–10 is recommended.
Silica	Greater than 50 mg/L
Silicate	Greater than 10 mg/L
Turbidity or color	May cause inconsistent results because the acid in the powder pillow may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add the contents of one Phosphate Pretreatment[1] Powder Pillow to 25 mL of sample. Mix well. Use this solution to zero the instrument.
Zinc	Greater than 80 mg/L

[1] See *Optional reagents and apparatus*.

Sample collection, preservation and storage

- Collect sample in plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution* and rinsed with deionized water.
- Do not use commercial detergents containing phosphate for cleaning glassware used in phosphate analysis.
- For best results, analyze samples immediately.
- If prompt analysis is not possible, preserve samples by filtering immediately and storing at 4 °C (39 °F) for up to 48 hours.
- Return the sample to room temperature before analysis.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Phosphate 10-mL Ampule Standard, 50-mg/L PO_4^{3-}
- Ampule breaker
- TenSette Pipet and tips

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select **OPTIONS>MORE>STANDARD ADDITIONS** from the instrument menu.

* See *Optional reagents and apparatus*.

3. Accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open the standard solution ampule.
5. Prepare a 0.1-mL sample spike by adding 0.1 mL of standard to the unspiked sample. Press the timer icon. After the timer expires, read the result.
6. Prepare a 0.2-mL sample spike by adding 0.1 mL of standard to the 0.1-mL sample spike. Press the timer icon. After the timer expires, read the result.
7. Prepare a 0.3-mL sample spike by adding 0.1 mL of standard to the 0.2-mL sample spike. Press the timer icon. After the timer expires, read the result. Each addition should reflect approximately 100% recovery.

Standard additions method for AccuVac Ampuls (sample spike)
Required for accuracy check:

- Mixing cylinders (3)

1. Fill three mixing cylinders each with 50-mL of sample and spike with 0.2 mL, 0.4 mL and 0.6 mL of standard.
2. Transfer 40 mL from each of the three mixing cylinders to three 50-mL beakers.
3. Analyze each standard addition sample as described in the *PhosVer 3 (Ascorbic Acid) method for AccuVac® Ampuls*.
4. Accept each standard additions reading. Each addition should reflect approximately 100% recovery.

Standard solution method
Note: *Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- Phosphate standard solution, 50 mg/L
- Deionized water
- 100-mL Class A volumetric flask
- 4 mL Class A volumetric pipet and pipet bulb

1. Prepare a 2.00 mg/L phosphate standard solution as follows:
   a. Pipet 4.00 mL of Phosphate Standard, 50-mg/L, into a 100-mL volumetric flask.
   b. Dilute to volume with demineralized water. Mix well. Prepare this solution daily.

Note: *Alternately, use one of the mixed parameter standards listed in Recommended standards. These contain 2.0 mg/L phosphate.*

2. Use this solution in place of the sample. Follow the *PhosVer 3 (Ascorbic Acid) method for powder pillows* test procedure.
3. To adjust the calibration curve using the reading obtained with the standard solution, navigate to Standard Adjust in the software **OPTIONS>MORE>STANDARD ADJUST**.
4. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision—95% Confidence Limits of Distribution	Sensitivity—DConcentration per 0.010 DAbs
490	2.00 mg/L PO_4^{3-}	1.98–2.02 mg/L PO_4^{3-}	0.02 mg/L PO_4^{3-}
492	2.00 mg/L PO_4^{3-}	1.98–2.02 mg/L PO_4^{3-}	0.02 mg/L PO_4^{3-}

Summary of method

Orthophosphate reacts with molybdate in an acid medium to produce a mixed phosphate/ molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. Test results are measured at 880 nm

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
PhosVer® 3 Phosphate Reagent Powder Pillows, 10-mL	1	100/pkg	2106069
OR			
PhosVer® 3 Phosphate Reagent AccuVac® Ampuls	1	25/pkg	2508025

Required apparatus (powder pillows)

Description	Quantity	Unit	Catalog number
Stopper for 18 mm Tube	1	6/pkg	173106

Required apparatus

Description	Quantity	Unit	Catalog number
Beaker, 50-mL	1	each	50041H
Stopper for 18 mm Tube	1	6/pkg	173106
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	each	2122800
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402

Recommended standards

Description	Unit	Catalog number
Phosphate Standard Solution, 10-mL Voluette® Ampul, 50-mg/L as PO_4	16/pkg	17110
Phosphate Standard Solution, 50-mg/L as PO_4	500 mL	17149
Phosphate Standard Solution, 1-mg/L as PO_4	500 mL	256949
Standard, Drinking Water, Mixed Parameter, Inorganic: F, NO_3, PO_4, SO_4	500 mL	2833049
Wastewater Effluent Standard, for mixed parameters: NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC	500 mL	2833249
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Catalog number
Hydrochloric Acid Solution, 6.0N, 1:1	500 mL	88449
Mixing Cylinder, 50 mL	each	189641
Phosphate Treatment Powder Pillow	100/pkg	1450199
Pipet, TenSette®, Pipet, 0.1–1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001[1]	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001[1]	1000/pkg	2185628
Pipet, TenSette, Pipet, 1.0 - 10.0 mL	each	1970010

Optional reagents and apparatus

Description	Unit	Catalog number
Pipet Tips, for TenSette Pipet 1970010[1]	50/pkg	2199796
Pipet Tips, for TenSette Pipet 1970010[1]	250/pkg	2199725
Sampling Bottle with cap, low density polyethylene, 250 mL	12/pkg	2087076
pH Paper, 0–14 pH range	100/pkg	2601300
AccuVac snapper	each	2405200
AccuVac ampule blanks	25/pkg	2677925
Flask, volumetric, 100 mL	each	1457442
Pipet, volumetric, Class A, 4 mL	each	1451504
AccuVac ampule drainer	each	4103600

[1] Other sizes are available

Optional standards

Description	Unit	Catalog number
Voluette Ampule breaker 10 mL	each	2196800
Phosphate, Standard Solution, 10 mg/L	946 mL	1420416
Phosphate, Standard Solution, 15 mg/L	100 mL	1424342
Phosphate; Standard Solution, 100 mg/L	100 mL	1436832
Phosphate; Standard Solution, 500 mg/L, 10 mL Voluette Ampules	16/pkg	1424210
Phosphate; Standard Solution, 500 mg/L	100 mL	1424232

© Hach Company, 2007, 2010. All rights reserved. Printed in the U.S.A.

Phosphorus, Total

DOC316.53.01121

USEPA[1]
PhosVer® 3 with Acid Persulfate Digestion Method

Method 8190

0.06 to 3.50 mg/L PO_4^{3-} or
0.02 to 1.10 mg/L P

Test 'N Tube™ Vials

Scope and Application: For water, wastewater and seawater

[1] USEPA Accepted for reporting wastewater analyses (Standard Methods 4500 P-E).

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Light shield
DR 3900	LZV849
DR 3800, DR 2800, DR 2700	LZV646

Before starting the test:

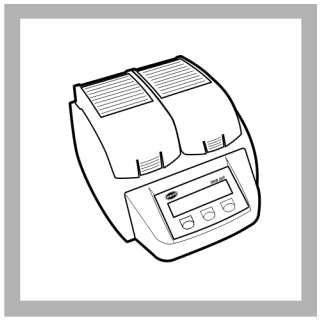
DR 3900, DR 3800, DR 2800 and DR 2700: Install the light shield in Cell Compartment #2 before performing this test.
For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust.
The test range for total phosphate is limited to 0.06 to 3.5 mg/L PO_4^{3-}. Values greater than 3.5 mg/L may be used to estimate dilution ratios, but should NOT be used for reporting purposes. If the value is greater than 3.5 mg/L, dilute the sample and repeat the digestion and the colorimetric test.
Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA. Refer to the current MSDS for safe handling and disposal instructions.

Collect the following items:

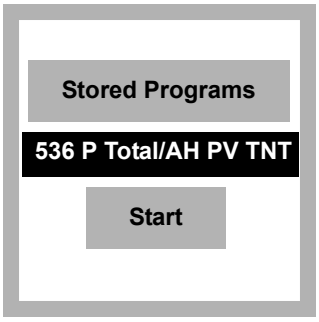
Description	Quantity
Total Phosphorus Test ‘N Tube™ Reagent Set	1
Deionized water	varies
DRB200 Reactor	1
Funnel, micro	1
Light Shield or Adapter (see *Instrument-specific information*)	1
Pipet, TenSette®, 1 to 10 mL, plus tips	1
Test Tube Rack	1

See *Consumables and replacement items* for reorder information.

PhosVer 3, acid persulfate digestion

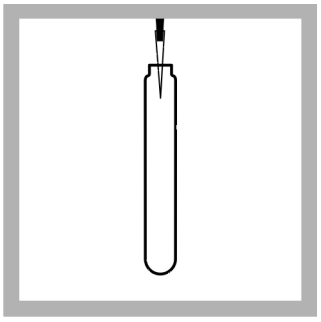


1. Turn on the DRB200 Reactor. Preheat to 150 °C.

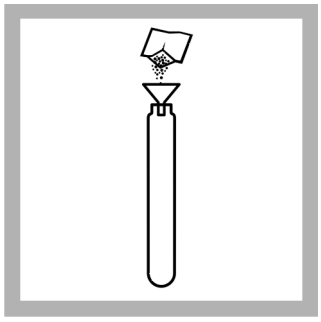


2. Select the test.

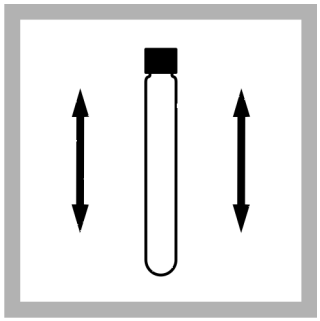
Insert an adapter if required (see *Instrument-specific information*).



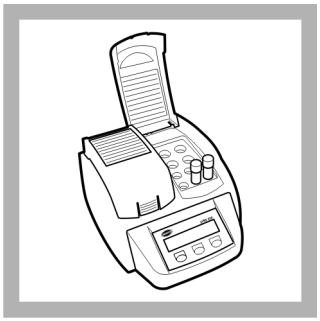
3. Use a TenSette® Pipet to add 5.0 mL of sample to a Total Phosphorus Test Vial.



4. Use a funnel to add the contents of one Potassium Persulfate Powder Pillow for Phosphonate to the vial.



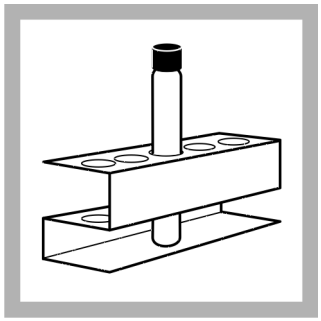
5. Cap tightly and shake to dissolve.



6. Insert the vial into the DRB200. Close the protective cover.

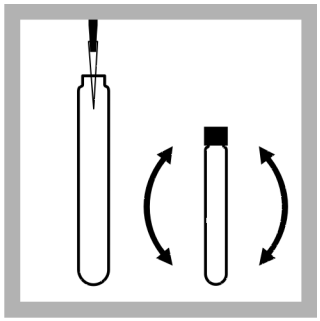
7. Set the instrument timer to 30 minutes and start.

A 30-minute heating period will begin.



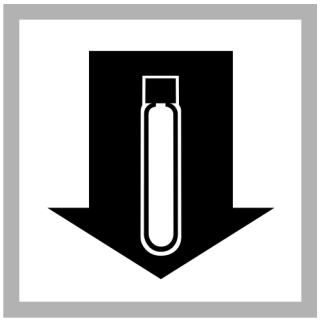
8. When the timer expires, carefully remove the hot vial from the reactor. Insert it in a test tube rack and cool to room temperature.

PhosVer 3, acid persulfate digestion (continued)

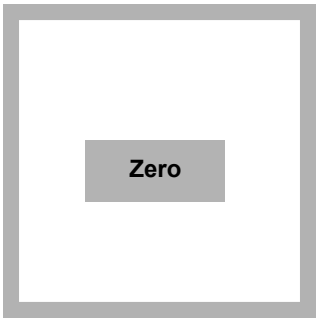


9. Use a TenSette Pipet to add 2 mL of 1.54 N Sodium Hydroxide Standard Solution to the vial. Cap and mix.

10. Wipe the outside of the vial with a damp cloth followed by a dry one.



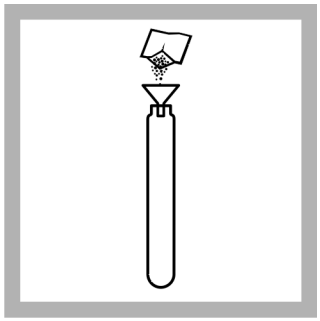
11. Insert the vial into the 16 mm cell holder.



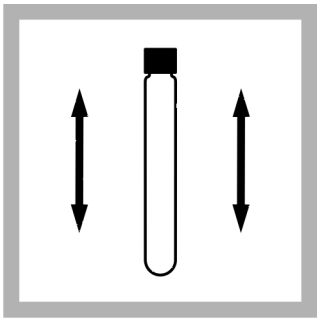
12. **ZERO** the instrument.

The display will show:

0.00 mg/L PO_4^{3-}



13. Use a funnel to add the contents of one PhosVer 3 Powder Pillow to the vial.



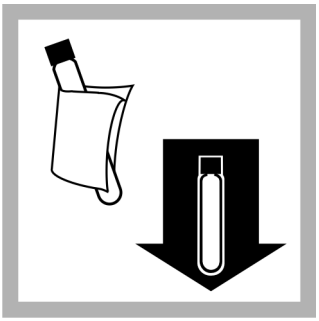
14. Immediately cap tightly and shake to mix for 20–30 seconds.

The powder will not dissolve completely.

15. Start the instrument timer.

A two-minute reaction period will begin.

Read the sample within 2–8 minutes after the timer expires.



16. After the timer expires, wipe the outside of the vial with a wet towel, then a dry one. Insert the prepared sample vial into the 16 mm cell.

READ the results in mg/L PO_4^{3-}.

Interferences

Table 2 Interfering substances

Interfering substance	Interference level
Aluminum	Greater than 200 mg/L
Arsenate	Interferes at any level
Chromium	Greater than 100 mg/L
Copper	Greater than 10 mg/L
Iron	Greater than 100 mg/L
Nickel	Greater than 300 mg/L
pH, excess buffering	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Silica	Greater than 50 mg/L

Table 2 Interfering substances (continued)

Interfering substance	Interference level
Silicate	Greater than 10 mg/L
Sulfide	Greater than 90 mg/L
Turbidity or color	May cause inconsistent results because the acid in the powder pillow may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.
Zinc	Greater than 80 mg/L

Sample collection, preservation and storage

- Collect samples in plastic or glass bottles that have been acid washed with 1:1 Hydrochloric Acid Solution* and rinsed with deionized water.
- Do not use commercial detergents containing phosphate for cleaning glassware used in this test.
- Analyze the samples immediately for the most reliable results.
- If prompt analysis is not possible, samples may be preserved up to 28 days by adjusting the pH to 2 or less with concentrated Sulfuric Acid* (about 2 mL per liter) and storing at 4 °C.
- Warm stored samples to room temperature and neutralize with 5.0 N Sodium Hydroxide* before analysis.
- Correct test results for volume additions.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Phosphate 10-mL Ampule Standard, 50-mg/L as PO_4^{3-}
- Ampule breaker
- TenSette Pipet and tips
- Mixing cylinders, (3)

1. Clean glassware with 1:1 Hydrochloric Acid Standard Solution. Rinse again with deionized water. Do not use phosphate detergents to clean glassware.
2. After reading test results, leave the sample cell (unspiked sample) in the instrument.
3. Select standard additions from the instrument menu **OPTIONS>MORE>STANDARD ADDITIONS**.
4. Accept the default values for standard concentration, sample volume and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
5. Open the standard solution ampule.
6. Use the TenSette Pipet to prepare spiked samples: add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 25-mL portions of fresh sample.
7. Use a 5-mL aliquot of the spiked sample in place of the sample. Follow the *PhosVer 3, acid persulfate digestion* test procedure for each of the spiked samples, starting with the 0.1 mL sample spike. Measure each of the spiked samples in the instrument.

* See *Optional reagents and apparatus*.

8. Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Standard solution method

Note: *Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- Phosphate standard solution, 3.0-mg/L

1. Use the 3.0 mg/L phosphate standard solution in place of the sample. Follow the *PhosVer 3, acid persulfate digestion* test procedure.
2. To adjust the calibration curve using the reading obtained with the standard solution, navigate to Standard Adjust in the software **OPTIONS>MORE>STANDARD ADJUST**.
3. Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision—95% Confidence Limits of Distribution	Sensitivity—DConcentration per 0.010 DAbs
536	3.00 mg/L PO_4^{3-}	2.93–3.07 mg/L PO_4^{3-}	0.06 mg/L PO_4^{3-}

Summary of method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphates by heating with acid and persulfate.

Orthophosphate reacts with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. Test results are measured at 880 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Total Phosphorus Test 'N Tube™ Reagent Set, 50 tests, includes:	—	—	2742645
PhosVer® 3 Phosphate Reagent Powder Pillows	1	50/pkg	2106046
Potassium Persulfate Powder Pillows	1	50/pkg	2084766
Sodium Hydroxide Solution, 1.54 N	2 mL	100 mL	2743042
Total and Acid Hydrolyzable Test Vials[1]	1	50/pkg	—
Water, deionized	varies	100 mL	27242

[1] Not sold separately

Required apparatus

Description	Quantity	Unit	Catalog number
DRB200 Reactor, 110 V, 15 x 16 mm	1	each	LTV082.53.40001

Required apparatus

Description	Quantity	Unit	Catalog number
DRB200 Reactor, 220 V, 15 x 16 mm	1	each	LTV082.52.40001
Funnel, micro	1	each	2584335
Light shield, DR 3900	1	each	LZV849
Light shield, DR 3800, DR 2800, DR 2700	1	each	LZV646
Pipet, TenSette®, 1.0 to 10 mL	1	each	1970010
Pipet Tips for TenSette Pipet 19700-10	1	250/pkg	2199725
Test Tube Rack	1	each	1864100

Recommended standards

Description	Unit	Catalog number
Drinking Water Standard, Mixed Parameter, Inorganic for F-, NO_3, PO_4, SO_4	500 mL	2833049
Phosphate Standard Solution, 10-mL Voluette® Ampule, 50-mg/L as PO_4^{3-}	16/pkg	17110
Phosphate Standard Solution, 1-mg/L as PO_4^{3-}	500 mL	256949
Phosphate Standard Solution, 3 mg/L as PO_4^{3-}	946 mL	2059716
Wastewater Standard, Effluent Inorganics, for NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC	500 mL	2833249
Voluette Ampule breaker 10 mL	each	2196800

Optional reagents and apparatus

Description	Unit	Catalog number
Cylinder, mixing, 25 mL	each	189640
Pipet, volumetric, Class A, 2.00 mL	each	1451536
Hydrochloric Acid Solution, 6.0 N, 1:1	500 mL	88449
Sodium Hydroxide, 5.0 N	1000 mL	245053
Sulfuric Acid, concentrated	500 mL	97949
Pipet, TenSette® Pipet, 0.1–1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
Sampling Bottle with cap, low density polyethylene, 250 mL	12/pkg	2087076
pH Paper, 0–14 pH range	100/pkg	2601300
Deionized Water	4 L	27256
Thermometer, Non-Mercury, -10 to 225 °C	each	2635700
Finger cots	2/pkg	1464702

Optional standards

Description	Unit	Catalog number
Phosphate, Standard Solution, 10 mg/L	946 mL	1420416
Phosphate, Standard Solution, 15 mg/L	100 mL	1424342
Phosphate, Standard Solution, 100 mg/L	100 mL	1436832
Phosphate, Standard Solution, 500 mg/L, 10 mL Voluette Ampules	16/pkg	1424210

Optional standards

Description	Unit	Catalog number
Phosphate, Standard Solution, 500 mg/L	100 mL	1424232

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

© Hach Company, 2007, 2010. All rights reserved. Printed in the U.S.A.

Phosphorus, Total, Digestion

DOC316.53.01112

USEPA[1] Acid Persulfate Digestion Method[2]

Method 8190

Scope and Application: For water, wastewater and seawater

[1] USEPA Accepted for wastewater analyses when used with the ascorbic acid (PhosVer 3) method.

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater* 4500-P B & E

Test preparation

Before starting the test:

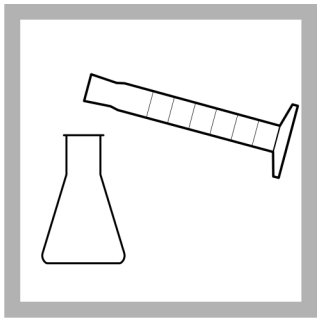
Rinse all glassware with 1:1 hydrochloric acid. Rinse again with deionized water.

Collect the following items:

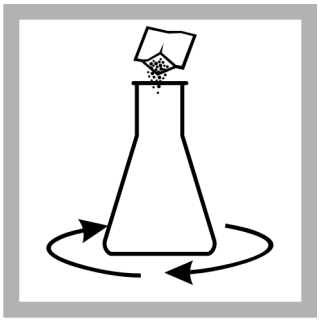
Description	Quantity
Potassium Persulfate Powder Pillows	1
Sodium Hydroxide Solution, 5.0 N	2 mL
Sulfuric Acid Solution, 5.25 N	2 mL
Water, deionized	varies
Cylinder, graduated, 25-mL	1
Flask, Erlenmeyer, 125-mL	1
Hot Plate	1

See *Consumables and replacement items* for reorder information.

Acid Persulfate Digestion

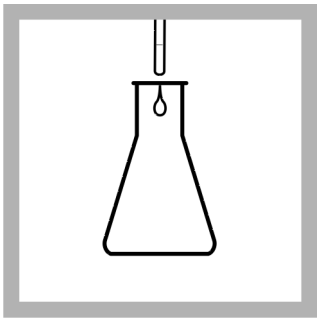


1. Use a graduated cylinder to measure 25 mL of sample. Pour the sample into a 125-mL Erlenmeyer flask.

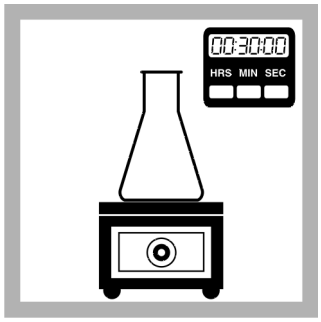


2. Add the contents of one Potassium Persulfate Powder Pillow.

Swirl to mix.

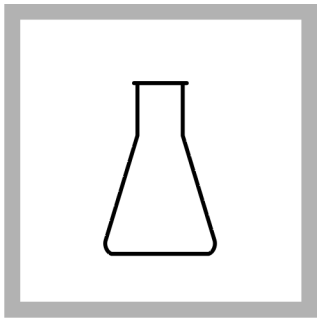


3. Use a 1-mL calibrated dropper to add 2.0 mL of 5.25 N Sulfuric Acid Solution to the flask.

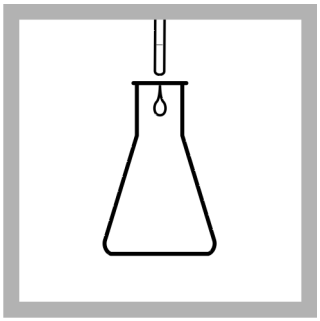


4. Place the flask on a hot plate. Boil gently for 30 minutes. Do not boil dry.

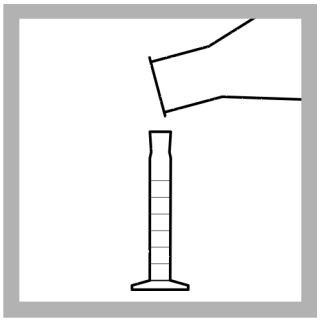
Concentrate the sample to less than 20 mL for best recovery. After concentration, maintain the volume near 20 mL by adding small amounts of deionized water. Do not exceed 20 mL.



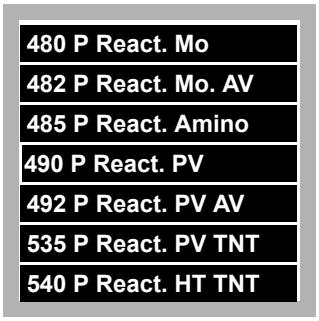
5. Cool the sample to room temperature.



6. Use a 1-mL calibrated dropper to add 2.0 mL of 5.0 N Sodium Hydroxide Solution to the flask. Swirl to mix.



7. Pour the sample into a 25-mL graduated cylinder. Adjust the volume to 25 mL with deionized water rinsings from the flask.



8. Proceed with a reactive phosphorus test of the expected total phosphorus concentration range.

Extend the color development time to 10 minutes for the PhosVer 3 (ascorbic acid) method.

Interferences

Table 1 Interfering substances

Interfering substance	Interference level
Alkaline or highly buffered samples	It may be necessary to add additional acid in step 3 to drop the pH of the solution below 1.
Turbidity	Use 50 mL of sample and double the reagent quantities. Use a portion of the reacted sample to zero the instrument in the reactive phosphorus procedure. This compensates for any color or turbidity destroyed by this procedure.

Sample collection, preservation and storage

- Analyze the samples immediately for the most reliable results.
- If prompt analysis is not possible, samples may be preserved up to 28 days.
- To preserve samples. adjust the pH to 2 or less with Concentrated Sulfuric Acid* (about 2 mL per liter). Store at 4 °C.
- Warm the sample to room temperature and neutralize with 5.0 N Sodium Hydroxide before analysis.
- Correct test results for volume additions.

Summary of method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulfate. Organically bound phosphates are thus determined indirectly by subtracting the result of an acid hydrolyzable phosphorus test from the total phosphorus result.

This procedure must be followed by one of the reactive phosphorus (orthophosphate) analysis methods for determining the phosphorus content of the sample. If the ascorbic acid (PhosVer 3) method is used to measure the reactive phosphorus, this method is USEPA accepted for NPDES reporting.

The following reagents and apparatus are required in addition to those required for the active phosphorus test.

* See *Optional reagents*.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Potassium Persulfate Powder Pillows	1	100/pkg	245199
Sodium Hydroxide Solution, 5.0 N	2 mL	100 mL MDB	245032
Sulfuric Acid Solution, 5.25 N	2 mL	100 mL MDB	244932
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity	Unit	Catalog number
Cylinder, graduated, 25-mL	1	each	50840
Flask, Erlenmeyer, 125-mL	1	each	50543
Hot Plate, 7” x 7” digital, 115 VAC	1	each	2881500
Hot Plate, Stirrer, 7” x 7” digital, 230 VAC	1	each	2881602

Optional reagents

Description	Unit	Catalog number
Sodium, Hydroxide, 5.0 N	1000 mL	245053
Sulfuric Acid, concentrated	500 mL	97949
pH paper, 0–14 pH range	100/pkg	2601300
Thermometer, Non-Mercury, –10 to 225°C	each	2635700
Sampling bottle with cap, low density polyethylene, 250 mL	12/pkg	2087076
Hydrochloric Acid, 6.0 N	500 mL	88449

© Hach Company, 2007, 2011. All rights reserved. Printed in the U.S.A.

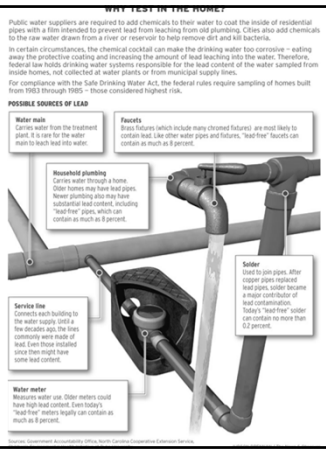
Section 9
Lead and Copper Sampling

Lead & Copper

Water Treatment Lab

TDEC - Fleming Training Center

1



TDEC - Fleming Training Center

2

Lead

- Primary cause of contamination in drinking water
  - Caused by corrosion of leaded materials in the water distribution system
    - Lead - based solder used to join copper pipe
    - Brass - and chrome-plated brass faucets
    - Lead service lines that connect houses to water mains

TDEC - Fleming Training Center

3

Health Effects of Lead Contamination

- Children
  - Altered physical/mental development
  - Interference with growth
  - Deficits in IQ, attention span and hearing
  - Interference with heme (blood) synthesis
- Women
  - Increased blood pressure
  - Shorter gestation period
- Men
  - Increased blood pressure

TDEC - Fleming Training Center

4

Health Effects of Copper Contamination

- Complications of Wilson's Disease
  - Wilson's Disease is a hereditary liver condition that restricts the body's ability to metabolize copper
- Stomach and intestinal distress
- Liver or kidney damage

TDEC - Fleming Training Center

5

Treatment Techniques

- Corrosion control – Lead & Copper
- Source water treatment – Lead & Copper
- Lead service line replacement – Lead
- Public education – Lead

TDEC - Fleming Training Center

6

Action Levels

- Lead = 0.015 mg/L
- Copper = 1.3 mg/L

- A system is often required to begin initiating treatment techniques when lead and/or copper levels in more than 10% of samples exceed these levels

TDEC - Fleming Training Center
7

Water Quality Parameters

- pH
- Alkalinity
- Calcium
- Conductivity
- Water temperature
- Orthophosphate or silica
  - If an inhibitor containing these compounds is used

TDEC - Fleming Training Center
8

Sample Site Selection

- All public water systems are required to sample at the customer's tap
- Specified targeting criteria have been selected to indicate probability of lead or copper contamination and to create a tiered system

TDEC - Fleming Training Center
9

How many sampling sites?

- The number of sampling sites are determined by the size of the population served by the system

TDEC - Fleming Training Center
10

Tier 1

- Consists of single family structures with:
  - Copper pipes with lead solder installed after 1982
  - Interior lead piping
  - Lead service lines
- May include multiple family residences if these comprise of more than 20% of the service connections to the public water supply

TDEC - Fleming Training Center
11

Tier 2

- Consist of buildings, including multiple family residences, with:
  - Copper pipes with lead solder installed after 1982
  - Interior lead piping
  - Lead service lines

TDEC - Fleming Training Center
12

Tier 3

- Consist of single family structures with:
  - Copper pipes with lead solder installed before 1983

TDEC - Fleming Training Center

13

Tap Water Samples

- First draw
  - Tap water that has remained motionless in the plumbing system for at least 6 hours
  - Collected without flushing the tap
- One liter
- Collected from a cold water kitchen tap or from a bathroom sink

TDEC - Fleming Training Center

14

Tap Water Samples

- Samples should be preserved with nitric acid (HNO_3) to a pH<2
- Plastic or glass container
- Holding time is 6 months

TDEC - Fleming Training Center

15

Reporting

- Results of all tap samples for lead and copper
  - Location of each site
  - Criteria used for site selection
- Certification that lead and copper samples were collected properly
- Certification that residents who collected lead and copper samples were informed of correct sampling procedures

TDEC - Fleming Training Center

16

Reporting

- Lead and copper 90th percentile concentrations
- Designation of any new sampling sites
  - Explanation of why sites have changed
- Result of all tap sampling for pH and other water quality parameters
- Results of all water quality samples collected at entry point(s) to the distribution system

TDEC - Fleming Training Center

17

90th Percentile Concentrations

- 0400-45-1.33(1)(c)(i) – The results of all lead or copper samples taken during a monitoring period shall be placed in ascending order from the sample with the lowest concentration to the sample with the highest concentration.
- Each sampling result shall be assigned a number, ascending by single integers beginning with the number 1 for the sample with the lowest contaminant level.

TDEC - Fleming Training Center

18

90th Percentile Concentrations

- 0400-45-1.33(1)(c)(i) cont. – The number assigned to the sample with the highest contaminant level shall be equal to the total number of samples taken.
- 0400-45-1.33(1)(c)(ii) – The number of samples taken during the monitoring period shall be multiplied by 0.9.

TDEC - Fleming Training Center

19

90th Percentile Concentrations

- 0400-45-1.33(1)(c)(iii) – The contaminant concentration in the numbered sample yielded by the calculation in (c)3(ii) is the 90th percentile contaminant level.
- 0400-45-1.33(1)(c)(iv) – For water systems serving fewer than 100 people that collect 5 samples per monitoring period, the 90th percentile is computed by taking the average of the highest and second highest concentrations.

TDEC - Fleming Training Center

20

90th Percentile Concentrations

- Copper Samples
  1. 0.03
  2. 0.11
  3. 0.23
  4. 0.27
  5. 0.28
  6. 0.59
  7. 0.63
  8. 0.98
  9. 1.31

0400-45-1.33(1)(c)(ii)
(0.9)(9) = 8.1

90th Percentile is less than the action level

TDEC - Fleming Training Center

21

Record Keeping

- Systems must retain on its premises original records of:
  - All sampling data and analyses
  - Reports
  - Surveys
  - Letters
  - Evaluations
  - Schedules
  - State determinations
- These records must be kept for 12 years

TDEC - Fleming Training Center

22

Lead and Copper
Review Questions

1. Name the primary cause of lead contamination in drinking water.

2. List two negative health effects of lead contamination.

3. List two negative health effects of copper contamination.

4. What are the treatment technique requirements specified in the Lead and Copper Rule?

5. What is the action level for lead and for copper?

6. For community water systems, Tier 1 sampling sites consist of single family structures with:
   a _____
   b _____
   c _____

7. All tap water samples must be _____ in volume and must have stood motionless in the plumbing system of the sampling site for at least _____ hours.

8. True or False. The number of sampling sites is determined by the size of the population served by the system.

9. The Lead and Copper Rule specifies that systems must monitor the following water quality parameters:
   a _____
   b _____
   c _____
   d _____
   e _____
   f _____
   g _____

10. How many years must the system keep records required by the Lead and Copper Rule?

11. How do you preserve a sample for Lead and Copper and what is the holding time?

Answers

1. Corrosion of lead-containing materials in distribution and plumbing systems.
2. Negative health effects of lead contamination include:
   a Increased blood pressure
   b Shorter gestational period for pregnant women
   c Brain, red blood cell and kidney damage
   d Deficits in IQ, attention span and hearing in children
   e Interference with growth in children
   f Interference with heme (blood) synthesis in children
   g Slowed mental and physical development in children
3. Negative health effects of copper contamination include:
   a Stomach and intestinal distress
   b Complications of Wilson's disease
   c Liver and kidney damage
   d Anemia
4. The treatment technique requirements specified in the Lead and Copper Rule are:
   a For lead: corrosion control treatment, source water treatment, lead service line replacement, public education
   b For copper: corrosion control treatment and source water treatment
5. The action level for lead is exceeded if more than 10% of samples have lead concentrations greater than 0.015 mg/L (15 ppb). The action level for copper is exceeded if more than 10% of samples have copper concentrations greater than 1.3 mg/L.
6. For CWSs, Tier 1 sampling sites consist of single family structures with:
   a Copper pipes with lead solder installed after 1982
   b Interior lead piping
   c Lead service lines
7. All tap water samples must be **1L** in volume and must have stood motionless in the plumbing system of the sampling site for at **6** hours.
8. True
9. The Lead and Copper Rule specifies that systems must monitor the following water quality parameters:
   a pH
   b Alkalinity
   c Orthophosphate
   d Silica
   e Conductivity
   f Calcium
   g Water temperature
10. at least 12 years
11. Preserve with HNO_3 (nitric acid) to a pH<2 in a plastic or glass container with a holding time of 6 months.

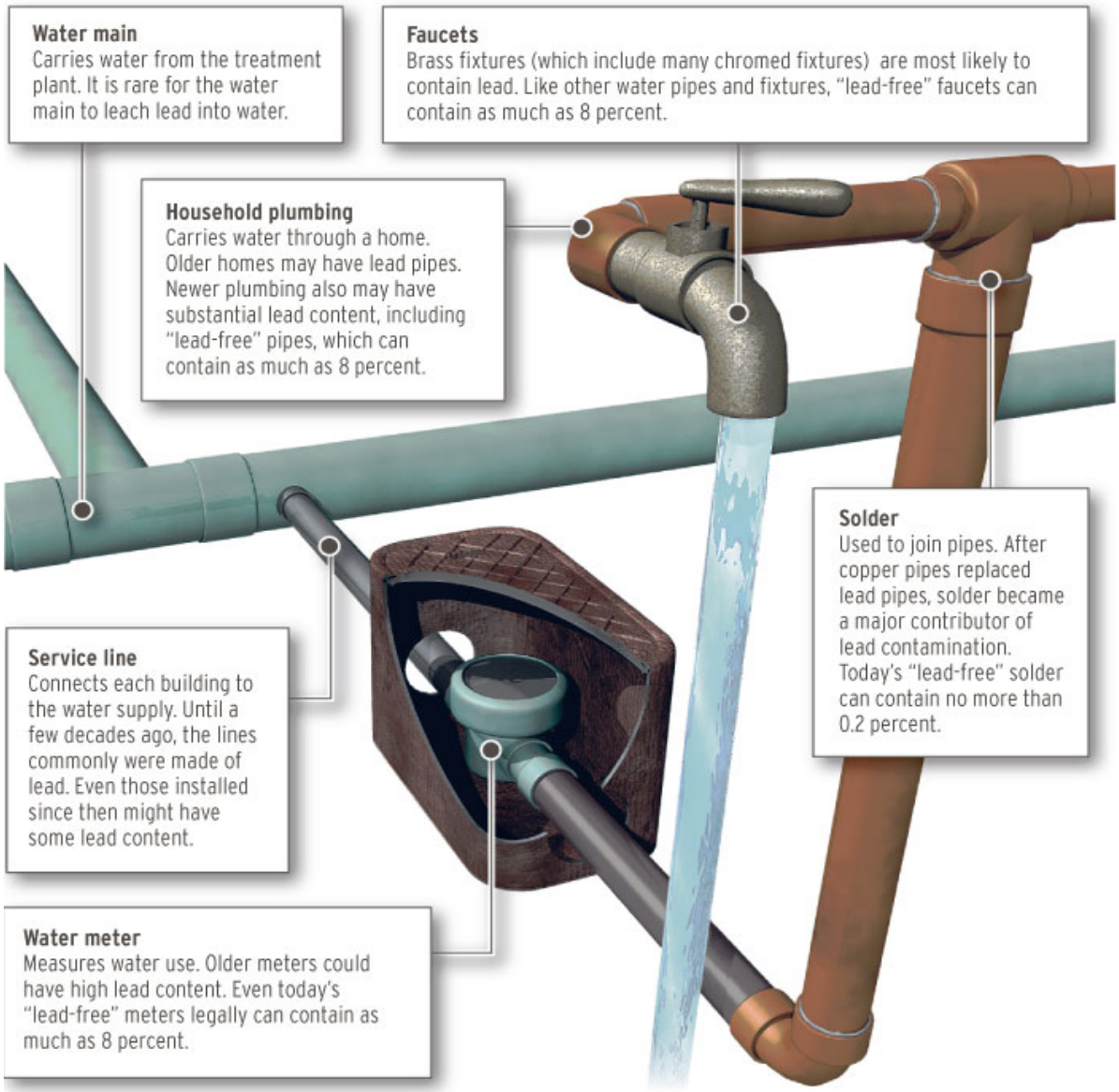
WHY TEST IN THE HOME?

Public water suppliers are required to add chemicals to their water to coat the inside of residential pipes with a film intended to prevent lead from leaching from old plumbing. Cities also add chemicals to the raw water drawn from a river or reservoir to help remove dirt and kill bacteria.

In certain circumstances, the chemical cocktail can make the drinking water too corrosive – eating away the protective coating and increasing the amount of lead leaching into the water. Therefore, federal law holds drinking water systems responsible for the lead content of the water sampled from inside homes, not collected at water plants or from municipal supply lines.

For compliance with the Safe Drinking Water Act, the federal rules require sampling of homes built from 1983 through 1985 – those considered highest risk.

POSSIBLE SOURCES OF LEAD



Sources: Government Accountability Office, North Carolina Cooperative Extension Service, Children's Environmental Health Initiative at Duke University

JUDSON DRENNAN / The News & Observer

Section 10
Turbidity

TURBIDITY

Water Treatment Lab

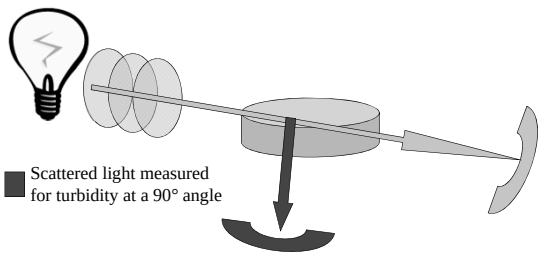
Turbidity

- A measure of the clarity of water
- It is an expression of the optical property that causes light to be scatter and absorbed in water
- It is caused by particulate, such as silt, clay, organic matter, algae and other microorganisms
- Amount of light absorbed is proportional to the concentration of particulate in the sample

Turbidity

- Caused by suspended and colloidal matter in water
- It is expression of light that is scattered or absorbed through a sample
- Does not indicate the number or size of particles in a sample
- General indicator of overall effluent water quality and a good process control test for operator

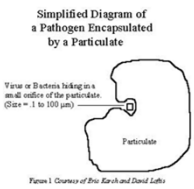
Turbidimeters



Scattered light measured for turbidity at a 90° angle

Light source from tungsten lamp passing through three precisely aligned lenses, the light is focused in a narrow, collimated beam

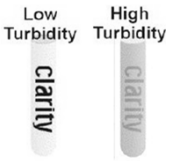
Importance



- Supports growth of microorganisms
- Reduces effectiveness of chlorination
- Interferes with chemical and microbiological analysis

Importance

- Is unacceptable for aesthetic reasons
- Is related to coagulation and filtration
- Is unacceptable for most industrial water



Measuring

- Use an instrument for measuring and comparing turbidity of liquids
- Nephelometers are instruments which measure turbidity by comparing the amount of light in a sample to the amount of light scattered by a standard
- The amount of scattered light is measured and converted to units of turbidity or NTU's (Nephelometric Turbidity Units)

Instruments

HACH 2100-N Laboratory Turbidimeter Benchtop

Portable Turbidimeter

Measuring Notes

- Always cap the sample cell to prevent spillage into instrument
- Close the sample compartment lid during measurement
- Do not leave sample cell in the cell compartment for extended periods of time
- Leave the instrument on 24 hours a day if instrument is used regularly

Measuring Notes

- Always use clean, scratch free sample cells and caps
- Always use silicone oil
- Measuring samples immediately to prevent changes in sample characteristics
- Remove air bubbles in sample cells
- Discard sample cells with scratches

Calibrations

- Use Gelex Secondary Turbidity Standards for periodic checks
- Primary Stable Cal Standards
  - Formazin Solution Primary Standards and Procedure for making solutions
- Record keeping requirements and recommendations for operators
- Calibrate at least quarterly

Calibrations

- Labtronix recommends a "Cold Start" when calibrating
  - Sets instrument back to factory settings
  - Erases past calibrations and any other manipulation of instrument
  - Hold Cal button down, turn off instrument, continue holding down Cal button and turn instrument back on

Frequently Asked Questions Regarding Turbidity from Hach

What is the difference between the turbidity units NTU, FNU, FTU, and FAU? What is a JTU?

Problem Solution:

NTU stands for Nephelometric Turbidity Unit and signifies that the instrument is measuring scattered light from the sample at a 90-degree angle from the incident light. FNU standards for Formazin Nephelometric Units and also signifies that the instrument is measuring scattered light from the sample at a 90-degree angle from the incident light. NTU is most often used when referencing the USEPA Method 180.1 or Standard Methods For the Examination of Water and Wastewater. FNU is most often used when referencing the ISO 7027 (European) turbidity method.

When formazin was initially adopted as the primary reference standard for turbidity, units of FTU or Formazin Turbidity Units were used. These units, however, do not specify how the instrument measures the sample.

FAU or Formazin Attenuation Units signify that the instrument is measuring the decrease in transmitted light through the sample at an angle of 180 degrees to the incident light. This type of measurement is often made in a spectrophotometer or colorimeter and is not considered a valid turbidity measurement by most regulatory agencies.

The turbidity units NTU, FNU, FTU, AND FAU are all based on calibrations using the same formazin primary standards. Therefore when a formazin standard is measured, the value for each of these units will be the same, however the value on samples may differ significantly.

A JTU or Jackson Turbidity Unit is a historical unit used when measurements were made visually using a Jackson Candle Turbidimeter. Water was poured into a tube until a flame underneath the tube could no longer be distinguished.

Why do I need to calibrate my turbidimeter? Aren't turbidimeters calibrated at the factory?

Problem Solution:

The light source used in turbidimeters has a specified temperature (required by USEPA regulations) at which it is required to operate. Because these lamps operate at a relatively high temperature, the output of the lamps can change over time, which can affect the amount of light that reaches the detector and thus the turbidity reading.

Hach lamps are specially designed for increased stability and are stable upon factory calibration. However, USEPA regulations mandate calibration upon receipt and set up of the instrument at the test site, as well as calibration on a quarterly basis.

Can I use Gelex standards to calibrate my turbidimeter?

Problem Solution:

Gelex standards should never be used to calibrate a turbidimeter. They are designed to check the calibration after the turbidimeter has been calibrated with a primary standard such as StablCal.

After calibrating the turbidimeter with StablCal or formazin standards, place each Gelex vial in the sample compartment, and write the NTU value of each Gelex standard on each vial. Place the Gelex vials in the turbidimeter on a regular basis and compare the NTU value with the value written on the vial. When the measured turbidity is greater than 5 percent different from the recorded value, the turbidimeter should be calibrated again using a primary standard.

Note: you may need to calibrate your turbidimeter more often than indicated by the reading from the Gelex vials in order to meet regulatory compliance

How do I use Gelex secondary standards?

Problem Solution:

Gelex standards are secondary standards in solid or gel form that require no dilution or mixing. They provide a quick and convenient way to check if the calibration of laboratory and portable turbidimeters has changed on a daily basis. To use, place the Gelex standard in the sample cell compartment in a defined orientation right after the turbidimeter has been calibrated with a primary

standard, and record the displayed value. Then periodically (daily or weekly, for instance) place the standard back in the instrument in the same orientation to verify that the calibration has not changed significantly. When the value of the Gelex standard differs by more than 5% from the value right after the turbidimeter was last calibrated, the turbidimeter should be calibrated again with a primary formazin or StablCal standard. Both formazin and StablCal are accepted primary standards for turbidimeter calibration. Gelex standards should never be used to calibrate a turbidimeter, only to check the calibration after the turbidimeter has been calibrated with a primary standard.

My laboratory turbidimeter reads higher than my on-line turbidimeter on the same sample. Which instrument is correct?

Problem Solution:

When measuring very clean water with very low turbidity (below about 0.2 NTU), it becomes more and more difficult to obtain an accurate reading with a laboratory turbidimeter. This is primarily due to contamination of the sample cells and stray light in the instrument, which can be caused by imperfections on the surface of the sample cells as well as dust on the optical lenses and other internal components.

Sample cells must be cleaned meticulously with 1:1 hydrochloric acid and rinsed thoroughly with distilled or deionized water and then sample water. Sonicating the cells in a sonicating bath is also helpful for dislodging particles attached to the cell walls. Once clean, sample cells should be stored with the caps on and rinsed with deionized water immediately after sample measurement.

When contamination is removed from the sample cells and silicone oil is properly applied to minimize the effects of scratches on the outer cell walls, the turbidity levels will drop and approach the readings obtained from the process turbidimeter. Because process turbidimeters do not use sample cells and the detector is placed directly in the sample stream, turbidity due to contamination and stray light are minimized.

Our new turbidimeter reads higher than the one we've used for decades (for example 2100A turbidimeter). We prefer the readings from the older instrument. What can we do?

Problem Solution:

Different turbidimeters may have different light sources, photodetectors, and optical systems that can result in differences in sensitivity and linearity between instruments. In addition, the way that the zero point is set and how calibrations are done has changed over the years to improve accuracy, especially at low concentrations. Many older turbidimeters did not incorporate the ratio mode for color interference and therefore give lower than actual results for samples having color. Some of the older turbidimeters also had zero knobs to zero out the reading from deionized water. Modern instruments do not zero on deionized water because even the cleanest water will have some turbidity. Zero knobs create a false negative condition where the instrument displays a lower than actual result. Newer instruments use the dark current (90-degree detector current with the lamp off) reading, made when the instrument is first turned on, to set the zero point. A dilution water (or <0.1 NTU StablCal) reading is taken and used to adjust the concentration of calibration standards for greatest accuracy. Modern turbidimeters incorporate the latest advances in electronics, optical components, and design, and will have the lowest stray light interference and give the most accurate results.

My 2100N or 2100AN Laboratory Turbidimeter does not display 0.000 when no sample is in the instrument. Does it need repair?

Problem Solution:

The empty cell reading (no sample cell in instrument, lid closed) in a turbidimeter displays stray light in the instrument and is normal. Stray light comes from light that reflects off internal surfaces in the instrument and reaches the detector. Stray light increases over time as dust collects on the optical lenses and other surfaces.

When the stray light reading gets above 0.03 NTU, clean the EPA filter (Catalog No. 3031200) with glass cleaner and a lint-free cloth. If the reading is still high, the instrument should be thoroughly cleaned by the Hach Service Department.

2100N LABORATORY TURBIDIMETER QUICK REFERENCE GUIDE

NEPHELOMETRIC MEASUREMENT PROCEDURE

1. Collect a representative sample in a clean container. Fill the sample cell to the line (approximately 30 mL). Take care to handle the sample cell by the top. Cap the sample cell. (*Note: Instrument warm-up stabilization time with Ratio on is 30 minutes and with Ratio off is 60 minutes. Typical application is to leave the instrument on 24 hours a day.)*

2. Hold the sample cell by the cap, and wipe to remove water spots and finger prints.

3. Apply a thin bead of silicone oil from the top to the bottom of the cell—just enough to coat the cell with a thin layer of oil. Using the oiling cloth provided, spread the oil uniformly. Then, wipe off the excess. The cell should appear nearly dry with little or no visible oil. (*Note: See Section 2.3.2 Applying Silicone Oil in the instrument manual.)*

4. Place the sample cell in the instrument cell compartment, and close the cell cover. (*Note: For immediate update of the display, press* **ENTER.**)

5. If necessary, insert the EPA filter. Select manual or automatic ranging by pressing the **RANGE** key.

6. Select the appropriate **SIGNAL AVERAGING** setting (on or off) by pressing the **SIGNAL AVG** key.

7. Select the appropriate **RATIO** setting (on or off) by pressing the **RATIO** key. (*Note: Values >40 NTU require Ratio on*.)

8. Select the appropriate measurement unit (NTU, EBC or NEPH) by pressing the **UNITS/EXIT** key.

9. Read and record the results.

CALIBRATION

Preparing Recommended Formazin Dilutions

Hach Company recommends use of 20-, 200-, 1000- and 4000-NTU Formazin standards for calibration of the Model 2100N Turbidimeter. Prepare all Formazin dilutions immediately before calibration, and discard the dilutions after use. While 4000-NTU stock solutions are stable for up to one year, diluted solutions deteriorate more rapidly. Prepare dilutions of 20, 200 and 1000 NTUs according to the directions in *Table 2 (Formazin Standard Preparation)* in *Section 3* of the Instrument Manual. The dilution water also is used to make an initial blank measurement (refer to *Section 3.2 Calibration* in the Instrument Manual).

NOTE

The calibration is based on a first order linear equation consisting of up to three independent variables. Unpredictable results may occur if standards other than the recommended calibration points are used. The factory-suggested calibration points are those determined by Hach Company chemists and engineers to provide the best calibration accuracy. Use of standards other than those specified may result in less accurate calibrations.

Calibrating with Formazin Standards

The electronic and optical design of the 2100N Turbidimeter provides long-term stability and minimizes the need for frequent calibration. The three-detector ratioing optical system compensates for electronic and optical system variations between calibrations. When data is used for USEPA reporting, recalibrate at least every 90 days, or as stipulated by the regulating authority. Refer to *Section 3.2 Calibration* in the Instrument Manual.

1. Fill a clean sample cell to the line (≅ 30 mL) with dilution water. Wipe the cell clean and apply a thin film of silicone oil.

2. Place the sample cell into the cell holder, and *close the cell cover.*

3. Press the **CAL** key. The S0 annunciator lights. The NTU value of the dilution water used in the previous calibration is displayed.

4. Press the **ENTER** key. The instrument display counts down from 60 to 0, and then makes a measurement. This result is stored and used to compensate for the turbidity of the dilution water.

5. The instrument automatically increments to the next standard, displays the expected NTU value (e.g., 20.00 NTU), and the S1 annunciator lights. Remove the sample cell from the cell holder.

6. Fill a clean sample cell to the line with well-mixed, 20-NTU Formazin standard. Wipe the sample cell clean, and apply a thin film of silicone oil on its surface. Place it into the cell holder, and *close the cell cover.*

7. Press the **ENTER** key. The display counts down from 60 to 0, and makes a measurement. The instrument automatically increments to the next standard, the display shows 200.0 NTU, and the S2 annunciator lights. Remove the sample cell from the instrument.

8. Fill a clean sample cell to the line with well-mixed, 200-NTU Formazin standard. Wipe the cell clean and apply a thin film of silicone oil to the surface. Place it into the cell holder, and *close the cell cover.* Press the **ENTER** key. The instrument display counts down from 60 to 0, and then makes a measurement. The instrument automatically increments to the next standard, the display shows 1000 NTU, and the S3 annunciator lights. Remove the sample cell from the instrument.

9. Fill a clean sample cell to the line with well-mixed, 1000-NTU Formazin standard. Wipe the cell clean and apply a thin film of silicone oil to the surface. Place it in the cell holder and *close the cell cover.* Press the **ENTER** key. The instrument display counts down from 60 to 0, and then makes a measurement. The display automatically increments to the next standard, the display shows 4000 NTU, and the S4 annunciator lights. Remove the sample cell from the instrument.

10. Fill a clean sample cell to the line with well-mixed, 4000-NTU Formazin standard. Wipe the cell clean and apply a thin film of silicone oil to the surface. Place it in the cell holder and *close the cell cover.* Press the **ENTER** key. The instrument counts down from 60 to 0, and then makes a measurement. The display automatically increments back to the dilution water standard. The S0 annunciator lights, and the previously measured value of the dilution water is displayed.

11. Press the **CAL** key. The instrument makes calculations based on the new calibration data, stores the new calibration and returns the instrument to the measurement mode.

Reviewing the Calibration Sequence

Press the **CAL** key and then use the **UP ARROW** key to scroll through the standards to review calibration data currently in effect. If the instrument is connected to a printer, pressing the **PRINT** key prints all of the calibration data in effect. Press the **UNITS/EXIT** key to return to the operating mode without altering the current calibration data.

Using Gelex® Secondary Turbidity Standards

Periodically, as experience or regulating authorities indicate, verify the instrument calibration using Gelex Secondary Standards. If the reading in the range of use is not within 5% of the standard's assigned value, recalibrate using Formazin primary standards (refer to *Section 3.2.5 Using Gelex Secondary Turbidity Standards* in the Instrument Manual).

1. Calibrate the instrument with Formazin (refer to *Section 3.2 Calibration* in the Instrument Manual).

2. Verify that the instrument is set for the NTU mode, Ratio on and Automatic Ranging.

3. Thoroughly clean the outside of the Gelex vials, and apply a thin coating of silicone oil.

4. Place the lowest NTU Gelex Standard in the sample compartment with the triangle on the vial aligned with the index mark on the instrument sample compartment. Close the sample cell cover.

5. Press the **ENTER** key. Record the value displayed. Remove the standard from the instrument, and mark this value on the vial with a water soluble marker.

6. Repeat steps 3 through 5 for the other Gelex standards.

NOTE

Reassign new values to the Gelex standards each time the instrument is calibrated with Formazin.

ERROR CODES

Error codes may result from instrument malfunction or operator error. **Errxx** error codes are cleared from the display by pressing the **ENTER** key. The meter continues operating in the error condition; a calibration in progress can be continued. Any calibration being calculated (at the time the message appears) is discarded; the old calibration is retained. *Table 1* lists the error codes displayed for specific conditions.

Table 1. Error Codes

Code	Probable Cause	Corrective Action
Err01	Dilution water calculated to be >0.5 NTU	Start calibration over with higher quality dilution water, or filter the water with a membrane filter before use.
Err02	Two calibration standards have the same value, or their difference is less than 60.0 NTU. Standard 1 is too low (<10 NTU)	Recheck preparation of standards and repeat calibration.
Err03	Low light error	Reinsert sample. Check that lamp is on. Dilution may be necessary.
Err04	Memory malfunction	Switch instrument off and back on with I/O. Call Hach Service.
Err05	A/D over-range	Contact Hach Service.
Err06	A/D under-range	Contact Hach Service.
Err07	Light leak	Contact Hach Service.
Err08	Bad lamp circuit	Contact Hach Service.
Err09	Printer timeout error	Check that external printer is properly connected. Check that external printer is selected (on-line).
Err10	System voltage out of range	Switch instrument off and back on with I/O. Call Hach Service.
Err11	System loop test error	Switch instrument off and back on with I/O. Call Hach Service.

Diagnostic Functions

The diagnostic mode accesses system function information that is useful primarily when the instrument function is in doubt. Hach service technicians use the information for precise troubleshooting, speeding repairs, and avoiding unnecessary service returns.

Access diagnostic information by pressing and holding the **RIGHT ARROW** key for 3 seconds. Use the **ARROW** keys to edit the display to read the diagnostic code number of interest. Press the **ENTER** key to display the diagnostic value. More information may be obtained by purchasing the instrument service manual, or contacting the service center nearest you.

Diagnostic Codes

Code	Display	Description
00	bP on/bP of	Keyboard Beeper On/Off
01	FS Pr/SL Pr	Fast/Slow Print Device
21	Pr In	Printer Test
22	*	Display Test
23	*	Keyboard Test
24	*	Memory Test

Refer to *Table 6 Diagnostic Codes* in *Section 8 Troubleshooting* of the instrument manual for a list of diagnostic codes.

HACH COMPANY
WORLD HEADQUARTERS
P.O. BOX 389
Loveland, Colorado 80539
Telephone: (970) 669-3050
FAX: (970) 669-2932

Section 11
Jar Testing

Water Treatment Laboratory

JAR TESTING

PURPOSE OF COAG/FLOC PROCESS

- Surface waters usually contain suspended particles that cause turbidity
- Particles can vary in size and amount
- Turbidity can be removed by adding a coagulant, followed by a brief mixing, slow mixing then finally a sedimentation period
- Jar tests imitate plant conditions

SOLIDS REMOVAL USING CHEMICALS

- Physical-chemical treatment
- Three step process, must occur in proper sequence
  - Coagulation Phase: Chemicals are added to the water and rapidly mixed forming "pinpoint floc"
  - Flocculation Phase: Gentle mixing to produce larger, denser floc particles that settle rapidly
  - Liquid/solids separation is almost always conventional sedimentation by gravity settling although air flotation is used occasionally

MOST IMPORTANT GUIDELINES

- Provide enough energy to completely mix chemicals
- Control intensity of mixing during flocculation
- Control chemical(s) dose

PRINCIPLES OF COAGULATION

- Coagulation involves both chemical (destabilization) and physical (mixing) processes.
- Coagulation produces solid particles that form strong enough to withstand shearing

PRINCIPLES OF COAGULATION

- Van Der Waals Force: attractive force existing between particles that allows coagulation to occur
- Zeta Potential: Measurement in millivolts of particle strength surrounding solids. The more negative the number, the stronger particle charge and repelling forces between particles

PRINCIPLES OF COAGULATION

- To achieve coagulation the electrostatic charges of particles must be modified to reduce Zeta Potential
- Add chemicals that have charge opposite of the suspended solids

FLOCCULATION PROCESS

- Selection of polymers depends on pH, conductivity, type and concentration of suspended solids, particle size ranges, type and amount of coagulant(s) added, and next stage in treatment process
- Most important to have sufficient paddle speeds during flocculation to keep floc from settling and not shearing (adjustable speed drives)

CHEMICALS USED TO IMPROVE SETTLING

- Aluminum Sulfate (Dry or Liquid)
- Ferric Chloride
- Lime
- Polymers

ALUMINUM SULFATE

- Very corrosive when mixed with water
- Supports bacterial growth and/or cause sludge deposits in feed lines
- Reduces alkalinity in water being treated during the coagulation process
- Hydrated lime, soda ash, or caustic soda may be required to adjust alkalinity for coagulation process to occur
- A 1% solution will have a pH of 3.5
- Alkalinity adjustment: 1 mg/L of chemical for alkalinity adjustment when using Alum

FERRIC CHLORIDE

- Very Corrosive
- Will leave stains
- Temperature rises as chemical dissolves
- Crystallizes in temperatures below -1°C
- Positive displacement pumps should be used for accuracy
- Will lower pH

LIME

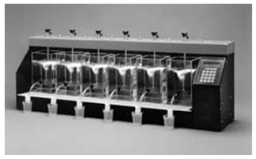
- Use to coagulate solids or adjust pH to improve coagulation
- Very irritating to skin, eyes, and mucous membranes
- High heat is generated when water is added to chemical
- Quicklime less expensive but slaking required

POLYMERS

- High molecular weight organic compounds
- Natural or synthetic origin
- Wide range available
- May be applied alone or in combination with other chemicals
- Extensive laboratory tests
- Anionic, Nonionic, and Cationic Polymers

JAR TESTING

- Must know volume of test jars and speed rates of stirrers prior to test
- Don't use laboratory grade chemicals
  - Use what you feed in plant



JAR TESTING

- Basic guidelines:
  - Jar test volume 2 Liters
  - working chemical strengths should be 0.1% (1,000 mg/L) or micro-pipet concentrated chemical
    - Anything less than 1% solutions should be prepared daily

JAR TESTING

- Basic guidelines:
  - Rapid mix at 140-160 RPM for 10-15 seconds for polymers: 3-5 minutes for aluminum and/or iron metal salts (Ferric Chloride)
  - Slow mix 15-20 RPM for 1-2 minutes for polymers; slow mix not used for aluminum and/or iron metal salts

JAR TESTING

- Ranges for times represent normal operating conditions
- Actual times based on composition of flow stream examined (detention and force gradients)

DETERMINE DOSE

- Bracket expected "best" dosage
  - If 15 mg/L alum is expected to be best, test 5, 10, 15, 20 , 25 and 30 mg/L
- Change only one variable (i.e. pH adjustment chemical dose) during each test run
  - Perform multiple runs if multiple variable changes are necessary

SELECTION OF CHEMICALS AND DOSAGES

- Three Step Process
  - Preliminary Screening
  - Dosage Testing
  - Full-Scale Trial
- Tested water treated must be freshly drawn samples from actual flow stream
- System performance optimization: regular testing of water upstream of chemical application

19

SOLUTION PREPARATION

- Accuracy is critical - Small errors are compounded by large dilution
- Dilute solutions of 1g/L or less of coagulants or polymers should be prepared daily

20

SOLUTION PREP - DRY PRODUCTS

- Dissolve 1 gram of a chemical that is 100% in 1000 ml of DI water
  - This is a 0.1% solution by weight or 1,000 mg/L
- In a 1 liter test beaker, 1 ml of the above equals 1 mg/L
- If the chemical is not 100%, then divide by the percent of the chemical available

21

SOLUTION PREP - DRY PRODUCTS

- Useful dilution for alum, iron salts, carbons and alkalis
- Lower this dilution for polymers, fluorides and potassium permanganate

22

EXAMPLE

- How do you make a solution of chlorine containing 1000 mg/L from HTH, which has 65% available chlorine?
- Grams = $\frac{1 \text{ gram}}{0.65}$ = 1.54 grams HTH into 1 Liter

23

DRY ALUM

- Use a 1-L volumetric flask
- Dissolve 10 grams in 600 mL DI water
- Fill to the mark and mix
- Solution contains 10,000 mg/L
- Therefore, 1mL of the stock solution added to a 2-L jar will equal a 5 mg/L alum dose

24

TDEC - Fleming Training Center

SOLUTION PREP - LIQUID PRODUCTS

- To make a 10 g/L solution (1% or 10,000 mg/L) of a liquid product, divide 10 gram by specific gravity
  - This is the mL of chemical to dissolve in 1000 ml DI water
  - In a 1 liter test beaker, 1 ml of the above equals 10 mg/L of liquid product
- For solutions like PACl

Remember, Jar Test beakers are usually 2L, therefore double dose

25

TDEC - Fleming Training Center

SOLUTION PREP - LIQUID PRODUCTS

- For liquids sold on a dry basis, correct for concentration as follows
  - 10 gm/(sp.grav. x conc.)
  - In a 1 liter test beaker, 1 ml of the above equals 10 mg/L of liquid product
- For solutions like alum, ferric, sodium permanganate, etc.

Again, remember Jar Test beakers are usually 2L, double the dose

26

TDEC - Fleming Training Center

SOLUTION PREP - LIQUID PRODUCTS

- Example:
  - Liquid aluminum sulfate is typically sold on a dry basis.
  - 48.5% $Al_2(SO_4)_3 \bullet 14\ H_2O$ and specific gravity of 1.335
  - $\frac{10 g/L}{(1.335)(0.485)}$ = 15.4 ml liquid alum into 1 L for a 10 gram/liter dry basis solution
  - 1 ml of this solution = 10 mg/L dry alum

27

TDEC - Fleming Training Center

CHEMICAL PREPARATION

- Caustic Soda
  - 1 mL = 2 mg/L dose
    - .1 N solution is generally sufficient
    - Dry: 4 grams of NaOH pellets mixed well into 1 L
- Liquid Sodium Hypochlorite(5.25 %)
  - 38 mL into 1-Liter Volumetric = 2 mg/mL strength
  - 1 mL added to 2-Liter jar equivalent to a dose of 1 mg/L

28

TDEC - Fleming Training Center

SOLUTION PREP - LIQUID PRODUCTS

- Micropipets dispense neat product
- Specific gravity must be accounted for (liquid chemicals weigh more than water, so 1 ml of product weights more than 1 gram)
  - $\frac{mg/L}{\text{sp. grav.}}$ = μL product / liter of test sol'n

29

TDEC - Fleming Training Center

SOLUTION PREP - LIQUID PRODUCTS

- For dose on a dry active product basis, divide by concentration:
  - $\frac{mg/L}{(sp.grav.)(conc.)}$ = μL product/L of test sol'n

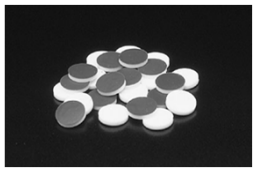
30

MICRO-PIPETING

- μL used/jar = (dose, mg/L)(2 Liters/jar) / specific gravity
- Example: 35 mg/L dose with 1.305 specific gravity
- (35)(2) / 1.305 = 52.1 μL/jar

MICRO-PIPETING

- Try to place dose on an object that can perch on the rim of the jar until you are ready to add all at the same time
  - Septas from TOC vials
  - Powder pillows

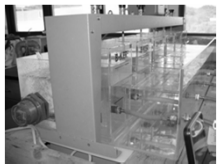


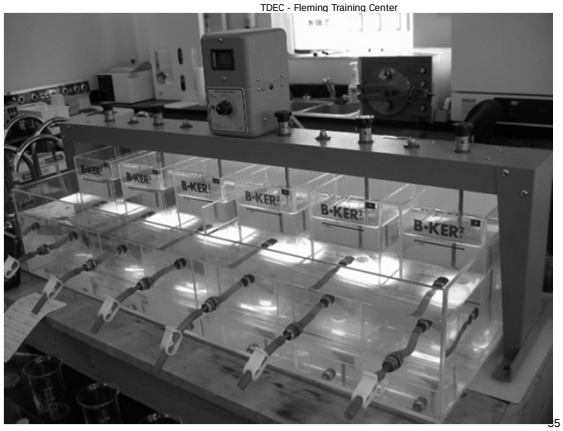
TROUBLESHOOTING

- Incomplete Floc???
  - Take sample after settling basin
  - Put on jar tester and set paddles to slow mix
  - If floc appears, you have incomplete flocculation

WATER BATH

- Jars set in a rectangular tank with raw water circulating around them
- This is only necessary for cold water





WATER BATH

- Determination for use of water bath:
  - Take a raw sample
    - Run jar test immediately
  - Take another sample
    - Let warm 5-10 degrees
    - Run same test and take note in difference

TDEC - Fleming Training Center

RULES TO REMEMBER

- Use 2 liters of water per jar
- Drain water out of sample line before taking sample
- Check pH at flash mix and jar to compare
- Light heats up water – leave off

37

TDEC - Fleming Training Center

RULES TO REMEMBER

- Keep equipment clean
  - Rinse jars and paddles with DI water
- Use fresh chemicals
- Add chemicals in correct order
- Pre-measure chemicals

38

Fleming Training Center

Date			Time			Analyst				
Jar	Chemical	Raw Turbidity	Raw pH	Chemical Dose, mg/L	Specific Gravity	Chemical Purity, %	uL used for 2L jar	Settled pH	Settled Turbidity at 2.5 min	Settled Turbidity at 10 min
1							#DIV/0!			
2							#DIV/0!			
3							#DIV/0!			
4							#DIV/0!			
5							#DIV/0!			
6							#DIV/0!			

Date			Time			Analyst				
Jar	Chemical	Raw Turbidity	Raw pH	Chemical Dose, mg/L	Specific Gravity	Chemical Purity, %	uL used for 2L jar	Settled pH	Turbidity at 2.5 min	Turbidity at 10 min
1							#DIV/0!			
2							#DIV/0!			
3							#DIV/0!			
4							#DIV/0!			
5							#DIV/0!			
6							#DIV/0!			

Jar Test Lab Math

1. The average flow for a water plant is 3.25 MGD. A jar test indicates that the best alum dosage is 2.5 mg/L. How many pounds per day will the operator feed?

2. Determine the setting on a dry alum feeder in pounds per day when the flow is 1.3 MGD. Jar tests indicate that the best alum dose is 12 mg/L.

3. A water treatment plant used 27 pounds of cationic polymer to treat 1.6 million gallons of water during a 24-hour period. What is the polymer dosage in mg/L?

4. Liquid polymer is supplied to a water treatment plant as an 8% solution. How many gallons of this liquid polymer should be used to make 200 gallons of a 0.7% polymer solution?

5. Liquid alum delivered to a water treatment plant contains 642.3 milligrams of alum per milliliter of liquid solution. Jar tests indicate that the best alum dose is 8 mg/L. Determine the setting on the liquid alum chemical feeder in milliliters per minute if the flow is 2.2 MGD.

6. A water plant is treating 8.2 MGD with 2.0 mg/L liquid alum. How many gpd of liquid alum will be required? The liquid alum contains 5.36 lbs dry alum/gallon.

7. An operator has decided to switch from dry alum to liquid alum. If he feeds an average of 100 lbs of dry alum a day, how many gallons of liquid alum will he need to feed on average given the following information:

Alum, liquid:	42.24% concentration
	11.07 lbs/gallon
	6.38 lbs dry alum/gallon
	1.3278 Specific Gravity

PROCEDURE

Procedure

Using the 1000 mL graduated cylinder, add 1000 mL (or 2000 mL if using the B-Ker^2 2-liter square jar) of the raw water to be coagulated to each of the jar test beakers. Using the prepared alum (or other coagulant) stock solution dose each beaker with increasing amounts, using the following schedule as an example (Double the dosage when using B-Ker^2 2-liter square jars). If necessary, add lime or soda ash stock solution to maintain correct alkalinity.

Jar #	mL Alum Stock	mL Lime\ Soda Ash	mg\L Alum	mg\L Lime Soda Ash
1	0.5	0	5.0	0
2	1.0	0	10.0	0
3	1.5	0	15.0	0
4	2.0	0.5	20.0	5.0
5	2.5	1.0	25.0	10.0
6	3.0	1.5	30.0	15.0

The above schedule is meant as an example. You should through trial and error establish your own sampling schedule that takes into account your own plant's operation and quality of the water at the intake. **IMPORTANT: ALWAYS KEEP ACCURATE NOTES PERTAINING TO DOSING WHILE PERFORMING JAR TESTS.**

Example: Your plant has a static mixer after the chemicals are injected, followed by 30 minutes in a flocculator, then 2 hours settling time before the filter.

After dosing each beaker, operate the stirrer at high rpm for approximately 1 minute. This simulates the static mixer. Then, slow to the rpm which matches the turbulence created in your flocculators and allow to stir for 30 minutes while observing the floc formation. At the end of the 30 minutes turn the stirrer off and allow to settle. Because there are 2 hours of settling time in this plant, at the end of 1 hour most of the settling will be complete.

A coagulant underfeed will cause the sample to appear cloudy, with little or no floc and almost no settling. A coagulant overfeed will form dense floc, however, it will appear fragile and fluffy; when the stirrer is turned off, it will not settle well. Floc formed by an overfeed is false floc which is very light and will carry to the filter. This is one of the most common treatment problems. A good floc will appear heavy and tight, not too dense, with spaces of bright, clear water between the particles and will begin to settle as soon as the stirrer is turned off.

INFORMATION

More Information

A tap installed in the raw water immediately after the chemicals are injected is indispensable. A sample taken from this tap can be placed on the stirrer to quickly determine the effectiveness of the dosage being used.

In order to add chemicals accurately, feeders must be calibrated.

If you are experiencing trouble when the raw water is clear and cold, and if your flocculators are adjustable, speed them up. This will improve the collision rate during cold water conditions.

A good formula to use for chemical application:

PPM x GPM / 2,000 = lbs. per hour

PPM you determine by the jar test. GPM is the gpm at which your plant operates. 2,000 is a given number.

If you use alum as a coagulant you should test the finished water for aluminum content. This is a good indicator of how well the coagulation flocculation process is working. An elevated aluminum level could indicate alum overfeed.

Placing a black background behind the jar test will give you a better view of the floc process.

When purchasing jar test apparatus there are two very important features to look for: Adjustable stirring rate and an illuminated base. Without adjustable speeds you will be unable to simulate conditions in your plant. The light base provides a full and clear view of all the beakers simultaneously. Light bases using fluorescent bulbs will not change the temperature of the sample significantly.

The jar test is intended to simulate the coagulation flocculation process in your plant. Designing a jar test procedure to match conditions in your plant takes a little thought and practice on the operator's part. However, when you have developed the proper routine and then properly applied the results, you will be producing the best water possible at the lowest cost.

Back to Menu PHIPPS&BIRD

Request Further Information