CHLORINE RESIDUAL TESTING FOR DRINKING WATER SYSTEMS USING DPD COLORIMETRIC TEST KITS

INTRODUCTION

Chlorine Residual Testing

- The one chemical analysis that operators/samplers in all public water systems perform.
- Water and wastewater operators perform it.
- How do you make sure you are getting accurate and reliable results?
- State must approve the use of DPD colorimetric test kits to measure residual concentrations of chlorine, chloramines, and chlorine dioxide.

DPD Colorimetric Method - Overview

- Colorimetric Analysis – The use of a colored reagent to determine the concentration of a contaminant
- This is a colorimetric version of the DPD method
- DPD = *N,N*-diethyl-*p*-phenylenediamine
- Method most used by water operators (it is relatively easy to perform)

DPD Colorimetric Method

- While it is a simple method, it is important to perform the tests properly.
- Too often it seems that operators hurry and take shortcuts.
- This leads to inaccurate and unreliable results.

Quality Systems

- A quality system should be in place to ensure the quality and reliability of your results.
- This consists of both Quality Assurance and Quality Control.

Quality Assurance

- Quality Assurance
  - Your plan for determining the quality of data from internal and external quality control measures.
  - Basically it answers who, how, why, when, and what.
  - The quality assurance plan can be quite large and highly involved….

Quality Assurance Plan

- Cover Sheet with Approvals
- Quality Policy Statement
- Organizational Structure
- Staff Responsibilities
- Analyst training and performance
- Tests performed by the laboratory
- Handling and receipt of samples
- Sample control and documentation
- Traceability of Measurement
- Major Equipment, Instrumentation, and Reference Standards Used
- Standard Operating Procedures (SOP)
- Approval and Control of Procedures
- Procurement of Reference Materials and Supplies
- Procurement of Subcontractors' Services
- Internal QC Activities
- Calibration, Verification, and Maintenance of Instrumentation
- Audits and Reviews
- Corrective Action
- Departure from Documented Policies
- And so forth…….

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Requirements…..

- All of the items mentioned in the prior slides are REQUIRED FOR CERTIFIED LABS.
- As a small system only analyzing chlorine residuals, applicability of items is totally dependent on your local public health official.
- We will look at those items in bold type, as they should be part of your operations.

Traceability of Measurement

- You should be using certified materials while performing your analyses.
- Verify this by obtaining a Certificate of Analysis from the manufacturer.
- This will connect your measurements back to a national or international standard.

Internal QC Activities

- Quality Control "QC"
  - This is the actual procedure that provides the support for your results
  - A little math, a little statistics, and a little science…..
  - Each test method has a list of required QC elements

Standard Operating Procedures

- A Standard Operating Procedure (SOP) can address all the bold items.
- This SOP can serve as you quality assurance plan.
- We will discuss some items that should be in a DPD Method SOP

OBJECTIVES/GOALS OF TODAY'S TRAINING

- Provide Attendees with an understanding of the history of water chlorination, water system requirements for measuring residual chlorine (disinfectant), conducting chlorine residual measurement tests, QA/QC activities to ensure accurate and reliable results.

- Assist the water systems in preparing a quality system to ensure the quality and reliability of your results.

- Provide necessary training that leads to state approval of the use of DPD colorimetric test kits.

OVERVIEW OF WATER DISINFECTION

- Water Disinfection and History of Chlorination
- Chemicals Used in Chlorination
- Chlorine Disinfection Chemistry
- What is Chlorine Residual (Total, Combined, Free?

OVERVIEW OF WATER DISINFECTION

Water Disinfection and the History of Chlorination

- Chlorine “discovered” in Sweden (1744).
- Identified as a chemical element in 1810.
- Chlorine and chlorine-containing products evaluated and demonstrated to be effective disinfectants.

OVERVIEW OF WATER DISINFECTION

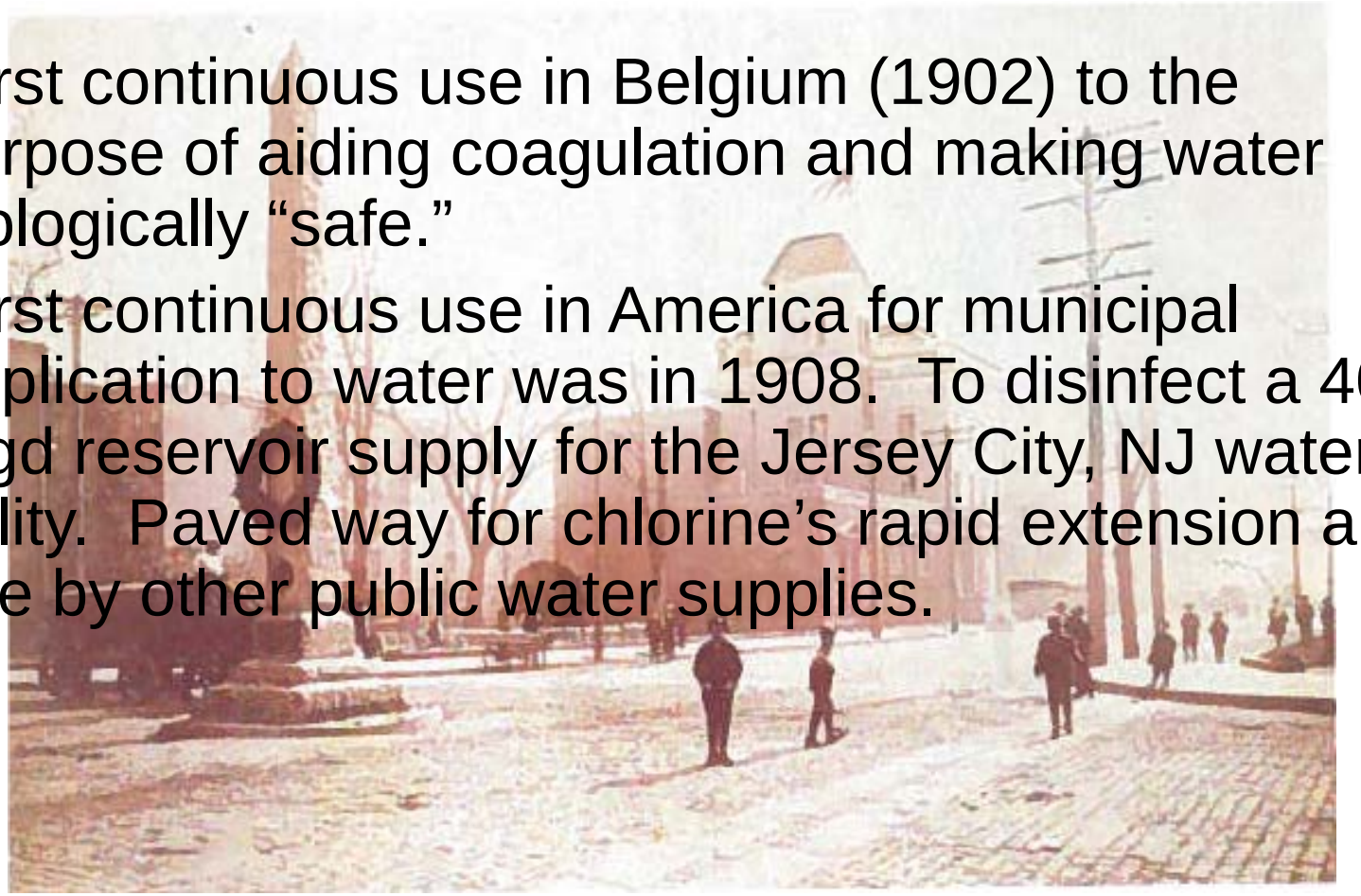
Water Disinfection and the History of Chlorination

- Disinfection of water practiced for millenniums.
- Historical records show that boiling of water was recommended (as early as 500 B.C.).
- Earliest record of chlorine used for disinfection was in Louiville, Kentucky in 1896.
- Used in 1897 in England to sterilize water-distribution main after a typhoid epidemic.

OVERVIEW OF WATER DISINFECTION

Water Disinfection and the History of Chlorination

- First continuous use in Belgium (1902) to the purpose of aiding coagulation and making water biologically “safe.”
- First continuous use in America for municipal application to water was in 1908. To disinfect a 40-mgd reservoir supply for the Jersey City, NJ water utility. Paved way for chlorine’s rapid extension and use by other public water supplies.



CHLORINE RESIDUAL TESTING FOR DRINKING WATER SAMPLING

Chlorination may produce adverse effects. Taste and odor characteristics of phenols and other organic compounds present in a water supply may be intensified.

Potentially carcinogenic chloroorganic compounds such as chloroform may be formed.

To fulfill the primary purpose of chlorination and to minimize any adverse effects, it is essential that proper testing procedures be used with a foreknowledge of the limitations of the analytical determination.

OVERVIEW OF WATER DISINFECTION

Chemicals Used in Chlorination

- **Elemental Chlorine, Cl_2**

- **Hypochlorite**
  - **Calcium Hypochlorite, $Ca(OCl)_2$**
  - **Sodium Hypochlorite, NaOCl**

CHLORINE

- Most Frequently Used Disinfectant
- Hydrochloric and Hypochlorous Acid formed when added to water
- Exist in Water as Free, Total, and Combined Available

CHLORINE CHEMISTRY

- Chlorine is added to water as chlorine gas or as sodium or calcium hypochlorite.

Chlorine Gas:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Sodium Hypochorite:

$$NaOCl + H_2O \rightarrow Na^+ + HOCl + OH^-$$

CHLORINE CHEMISTRY

- The two chemical species formed by chlorine in water are hypochlorous acid and hypochlorite ion.

$$HOCl \leftrightarrow H^+ + OCl^-$$

Hypochlorous Acid Hypochlorite Ion

CHLORINE CHEMISTRY

- Hypochlorous acid is the stronger disinfectant.
- Below pH 7.5 free chlorine exists predominantly in the HOCl form.
- Above pH 7.5 free chlorine exist predominantly in the OCl^- form.

Chlorine Chemistry & Disinfection Efficiency:

Free Chlorination:

$Cl_2 + H_2O \rightarrow HOCl + OCl^-$ (strong)

Chloramination:

$NHCl_2 + HOCl \rightarrow H_2O + NCl_3$

$NH_2Cl + HOCl \rightarrow H_2O + NHCl_2$

$NH_3 + HOCl \rightarrow H_2O + NH_2Cl$

decreasing disinfection efficiency

Organic Amines:

Org. N + HOCl → OrgN-Cl (~none)

OVERVIEW OF WATER DISINFECTION

<u>What is Chlorine Residual (total, combined, free, …)</u>

- Total: The sum of free and combined available forms of chlorine.
- Combined: Chloramines including monochloramines, dichloramines, and nitrogen trichloride. (combined available)
- Free: Chlorine existing in water as hypochlorous acid or the hypochlorite ion. (free available)

WHY/WHEN DO WE CONDUCT CHLORINE RESIDUAL MEASUREMENTS?

- Total Coliform Rule/Groundwater Rule
- Disinfectant/Disinfection By-Product Rule
- Surface Water Treatment Rule
- Drinking Water Compliance Monitoring
- System Repair/Maintenance
- Emergency Situations/Events

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

RTCR

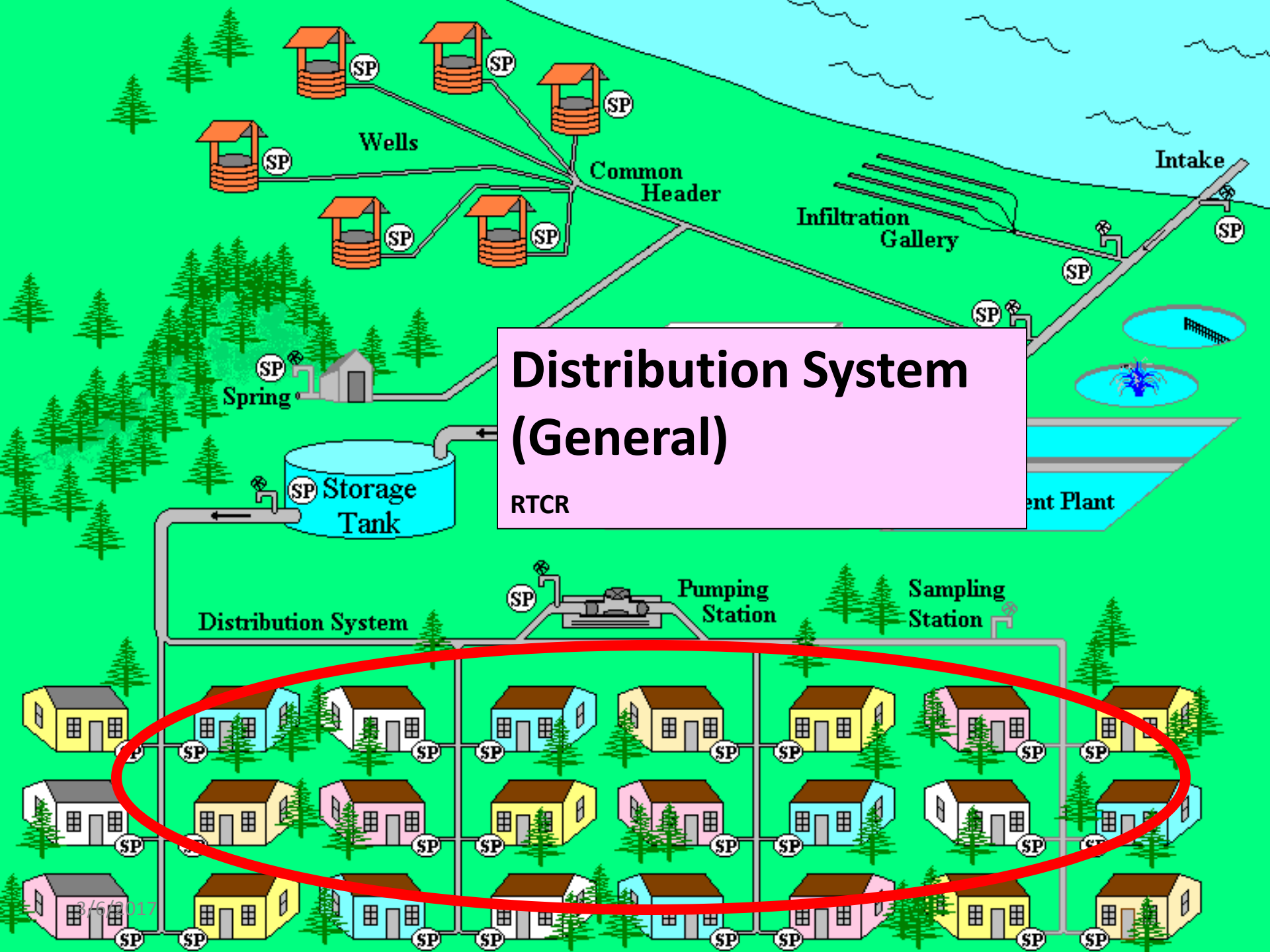
- Determine water treatment.

- Determine dechlorination requirement.

- Requires chlorine residual monitoring under the D/DBPR at the same and time and place as Coliform monitoring (routine and repeat). **40CFR141.21**

Distribution System (General)

RTCR

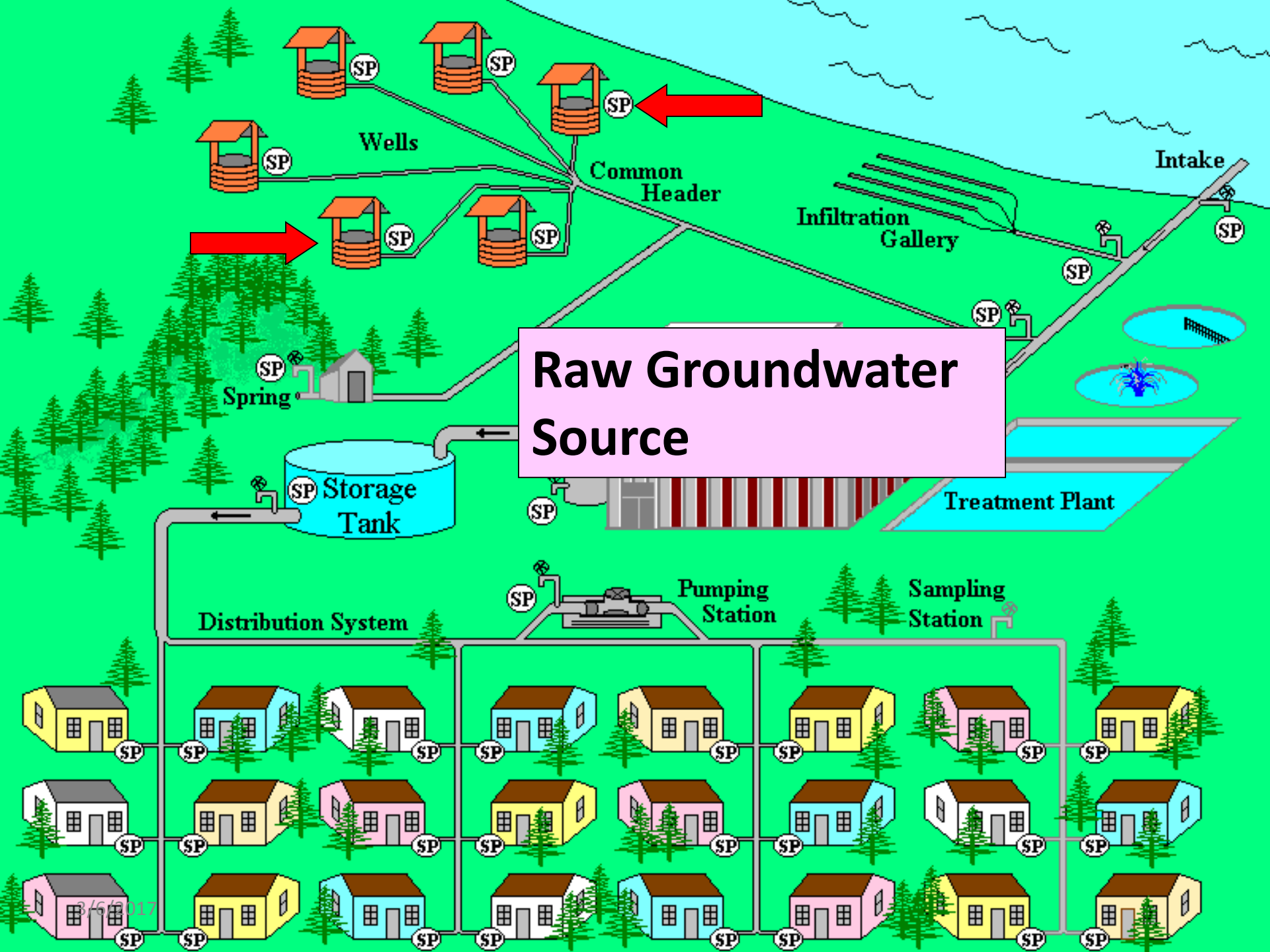


WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

GWR

- Ensure proper concentration of residual chlorine as required by Groundwater Rule. **SUGGESTED minimum of 0.2 mg/l.**

- Determine source samples. Ensure that source samples are raw water and not treated water when required to collected triggered source samples.



Raw Groundwater Source

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

D/DBPR

- Determine chlorine level and potential generation of disinfection by-products (THM & HAA5)
- Determine residual disinfectant in water.
- Determine requirements for dechlorination.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

DDBPR

Drinking Water Requirements for Chlorine Residual Analysis

40CFR141.131(c) Disinfectant residuals. (1) Systems must measure residual disinfectant concentrations of free chlorine, combined chlorine (chloramines), and chlorine dioxide by the methods listed in the following table:

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

DDBPR

APPROVED METHODS FOR DISINFECTANT RESIDUAL COMPLIANCE MONITORING

Methodology	Standard Method	ASTM method	Residual Measured1			
			Free Cl	Combined Cl	Total Cl	ClO2
Amperometric Titration	4500-Cl D	D 1253-86	X	X	X	
Low Level Amperometric Titration	4500-Cl E				X	
DPD Ferrous Titration	4500-Cl F		X	X	X	
DPD Colorimetric	4500-Cl G		X	X	X	
Syringaldazin e (FACTS)	4500-Cl H		X			
Iodometric Electrode	4500-Cl I				X	
DPD 4500-Cl O2 D						X
Amperometric Method II	4500-ClO2 D					X

1 X indicates method is approved for measuring specified disinfectant residual.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

DDBPR

(2) If approved by the State, systems may also measure residual concentration for chlorine, chloramines, and chlorine dioxide by using DPD colorimetric test kits.

(3) A party approved by EPA of the State must measure residual disinfectant concentration.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

<u>D/DBPR</u>

40CFR142.16(h) Requirements for States to adopt 40 CFR Part 141, subpart L. In addition to the general primacy requirements elsewhere in this part, including the requirements that State regulations be at least as stringent as federal requirements, an application for approval of the State program revision that adopts 40 CFR 141, subpart L, must contain a description of how the State will accomplish the following program requirements:

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

D/DBPR

(3) Section 141.131(c) of this chapter (DPD colorimetric test kits). Approve DPD colorimetric test kits for free and total chlorine measurements. State approval granted under §141.74(a)(2) of this chapter for the use of DPD colorimetric test kits for free chlorine testing is acceptable for the use of DPD test kits in measuring free chlorine residuals as required in 40 CFR part 141, subpart L.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

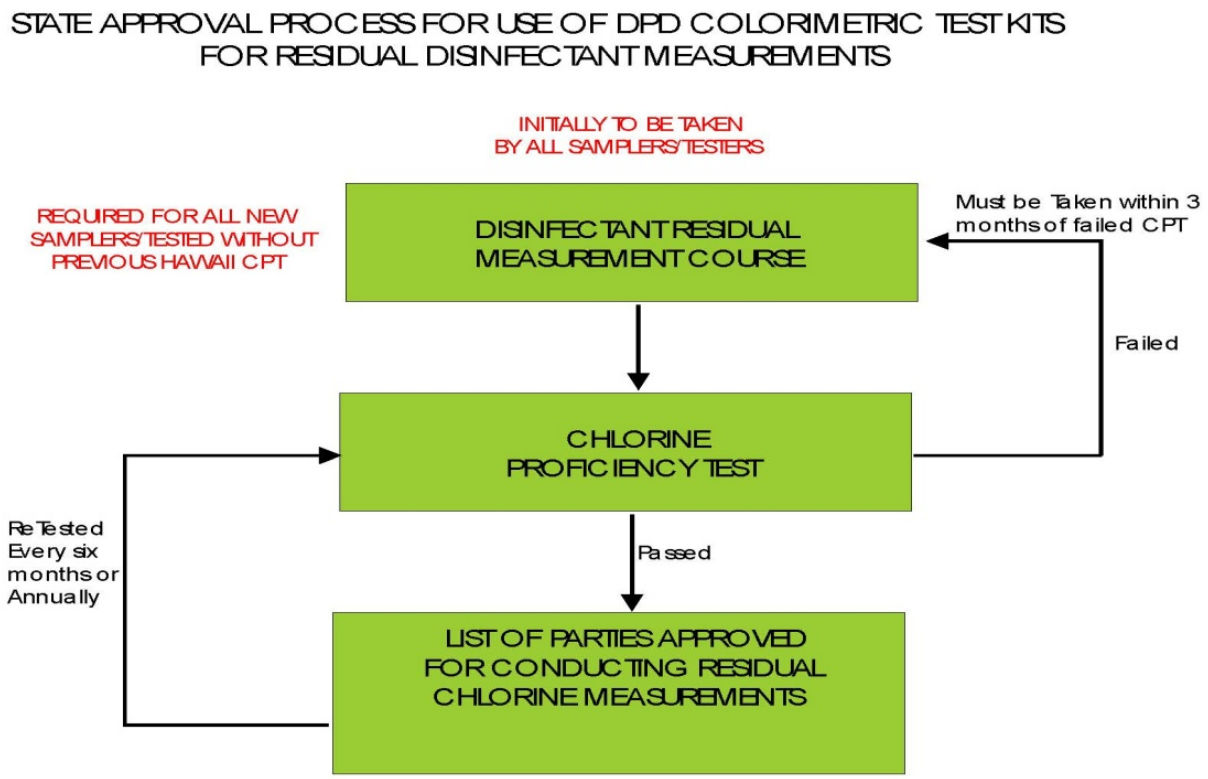
D/DBPR

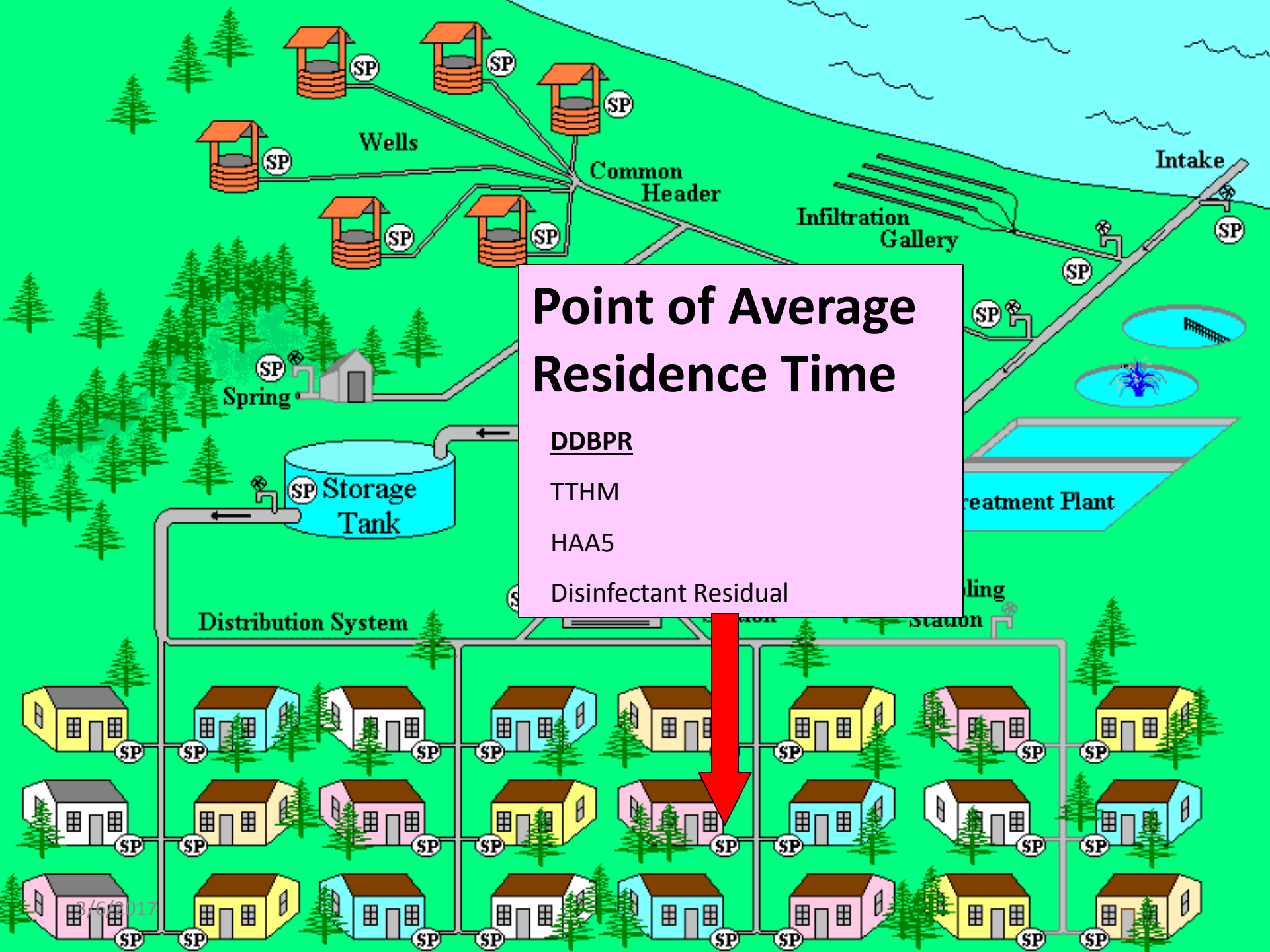
(4) Section 141.131(c)(3) and (d) of this chapter (State approval of parties to conduct analyses). Approve parties to conduct pH, bromide, alkalinity, and residual disinfectant concentration measurements. The State's process for approving parties performing water quality measurements for systems subject to 40 CFR part 141, subpart H requirements in paragraph (b)(2)(i)(D) of this section may be used for approving parties measuring water quality parameters for systems subject to subpartL requirements.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

STATE APPROVAL PROCESS FOR USE OF DPD COLORIMETRIC

<u>TEST KITS FOR RESIDUAL DISINFECTANT MEASUREMENT</u>





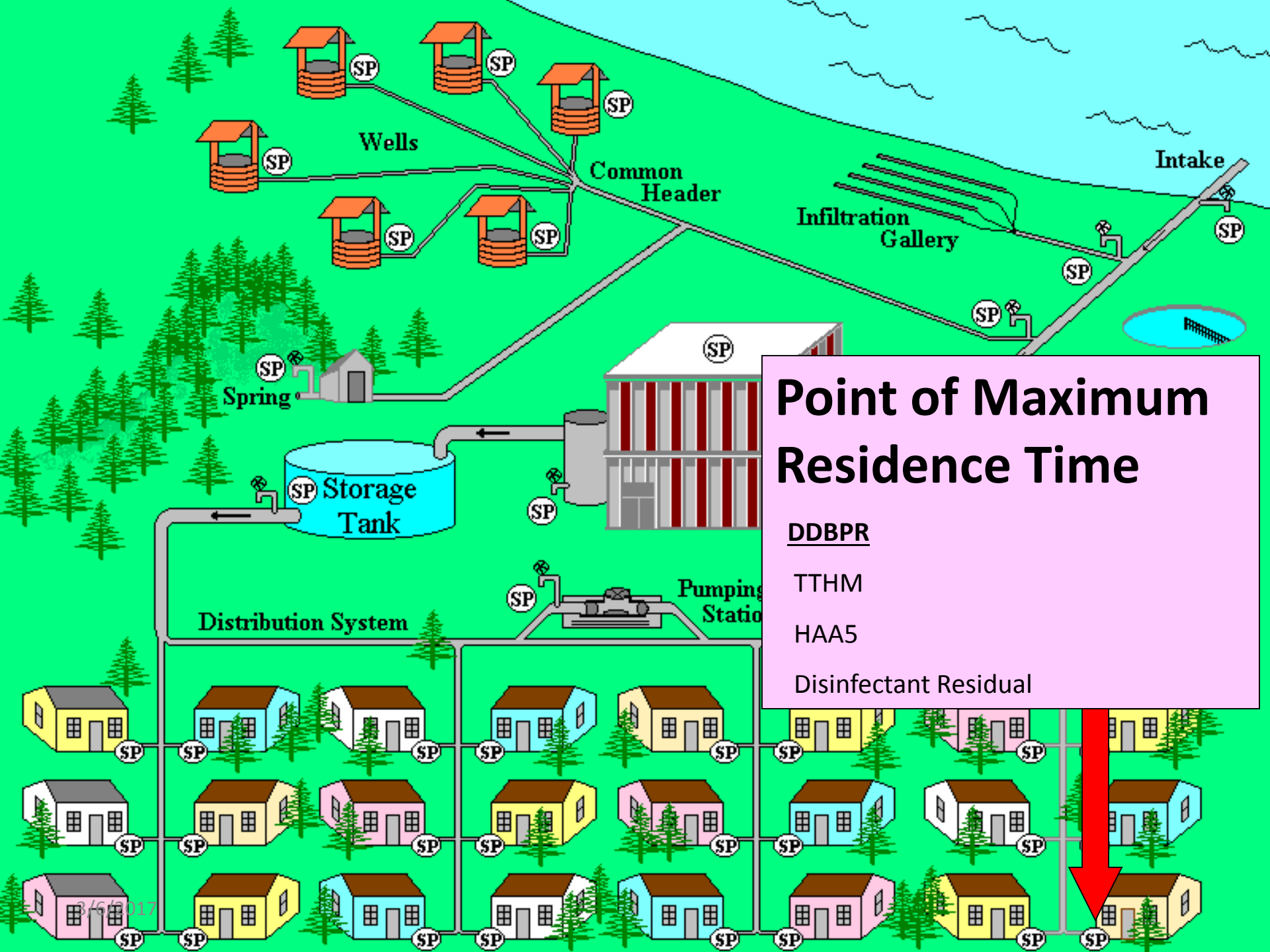
Point of Average Residence Time

DDBPR

TTHM

HAA5

Disinfectant Residual



Point of Maximum Residence Time

DDBPR

TTHM

HAA5

Disinfectant Residual

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

<u>Surface Water Treatment Rule</u>

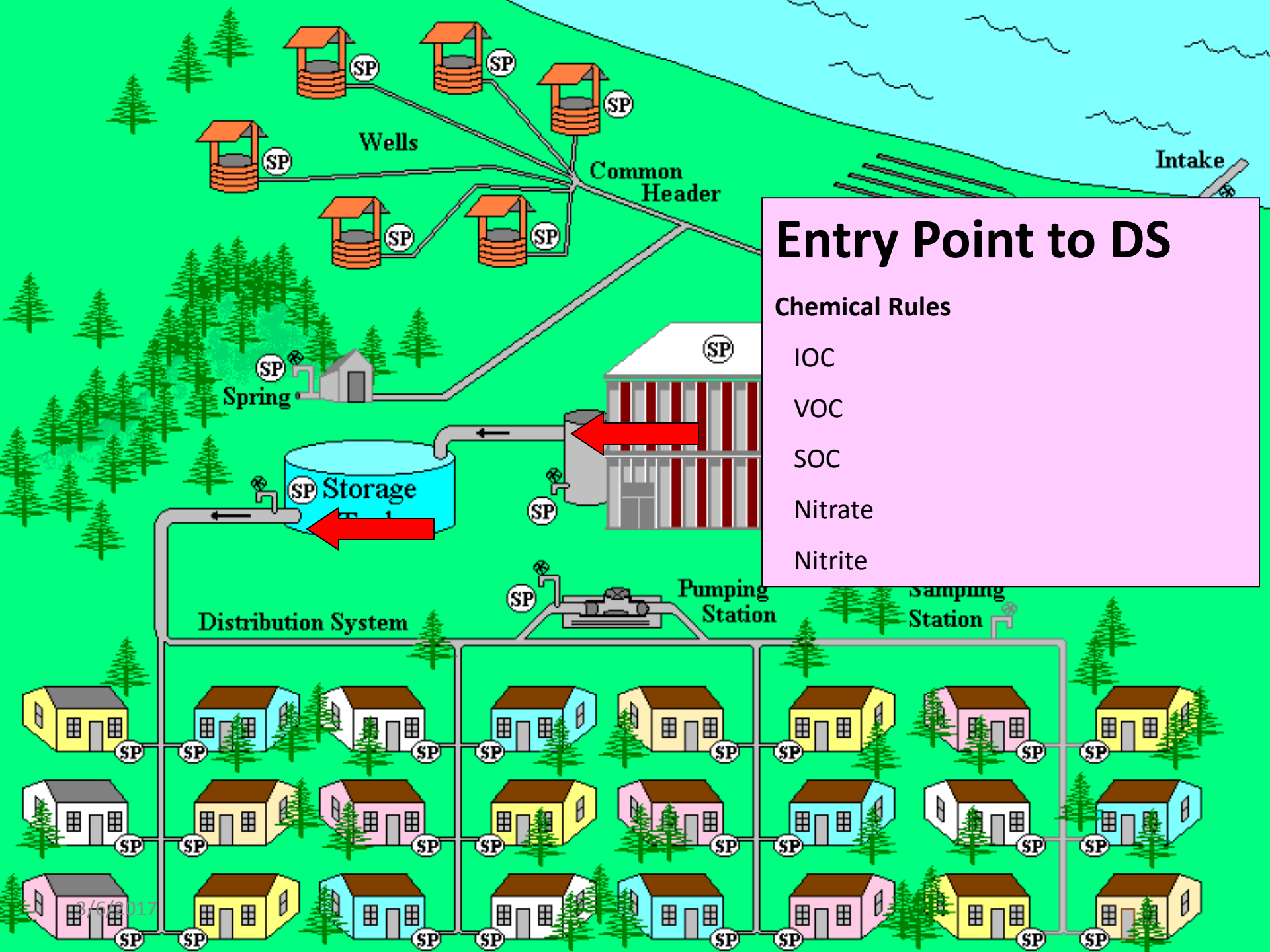
- Requires chlorine residual monitoring to determine contact time and Entry Points to distribution system monitoring. **40CFR141.74**

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

Chemical Monitoring

- Determine requirements for dechlorination. (particularly organic samples)

- Chlorine may cause analysis interference or generation of by-products



Entry Point to DS

Chemical Rules

- IOC
- VOC
- SOC
- Nitrate
- Nitrite

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (Flushing Pipelines)

- Removes aged water
- Reduces buildup of biofilms, scales, rust, and sediments
- Brings fresh water into the distribution system
- Restores disinfectant residual
- Flush dead-end mains

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (disinfection of water lines)

- Newly laid water line or lines that have been repaired should be disinfected before they are put into service
- Procedure should also apply for all water system components including wells and reservoirs

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

<u>System Repair/Maintenance (disinfection of water lines)</u>

- Flush the line
- Disinfect the line
- Flush the line again
- Refill the line → BACTI samples → BACTI(-) ↓

(OK–put line in service)

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (disinfection of water lines)

- Chlorine should be added at same time as water is introduced back into the line.
- Chlorine solution added to create a 50 mg/L dosage with a 5mg/L residual after 24 hours.
- Alternative: Flush line with water containing a free chlorine residual of 0.5 to 1.0 mg/L. Maintain chlorine residual until BACTI samples are negative.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (storage tank facility)

- New storage facilities and storage facilities that have been repaired, cleaned , has cathodic protection installed or been inspected must be disinfencted.
- Liquid chlorine, calcium hypochlorite, and sodium hypochlorite are commonly used.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (storage tank facility)

- Disinfection accomplished in several ways:

  (1) spraying or brushing the interior of the storage facility with 200mg/L chlorine solution and let stand for 30 minutes before filling to achieve at least a 3 mg/L chlorine residual for 3 to 6 hours.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (storage tank facility)

(2) filling tank with a 50 mg/L available chlorine concentration and letting tank stand for 24 hours. A chlorine residual of at least 10 mg/L must remain after 24 hours.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

System Repair/Maintenance (storage tank facility)

- After proper disinfection methods and time has been met,, BACTI samples must be collected.
- Once two consecutive BACTI samples are submitted with coliform negative results, system may request that storage facility be put back in service.
- If coliform bacteria are present, the tank must be disinfected until negative results are achieved.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS

Emergency Situations/Events

"TYPE A"

Major state or county disaster and include: nuclear disasters, tsunamis, earthquakes, volcano eruptions, floods and tornados.

"TYPE B"

Are limited situations affecting only water systems and include: drought, major contamination of a water system's basic water source, major destruction or impairment of a system's physical facilities which substantially interferes with quantity and quality of water delivered to the public.

"TYPE A"

Type A disasters will most likely be characterized by:

- ✓ Relatively widespread disruption of basic public services;
- ✓ Significant number of people affected and consequently, a significant extent and degree of public risk - - requiring greater assistance and cooperation; or
- ✓ Major strains on available resources – with greater likelihood that assistance priorities and allocation of resources will be set by an outside agency (Civil Defense, FEMA,…).

"TYPE B"

Type B disasters will most likely be characterized by:

- ✓ An impact essentially limited to the water system and not directly impacting other public services;
- ✓ A more limited number of affected people, but nonetheless a possibly high degree of health risk;
- ✓ More flexibility available to department of health in setting its assistance priorities and access by the department of health and water systems to other resources for assistance.

Responsibilities in emergency situations involving drinking water

<u>Major responsibilities include</u>:

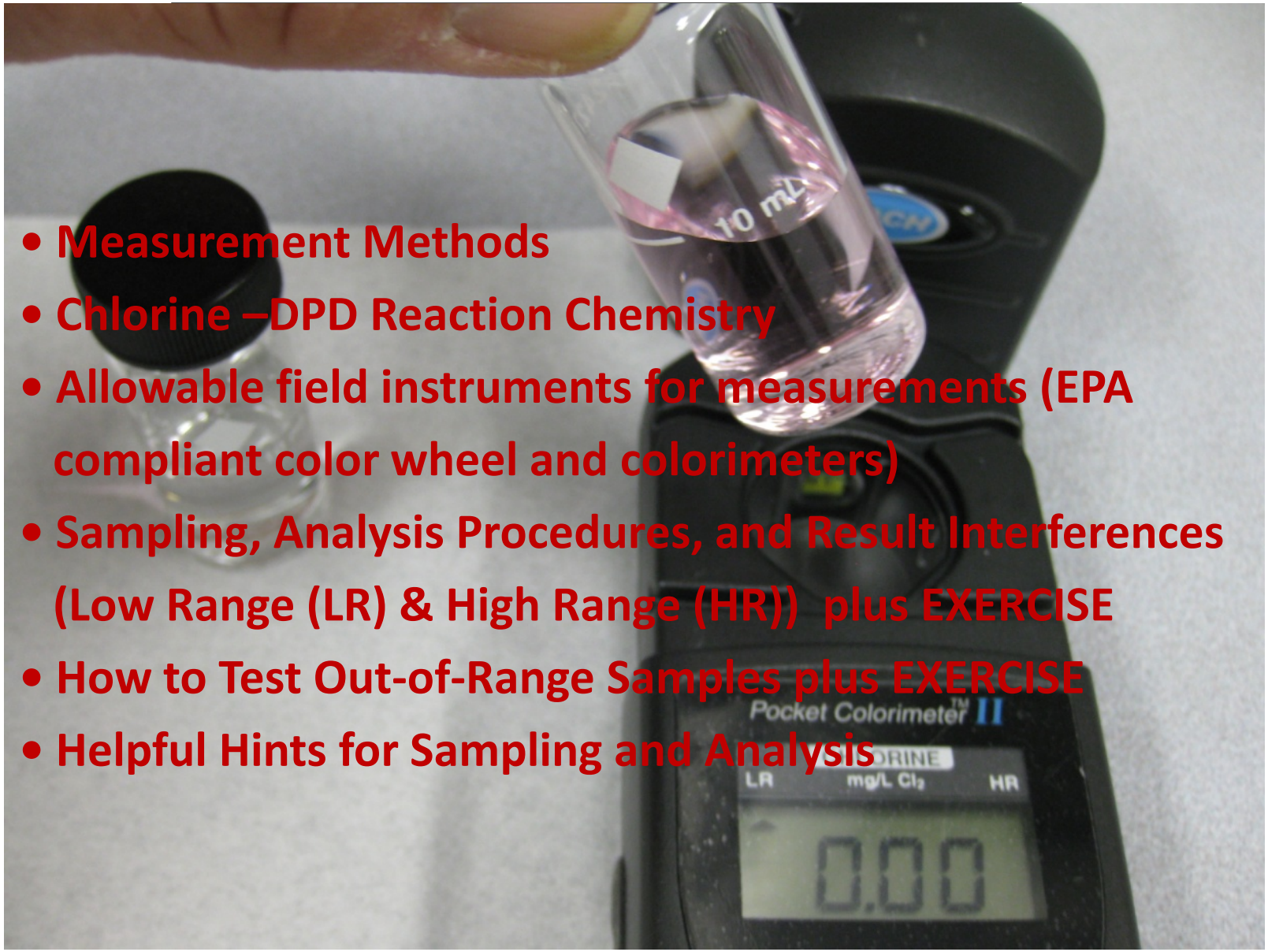
- To coordinate with other governmental agencies and the private sector to provide drinking water supplies to areas deprived of such supplies as a result of the emergency.
- To sample and analyze drinking water supplies to determine the existence of potential contamination of drinking water supplies as a result of the emergency.

Responsibilities in emergency situations involving drinking water

<u>Major responsibilities include</u>:

- If emergency drinking water supplies are to be provided from an alternative water source, to determine whether the alternative source is safe and whether the means of its transport or delivery have made or are likely to make the water unsafe when delivered for consumption..

USING THE DPD COLORIMETRIC TEST FOR MEASURING CHLORINE RESIDUAL



- Measurement Methods
- Chlorine –DPD Reaction Chemistry
- Allowable field instruments for measurements (EPA compliant color wheel and colorimeters)
- Sampling, Analysis Procedures, and Result Interferences (Low Range (LR) & High Range (HR)) plus EXERCISE
- How to Test Out-of-Range Samples plus EXERCISE
- Helpful Hints for Sampling and Analysis

Measurement Methods

- Amperometric titration
- Colorimetric DPD
- Titrimetric DPD
- Iodimetric titration

REACTION CHEMISTRY
Free Chlorine

- Free Chlorine oxidizes DPD indicator at a pH of 6.3-6.6 to form a magenta-colored compound.

Free Cl_2 + DPD $\rightarrow$ magenta-colored compound

REACTION CHEMISTRY
Total Chlorine

- Free Chlorine reaction + Potassium Iodine is added to the reagents.
- Chloramines oxidizes iodine to iodine which, along with free chlorine, oxidizes DPD to form pink color.

Free Chlorine + Chloramines + KI + DPD → magenta-colored compound

CHEMICAL REACTION

- Free Available Chlorine
- Total Chlorine

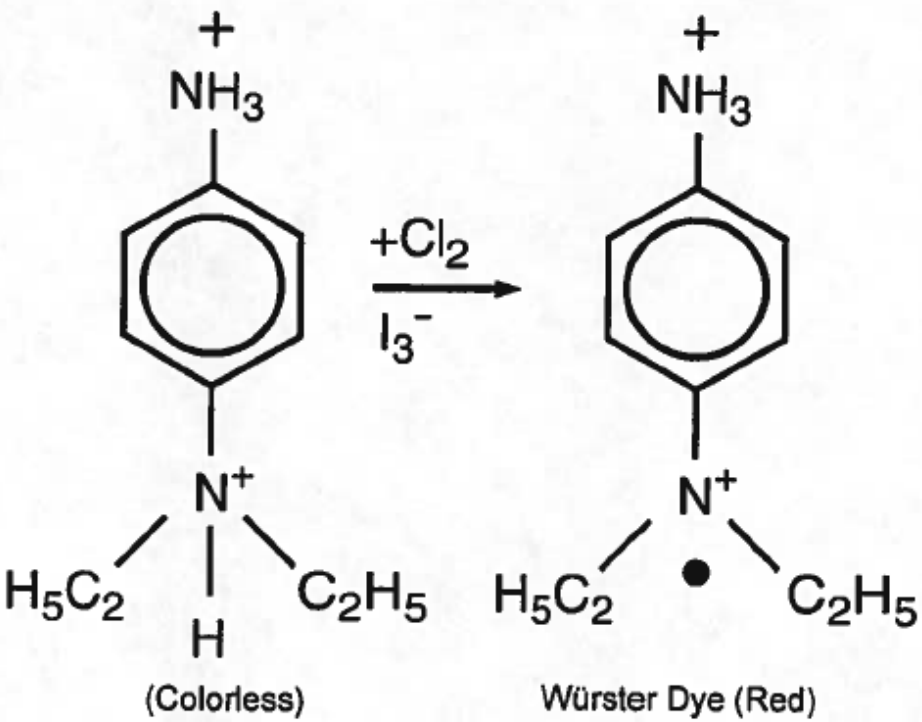


Figure 1 DPD chemical reactions

WAYS TO MEASURE CHLORINE RESIDUAL

- Digital Colorimeter
- Color Comparator Method (Color Wheel)
- SenSafe Free Chlorine Test Strips

  (EPA Approved)

Common EPA Approved Field <u>Instruments</u>

Non-EPA Approved Field Instruments

Watch for wording like this →

Features

No Reagents Required
Polarographic method enables measurement to be carried out easily without the need for reagent treatment and management. This reduces operating costs compared to using DPD method for measurements. It also allows more stable measurements without the human errors associated with colorimetric measurements.

Waterproof Construction
Meter is constructed to IP 67 standards and can withstand complete immersion into water (1m for 30 minutes). Provides worry free operation in outdoor environments.

CHLORINE RESIDUAL
SAMPLE COLLECTION AND ANALYSIS

CHLORINE RESIDUAL
SAMPLE COLLECTION AND ANALYSIS

CHLORINE RESIDUAL ANALYSIS
USING A
COLOR WHEEL TEST KIT

Free or Total Chlorine Test, 0–3.4 mg/L Cl_2

For Test Kits 223101 (CN-66), 223102 (CN-66F) and 223103 (CN-66T)

DOC326.98.00008

Additional copies available on www.hach.com

Test preparation

- Assemble the color comparator by placing the color disc on the center pin with the lettering facing out.
- Rinse vials with the sample water before testing. Rinse with deionized water after testing.
- Accuracy is not affected by undissolved powder.
- Monochloramine causes a gradual drift to higher values. Read immediately after the addition of the free chlorine reagent. At 3.0 mg/L monochloramine, a 0.1 mg/L increase in the reading will be obtained.
- Read the mg/L chlorine at the matching disc segment or at the value halfway between the two segments closest in color.
- If the disc becomes wet, carefully separate the two halves of the plastic case and dry them and the colored plastic insert with a soft cloth. Reassemble when the parts are completely dry.

CAUTION: Handle chemical standards and reagents carefully. Review Material Safety Data Sheets before handling chemicals.

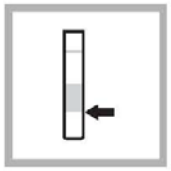
Replacement items

Description	Unit	Catalog no.
Color Comparator Box	each	173200
Color Disc, DPD Chlorine, 0–3.4 mg/L	each	990200
Color Viewing Tube, plastic, with cap	4/pkg	4660004
DPD Free Chlorine Reagent Powder Pillows	100/pkg	1407799
DPD Total Chlorine Reagent Powder Pillows	100/pkg	1407699

Optional items

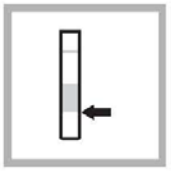
Description	Unit	Catalog no.
Caps, for plastic viewing tubes 4660004	4/pkg	4660014
Color Viewing Tube, glass	6/pkg	173006
Stoppers, for glass viewing tubes 173006	6/pkg	173106
Deionized Water	500 mL	27249

Free or total chlorine test procedure



1. Fill a tube to the first (5-mL) line with sample.

2. Insert the tube into the left opening of the comparator.



3. Fill another tube to the first (5-mL) line with sample.

4. If testing free chlorine, add one DPD Free Chlorine Reagent Powder Pillow to the second tube. Swirl to mix.

If testing total chlorine, add one DPD Total Chlorine Reagent Powder Pillow to the second tube. Swirl to mix.

***Note:** If testing free chlorine, complete the test and read the result within one minute of adding the reagent.*

***Note:** If testing total chlorine, read the test result after three minutes but before six minutes of adding the reagent.*

5. Insert the second tube into the right opening of the comparator.

6. Hold the comparator so that daylight or a florescent light source is directly behind the tubes. Rotate the color disc until the colors in the front windows match. The best match might occur between two color segments.

7. Read the result in mg/L in the scale window. If the best match occurs between two color segments, determine the value halfway between the two printed numbers.

DPD Colorimetric Method

- We will be looking at HACH© Colorimeter and reviewing procedures on using it.
- While there may be other DPD units in use, the procedures should be similar.
- Refer to your user manual when reviewing these procedures.

CHLORINE RESIDUAL
SAMPLE COLLECTION AND ANALYSIS

CHLORINE RESIDUAL ANALYSIS
USING A
DIGITAL COLORIMETER

PART 1: Low Range
PART 2” High Range

CHLORINE RESIDUAL MEASUREMENT

- Low Range (0.02 - - 2.0 mg/l)
- High Range (0.1 mg/l - - 8.0 mg/l)

Drinking Water Standard

MCLG: 4.0 mg/l

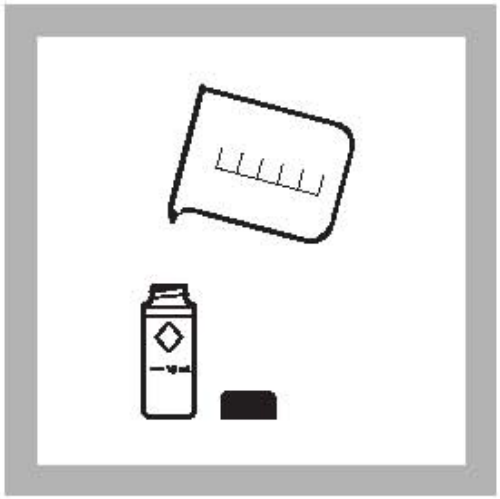
MCL: 4.0 mg/l

CHLORINE RESIDUAL
SAMPLE COLLECTION AND ANALYSIS

CHLORINE RESIDUAL ANALYSIS USING A DIGITAL COLORIMETER

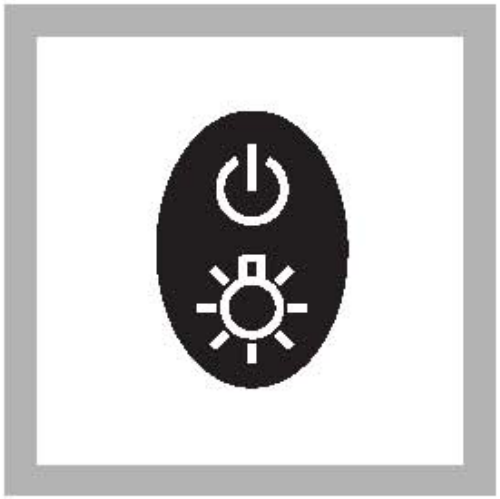
PART 1: Low Range

Using Powder Pillows (USEPA accepted for reporting)



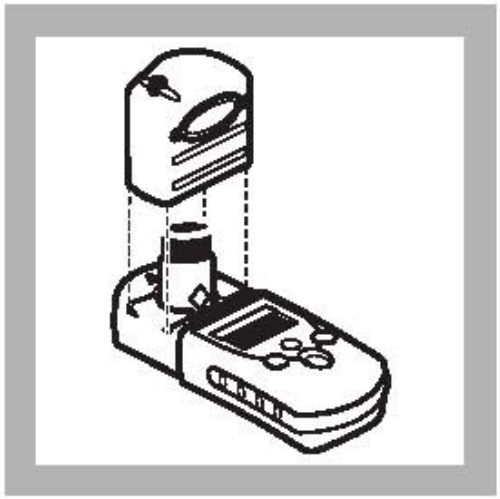
1. Fill a 10-mL cell with sample (the blank). Cap.

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



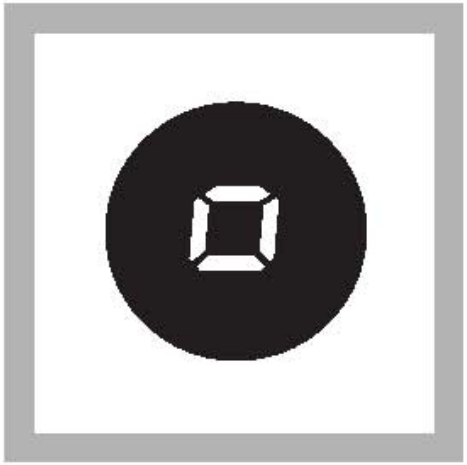
2. Press the **POWER** key to turn the meter on. The arrow should indicate the low range channel (LR).

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



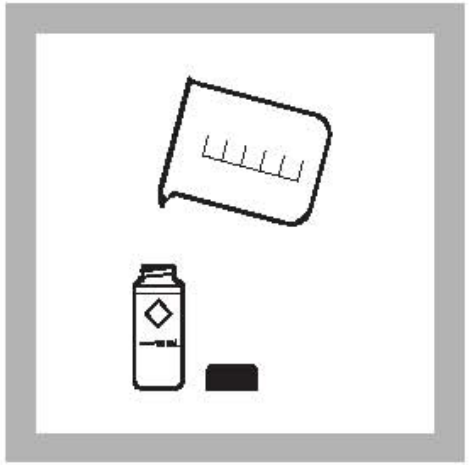
3. Remove the meter cap. Place the blank in the cell holder with the diamond mark facing the keypad. Fit the meter cap over the cell compartment to cover the cell.

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



4. Press **ZERO/SCROLL**. The display will show "- - - -" then "0.00".

Remove the blank from the cell holder.

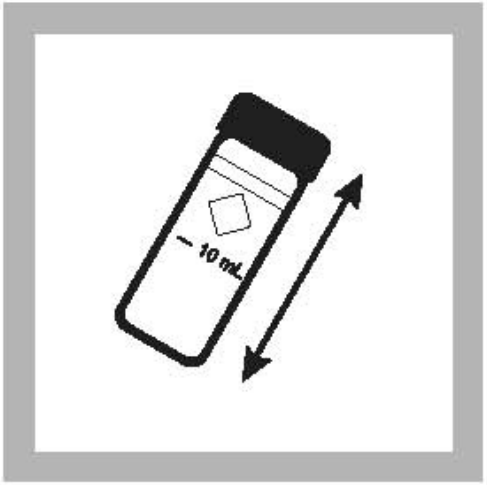


5. Fill a second 10-mL cell to the 10-mL line with sample.

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).

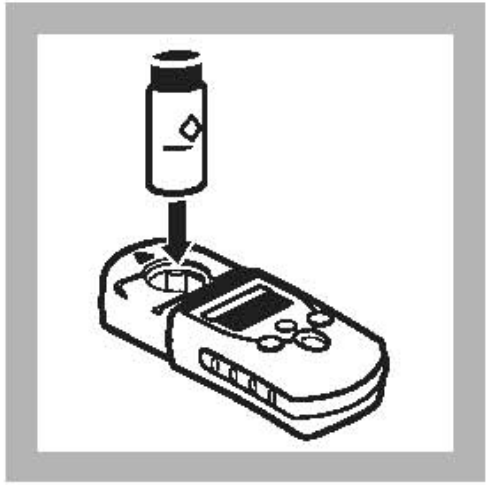
Note: *SwifTest™ Dispensers for Free or Total Chlorine can be used in place of powder pillows. See* *Using the SwifTest™ Dispenser (USEPA accepted for reporting) on page 1—26*.



7. Cap and shake gently for 20 seconds.

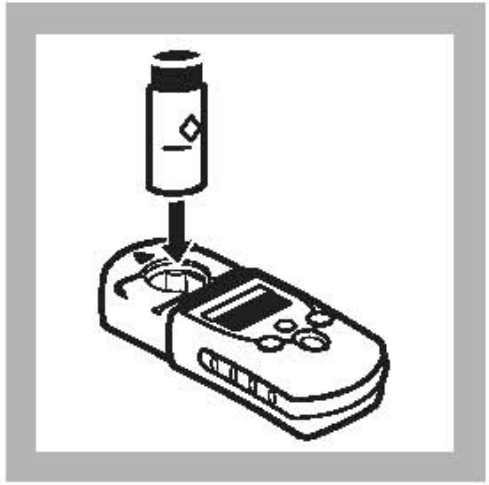
Note: *Shaking dissipates bubbles that may form in samples with dissolved gases.*

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



8. For **free** chlorine, wipe excess liquid and fingerprints from the sample cell. Put the prepared sample cell in the cell holder, then cover the cell with the instrument cap. Proceed to step 10 within **one** minute after adding the DPD Free Pillow.

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



9. For **total** chlorine, wait **3 to 6** minutes after adding the DPD Total Pillow. After the reaction time, wipe excess liquid and fingerprints from the sample cell. Put the prepared sample in the cell holder and cover the cell with the instrument cap. Proceed to step 10.

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.*

Interferences in Analytical Results (Low Range)

Interferences

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 a separate 10-mL sample, then add the same amount to the sample being tested. Correct for the additional volume.
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 a separate 10-mL sample, then add the same amount to the sample being tested. Correct for the additional volume.
Bromine, Br_2	Interferes at all levels

Interfering Substance	Interference Levels and Treatments
Hardness	No effect at less than 1,000 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) (Cat. No. 343-32) to a 10-mL sample. 3. Mix and wait one minute. 4. Add 3 drops Sodium Arsenite (5-g/L) (Cat. No. 1047-32) 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.

Interfering Substance	Interference Levels and Treatments
Monochloramine, LR method	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.

Method Performance

Estimated Detection Limit (EDL) = 0.02 mg/L

Typical precision (95% confidence interval) = 1.00 ± 0.05 mg/L

LOW RANGE CHLORINE RESIDUAL EXERCISE

CHLORINE RESIDUAL
SAMPLE COLLECTION AND ANALYSIS

CHLORINE RESIDUAL ANALYSIS USING A DIGITAL COLORIMETER

PART 2” High Range

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS (High Range)

Determine concentration of chlorine used for disinfection of a public water system

- Chlorine concentration of disinfection solution should be measured to determine proper dosage.
- Is the concentration of chlorine solution adequate for proper disinfection.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS (High Range)

System Repair/Maintenance (disinfection of water lines)

- Chlorine should be added at same time as water is introduced back into the line.
- Chlorine solution added to create a 50 mg/L dosage with a 5 mg/L residual after 24 hours.
- Alternative: Flush line with water containing a free chlorine residual of 0.5 to 1.0 mg/L. Maintain chlorine residual until BACTI samples are negative.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS
(High Range)

System Repair/Maintenance (storage tank facility)

- Disinfection accomplished in several ways:

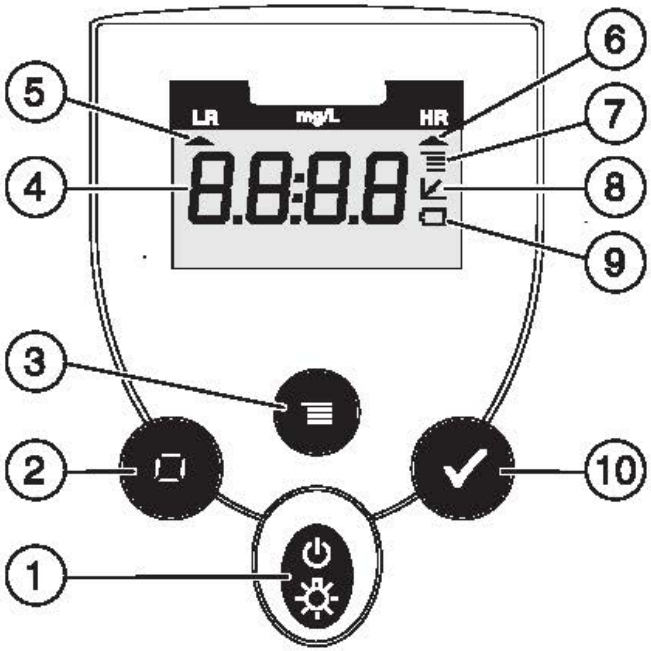
  (1) spraying or brushing the interior of the storage facility with 200mg/L chlorine solution and let stand for 30 minutes before filling to achieve at least a 3 mg/L chlorine residual for 3 to 6 hours.

WHY DO WE NEED TO CONDUCT CHLORINE RESIDUAL ANALYSIS
(High Range)

System Repair/Maintenance (storage tank facility)

(2) filling tank with a 50 mg/L available chlorine concentration and letting tank stand for 24 hours. A chlorine residual of at least 10 mg/L must remain after 24 hours.

Instrument Keys and Display



Item	Description
1	**POWER/BACKLIGHT** Key
2	**ZERO/SCROLL** Key
3	**MENU** Key
4	Numeric Display
5	Range Indicator
6	Range Indicator
7	Menu Indicator
8	Calibration Adjusted Indicator
9	Battery Low Indicator
10	**READ/ENTER** Key

Instrument Operation

Key Functions

Key	Description	Function
	POWER	On/Off/Backlight To turn on the backlight, turn on the instrument, then press and hold the power key until the backlight turns on. Press and hold again to turn off the backlight. This key functions the same in all instrument modes and ranges.
	ZERO/SCROLL	In measurement mode, sets the instrument to zero. In menu mode, scrolls through menu options. Also scrolls numbers when entering or editing a value.
	READ/ENTER	In measurement mode, initiates sample measurement. In menu mode, selects a menu option. When entering numbers, moves one space to the right and executes the function when the entry is complete.

Key	Description	Function
	MENU	Enter/Exit the menu mode Press and hold for approximately 5 seconds to enter user-entered method mode.

Menu Selections

Press the **MENU** key to access the menu selections.

Switching Ranges

1. Press the **MENU** key. The display will show “SEL”. A flashing arrow indicates the current range.
2. Press the **READ/ENTER** key to toggle between ranges.
3. Press **MENU** again to accept and exit back to the measurement screen.

Setting the Time

1. Press the **MENU** key, then press the **ZERO/SCROLL** key until the display shows a time in the “00:00” format.

2. Press **READ/ENTER**. The digit to be edited will flash.
3. Use the **ZERO/SCROLL** key to change the entry, then press **READ/ENTER** to accept and advance to the next digit. The time is entered in 24-hour format.

Recalling Stored Measurements

1. Press the **MENU** key, then press the **ZERO/SCROLL** key until the display shows RCL. The instrument automatically stores the last 10 measurements.
2. In RCL, press **READ/ENTER** to recall the stored measurements, beginning with the most recent measurement taken. The meter stores the measurement number as 01 (most recent) through 10 (oldest), the time the measurement was taken, and the measurement value. The **ZERO/SCROLL** key allows for selection of a specific measurement by number. The **READ/ENTER** key scrolls through all stored data points.

Chlorine, Free and Total, HR (0.1 to 8.0 mg/L Cl_2)

For water, treated water, estuary water, and seawater (Free Chlorine)
For water, treated waters, wastewater, estuary water, and seawater (Total Chlorine)

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*

DPD Method*

USEPA accepted for reporting drinking water analyses (free and total chlorine) and wastewater analyses (total chlorine).

Measuring Hints

- If the chlorine concentration is typically less than 2 mg/L, use the low range procedure.
- Analyze samples immediately. Do not use plastic containers to collect samples. For best results, dedicate a set of sample cells to each test (free and total).

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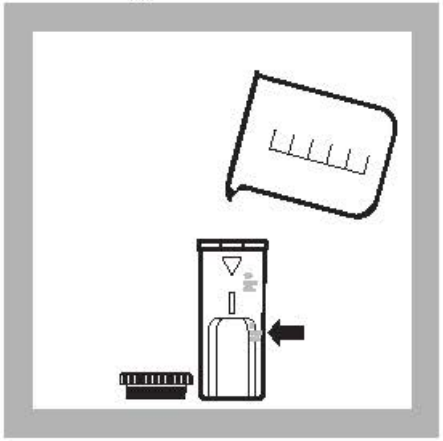
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

- If the sample temporarily turns yellow after reagent addition or shows overrange (page 2—12), dilute a fresh sample and repeat the test. A slight loss of chlorine may occur. Multiply the result by the dilution factor.
- High range free chlorine determinations are subject to variable levels of interferences from monochloramine. See Interferences on page 1—47.
- Cold waters can cause condensation on the sample cells during color development. Examine the sample cells for condensation before reading.

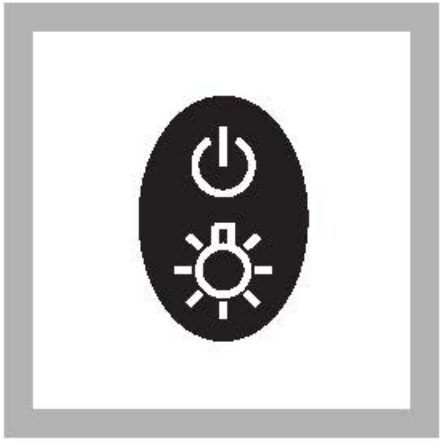
Note: *The Pocket Colorimeter II is designed to measure solutions contained in sample cells.* ***DO NOT*** *dip the meter in the sample or pour the sample directly into the cell holder.*

Using Powder Pillows



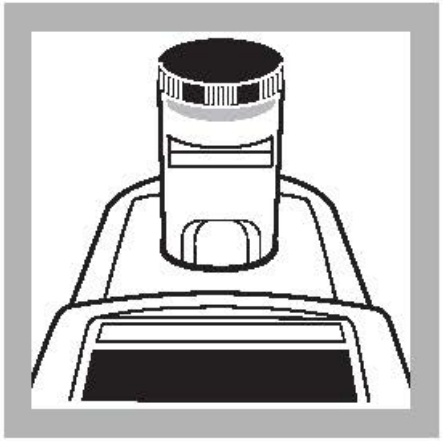
1. Fill a 1-cm/10-mL cell with sample (the blank). Cap.

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



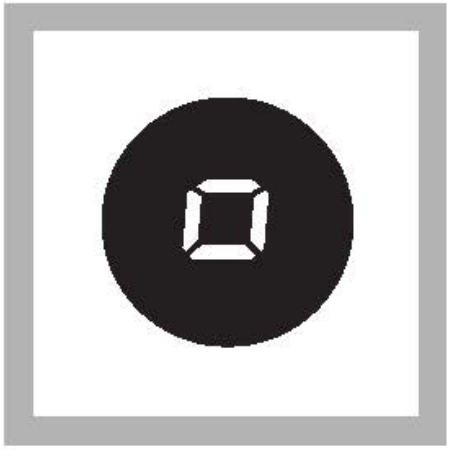
2. Press the **POWER** key to turn the meter on.
The arrow should indicate the high range channel (HR).

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



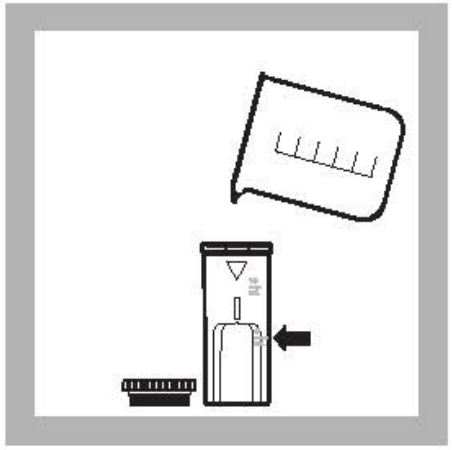
3. Remove the meter cap. Place the blank into the cell holder, with the diamond mark facing the back of the cell holder. Cover the cell with the cap.

Note: *Wipe liquid off sample cells.*

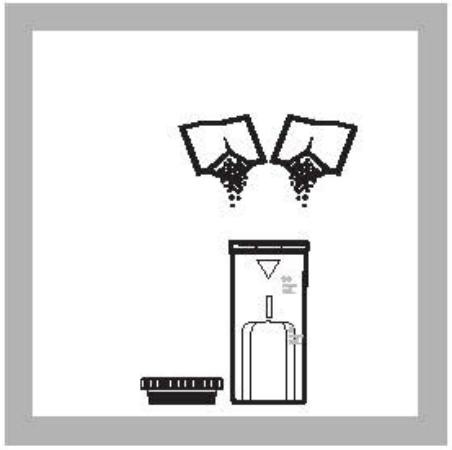


4. Press: **ZERO/SCROLL**
The display will show "- - - -" followed by "0.0".

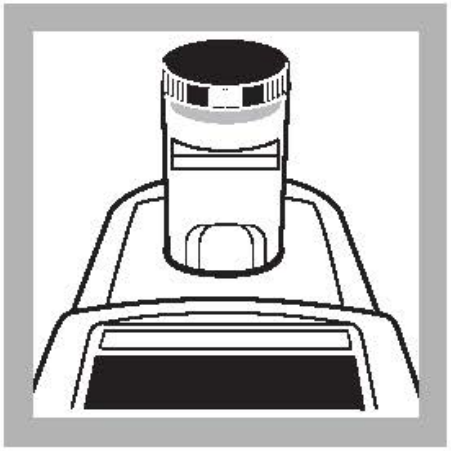
Remove the blank.



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.*

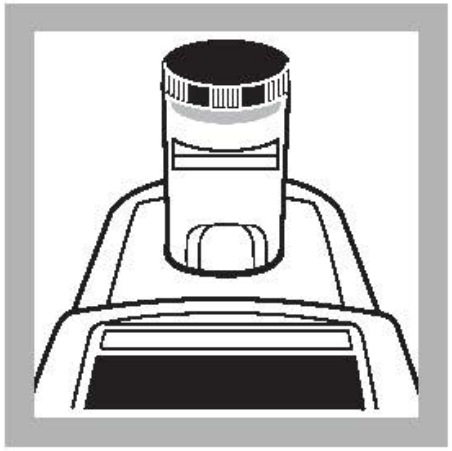


6. Add the contents of two DPD **Free** Chlorine or two DPD **Total** Chlorine Powder Pillows to the sample cell (the prepared sample). Cap the cell and shake gently for 20 seconds.
Note: *Gentle shaking dissipates bubbles which may form in samples containing dissolved gases.*



7. For **free** chlorine, wipe excess liquid and fingerprints from the sample cell. Put the prepared sample cell in the cell holder, then cover the cell with the instrument cap. Proceed to step 9 within **one** minute after adding the DPD Free Pillows.

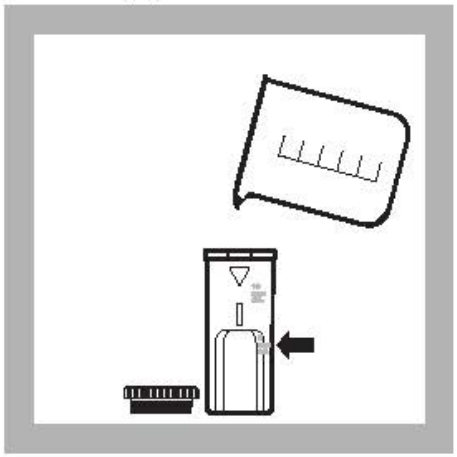
Note: *The SwifTest™ Dispenser can be used in place of the powder pillows (see page 1—42).*



8. For **total** chlorine, wait **3 to 6** minutes after adding the DPD Total Pillows. After the reaction time, wipe excess liquid and fingerprints from the sample cell. Put the prepared sample in the cell holder and cover the cell with the instrument cap. Proceed to step 9.

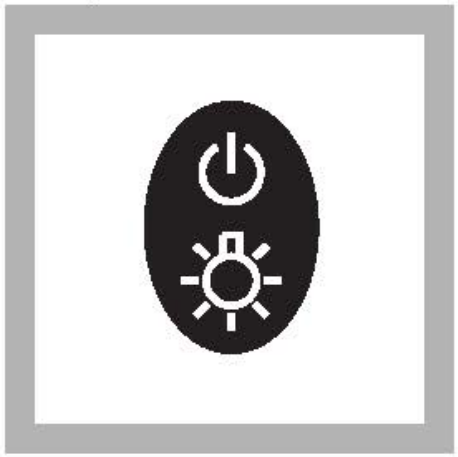
9. Press **READ/ENTER**. The instrument will show "- - - -" followed by the results in mg/L chlorine (Cl_2).

Using the SwifTest™ Dispenser



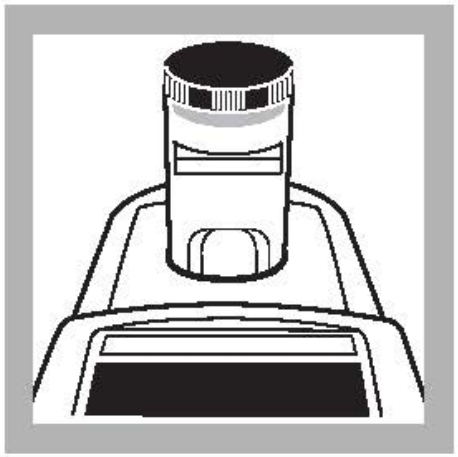
1. Fill a 1-cm/10-mL cell with sample (the blank). Cap.

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



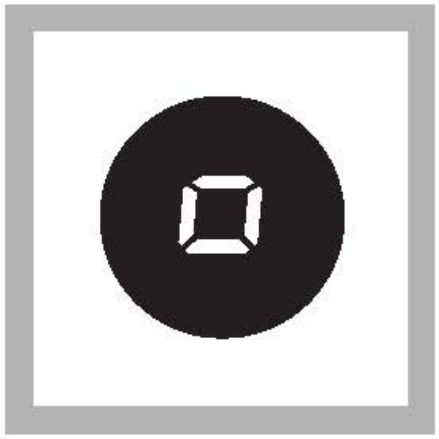
2. Press the **POWER** key to turn the meter on.
The arrow should indicate the high range channel (HR).

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



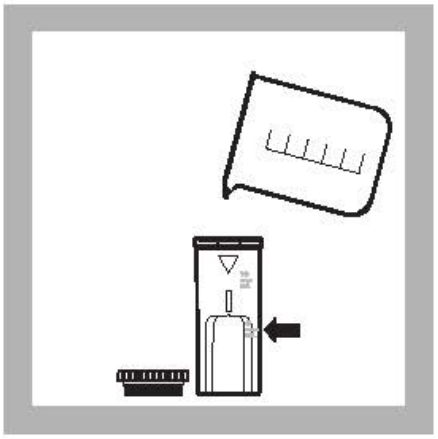
3. Remove the meter cap. Place the blank into the cell holder, with the diamond mark facing the back of the cell holder. Cover the cell with the cap.

Note: *Wipe liquid off sample cells.*

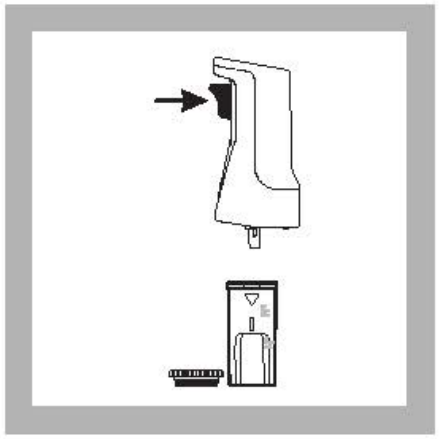


4. Press: **ZERO/SCROLL**
The display will show "- - - -" followed by "0.0".

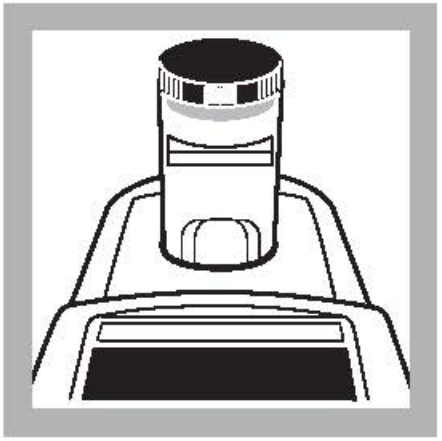
Remove the blank.



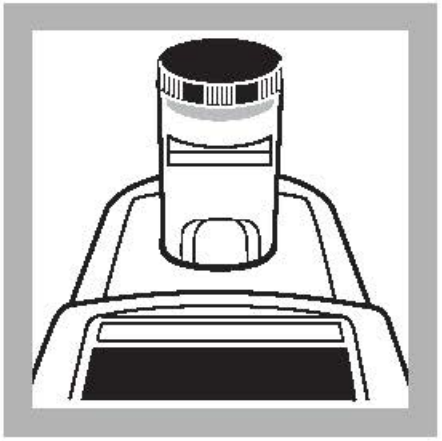
5. Fill another 1-cm/10-mL sample cell to the 5-mL line with sample. Cap.
Note: *Do not use the same sample cells for free and total chlorine without thoroughly rinsing the cells between the free and total tests.*



6. Use the SwifTest™ Dispenser to add two dispensations of DPD **Free** Chlorine reagent or DPD **Total** Chlorine reagent to the sample cell (the prepared sample). Cap the cell and shake gently for 20 seconds.
Note: *Gentle shaking dissipates bubbles.*



7. For **free** chlorine, wipe excess liquid and fingerprints from the sample cell. Put the prepared sample cell in the cell holder, then cover the cell with the instrument cap. Proceed to *step 9* within **one** minute after adding the DPD Free reagent.



8. For **total** chlorine, wait **3 to 6** minutes after adding the DPD Total reagent. After the reaction time, wipe excess liquid and fingerprints from the sample cell. Put the prepared sample in the cell holder and cover the cell with the instrument cap. Proceed to *step 9*.

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

Accuracy Check

Standard Additions Method

a. Use the ampule breaker to snap the neck off a high range Chlorine Standard Solution Ampule, 50–70 mg/L Cl_2.

b. Use a TenSette® pipet to add 0.1, 0.2, and 0.3 mL of standard to three 5-mL samples. Swirl gently to mix.

c. Analyze each sample as described in the procedure. Each 0.1 mL of standard will cause an incremental increase in chlorine. The exact value depends on the concentration of the ampule standard. Check the certificate enclosed with the ampules for calculation of the expected increase in the chlorine concentration.

Standard Solution Method

Standard solutions for chlorine are difficult and time-consuming to prepare. Errors can occur if attention to detail is not addressed during preparation of the standards. The calibration curve is prepared under rigorous analytical laboratory conditions. Use the factory calibration for most normal testing.

A user calibration or a user-prepared chlorine standard may be required by a regulatory official or agency. Two options are available on the Pocket Colorimeter™ II to meet this requirement.

A chlorine standard may be prepared and used to validate the calibration curve using the Standard Calibration Adjust feature (see page 2—13 for more information). The concentration of the prepared standard must be determined with an alternate instrument such as a spectrophotometer, colorimeter, or by using an alternate method such as amperometric titration. The concentration of the chlorine standard for the HR procedure must be between 4.5 and 7.0 mg/L chlorine.

In addition, a user-generated calibration curve can be programmed into the Pocket Colorimeter™ II. See User-Entered Calibration on page 2—15 for more information.

Interferences in Analytical Results (High Range)

Interferences

Interfering Substance	Interference Levels and Treatments
Monochloramine	For conventional free chlorine disinfection (beyond the breakpoint), monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test varies with the temperature, the relative amount of monochloramine to free ammonia, and the time required to do the analysis. Approximate interference levels of monochloramine in the free chlorine test are listed below (as mg/L Cl_2).

NH_2Cl	Sample Temperature °C (°F)			
(as Cl_2)	5 (40)	10 (50)	20 (68)	30 (83)
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

See additional Interferences on page 1—34.

Chlorine, Free and Total, LR, continued

Interferences

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 a separate 10-mL sample, then add the same amount to the sample being tested. Correct for the additional volume.
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 a separate 10-mL sample, then add the same amount to the sample being tested. Correct for the additional volume.
Bromine, Br_2	Interferes at all levels

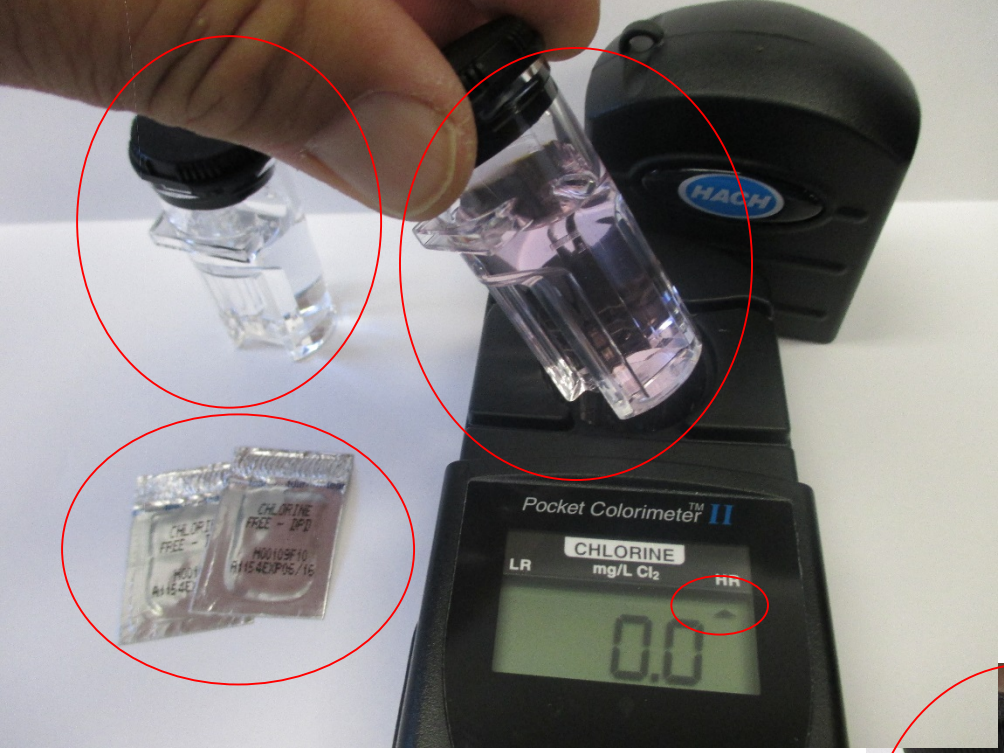
Interfering Substance	Interference Levels and Treatments
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine, I_2	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	1. Adjust sample pH to 6–7. 2. Add 3 drops Potassium Iodide (30-g/L) (Cat. No. 343-32) to a 10-mL sample. 3. Mix and wait one minute. 4. Add 3 drops Sodium Arsenite (5-g/L) (Cat. No. 1047-32) 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.

Summary of Method

Chlorine can be present in water as free chlorine and as combined chlorine. Both forms can coexist in the same solution and can be determined together as total chlorine. Free chlorine is present as hypochlorous acid or hypochlorite ion. Combined chlorine represents a combination of chlorine-containing compounds including but not limited to monochloramine, dichloramine, nitrogen trichloride, and other chloro derivatives. The combined chlorine oxidizes triiodide ion (I_3^-) 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 total chlorine concentration. To determine 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 range of analysis using the DPD method for chlorine can be extended by adding more indicator in proportion to sample volume. For example, two powder pillows of DPD Chlorine Reagent are added to a 5-mL sample portion to extend the range of analysis.

FIND THE DIFFERENCES?



HIGH RANGE

LOW RANGE

SWITCHING YOUR COLORIMETER BACK TO THE LOW RANGE SETTING

Switching Ranges

1. Press the **MENU** key. The display will show “SEL”. A flashing arrow indicates the current range.
2. Press the **READ/ENTER** key to toggle between ranges.
3. Press **MENU** again to accept and exit back to the measurement screen.

HIGH RANGE CHLORINE RESIDUAL EXERCISE

HOW TO TEST OUT-OF-RANGE SAMPLES

LOW RANGE COLORIMETER TEST KITS CAN BE USED TO MEASURE FREE CHLORINE CONCENTRATIONS HIGH THAN THE RANGE OF THE TEST KIT BY DILUTING THE SAMPLE TO REDUCE THE FREE CONCENTRATION TO BE WITHIN RANGE OF THE TEST KIT.

SAMPLES MAY BE DILUTED USING EITHER THE GRADUATED CYLINDER METHOD OR THE DPD DROP DILUTION METHOD.

GRADUATED CYLINDER DILUTION METHOD

- Collect 2ml sample of the highly chlorinated water.
- Pour sample into an empty 50ml graduated cylinder.
- Add distilled or deionized water for a total of 50ml and gently mix.

- Transfer from the graduated cylinder the volume of diluted chlorinated water specified by the test kit to the sample vial or tube.
- Add DPD reagent and mix. Determine the free chlorine concentration of the diluted sample using the test kit.

GRADUATED CYLINDER DILUTION METHOD

- Multiple the free chlorine concentration by the dilution factor. Which is calculated as follows:

$$\frac{\text{(Volume of distilled water + Volume of chlorinated sample)}}{\text{(Volume of chlorinated sample)}} = \text{Dilution Factor}$$

- When 2ml of sample is combined with 48ml of distilled water in the graduated cylinder, the dilution factor is 25 as determined below:

$$\frac{\text{(48ml of distilled water + 2ml of chlorinated sample)}}{\text{(2ml of chlorinated sample)}} = \text{Dilution Factor of 25}$$

GRADUATED CYLINDER DILUTION METHOD

- EXAMPLE: Diluted sample has a free chlorine residual of 1 mg/l, the undiluted sample would have a residual 25 x 1 mg/l or 25 mg/l.

- If it is not possible to accurately determine the chlorine residual of the undiluted sample, it may be necessary to apply a different dilution factor.

(EXAMPLE: If the anticipated level of chlorine residual is around 100mg/l, a more appropriate dilution factor would be 50. The level of dilution could be obtained by diluting 1mg/l of sample with 49ml of distilled water.)

DPD DROP DILUTION METHOD

- Add 10ml of distilled or deionized water and one premeasured packet or powder pillow of DPD reagent (or 0.5ml of DPD solution) to the DPD test kit's sample vial or tube.
- Using an eye dropper, add a sample of the highly chlorinated water on a drop-by-drop basis to the sample vial or tube until a color is produced.

DPD DROP DILUTION METHOD

- Record the number of drops added to the sample vial or tube. Assume one drop equals 0.05ml.
- Determine free chlorine concentration in the sample vial or tube containing # drops of sample, 10ml of distilled or deionized water and DPD reagent by using the colorimetric test kit.

- Estimate the chlorine residual in the sample using the following equation:

$$\frac{(Cl_2\ \text{Residual}_{\text{sample-tube}}, \frac{mg}{L}) * (\text{Vol}_{\text{distilled-water}}, mL)}{(\text{Vol}_{\text{sample}}, \text{drops}) * (0.05 \frac{mL}{drop})} = Cl_{2\ \text{residual-sample}}, \frac{mg}{L}$$

DPD DROP DILUTION METHOD

- EXAMPLE: Assume three (3) drops of chlorinated water from a disinfected water main determine a free chlorine concentration of 0.6mg/l in 10ml if distilled water in the sample vial. Determine the free chlorine concentration in the sample of chlorinated water from the disinfected water main:

$$\frac{(0.6\text{mg/l}) \times (10\text{ml})}{(3\text{ drops}) \times (0.05\text{ml/drop})} = \underline{\mathbf{40mg/l}}$$

OUT-OF-RANGE CHLORINE RESIDUAL EXERCISE

Chlorine Residual Sampling Hints and Tips

GOOD SAMPLING HINTS/TIPS

- **Sampling Hints/Tips**
  - Analyze immediately after collection

    (Chlorine in aqueous solution is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly.)
  - Avoid Plastic containers
  - Dedicated different sample cells for Free and for Total Chlorine testing.
  - If chlorine concentration is less than 2 mg/L use the Low Range setting and procedure.

GOOD SAMPLING HINTS/TIPS

- **Sampling Hints/Tips**
  - Exposure to sunlight or other strong light or agitation will accelerate the reduction of chlorine.

- Therefore, start chlorine determinations immediately after collecting the sample to avoid excessive light of agitation.

- Do not store samples to be analyzed for chlorine.

GOOD SAMPLING HINTS/TIPS

- **Sampling Hints/Tips**
  - Pretreat glassware by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of D.I. Water for at least one hour.
    - Thoroughly rinsing after each use allows for only occasional pre-treatment.
    - Air dry the sample cells and sampling containers.

TESTING TIPS

1.

Samples should be collected in a clean glass or polyethlylene container.

2.

Samples should be analyzed as soon as possible after collection.

3.

Discard tubes that are badly scratched.

4.

Observe the shelf-life recommendations for reagents.

5.

Protect reagents and components from extreme heat and cold.

6.

Never put wet tubes in colorimeter.

NOTES ON DPD COLORIMETRIC METHOD

- Keep glassware clean and scratch-free
  - Rinse after analyzing a sample.
  - Wipe with a soft towel so as to not scratch the vial
  - Rinse with distilled or deionized water when back from field, then leave open to dry
  - Weekly, put bleach into the vial and seal overnight to disinfect.
  - **Do Not** leave sample in vial with DPD. The color will stain the glass and give inaccurate results!!!


10 ml

NOTES ON DPD COLORIMETRIC METHOD

- Keep colorimeter clean and dry
  - Make sure sample vial is wiped off before placing into the unit
  - Wipe out the colorimeter if liquid or dirt get in it
- Use the cap supplied with the sample vial
  - Do not put the vial in the instrument while open
  - **Do Not** cover the vial with your thumb and shake
  - Swirl the sample to stir after you put the cap on
- Store the colorimeter in a case
  - While some of these units are relatively rugged, banging it around as you toss it in your truck could damage the optics or electronics in the unit.

NOTES ON DPD COLORIMETRIC METHOD

- **Keep your DPD clean and dry!!** It is critical to your work and cannot get contaminated. If your reagent is clumped and/or dirty, get new reagent.
- If you have to use the contaminated reagent, make a note and permanently attach it to your sample records.

OTHER CHLORINE RESIDUAL MEASUREMENT ISSUES

- STANDARDS – Primary and Secondary Standards for Calibration and Performance Verification
- Initial Demonstration of Capability (IDOC)
- Preparing an Standard Operating Procedure (SOP)

Primary Chlorine Standards

- Utilizes an actual water sample with a known chlorine concentration.
- Can be purchased from laboratory supply business.
- For stability reasons, primary chlorine standards are sold at a minimum concentration of 50 mg/l.
- Dilution on-site is required to use primary standards
- Requires clean glassware and GLP to create an accurate standard.

Chlorine Standards

- Sealed ampoule containing a known chlorine concentration.

- Is then diluted with sterile water **or** distilled/deionized water if DPD is added first
  - (Chlorine demand in water could affect the expected result.)

- These are considered *primary standards* and can be used for calibrating the unit

Chlorine Standards

- **Standard Solutions**
  - Used as accuracy check (standard solution or standard additions)
  - Could be used for calibration

DPD Colorimetric Method – Calibration Check

Chlorine Standards

An ampoule containing a known concentration of chlorine.

The lot being used for this example contains 65.0 mg/l chlorine

They need to be stored in a refrigerator. Not the lunch room one….

Primary vs. Secondary Standard

- A primary standard can be used to calibrate an instrument and/or check calibration
  - Based on experience, HACH colorimeters are quite accurate and do not require a new calibration input. If your unit does, there may be a problem with the unit or your method. Investigate before changing the calibration.
- A secondary standard is meant as a check of calibration only – cannot be used to calibrate a unit

Chlorine Standards - Math

- To determine the concentration of the prepared standard:
  - Volume Standard Added / (Volume Standard + Sample Volume) x Standard Concentration
  - Example: 64.79 mg/L, 0.10 ml added to 10 ml
    - (0.1 ml / (0.1 ml + 10 ml)) x 64.79 mg/L
    - (0.0099) x 64.79 mg/L = 0.64 mg/L

- To make a standard of a specific concentration, change the volume added and recalculate until you get the concentration needed.

Chlorine Standards

- HACH's procedure recommends adding the DPD to the sample vial and water before adding the chlorine standard.
- This minimizes any chlorine demand that may be in the water.
- This method checks for glassware, reagent, colorimeter, and analyst effectiveness

Chlorine Standard Addition and Check

Use at least four (4) vials; 5 are used in this example.

Make sure sample vials are clean and dry.

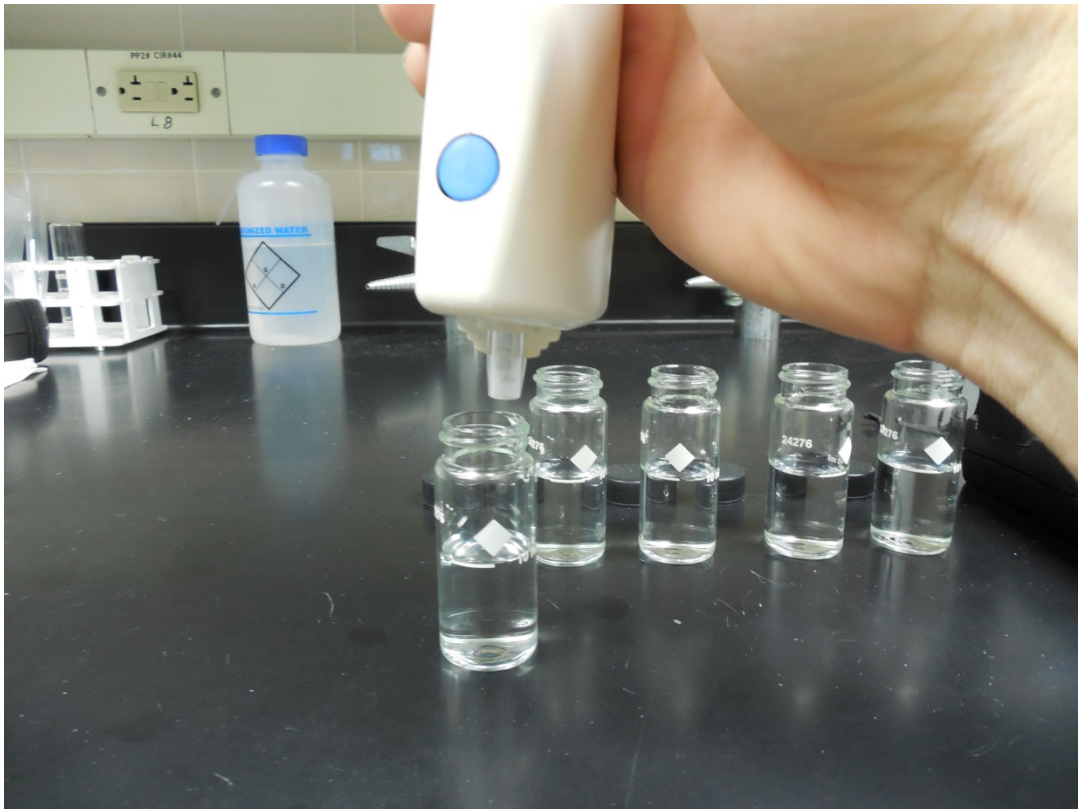
The micro-pipettes will be used in dispensing the chlorine standard

Chlorine Standard Addition and Check

After adding 10 ml of distilled or deionized water to the vials, dispense the required amount of DPD to the vial.

Using the line on the vial is acceptable for accuracy.

This is an automatic dispenser using powder DPD.



Chlorine Standard Addition and Check

One vial will be used as a blank.

Accurately pipette the volume of chlorine standard to each of the other vials.

Cap and swirl each one after adding the standard.

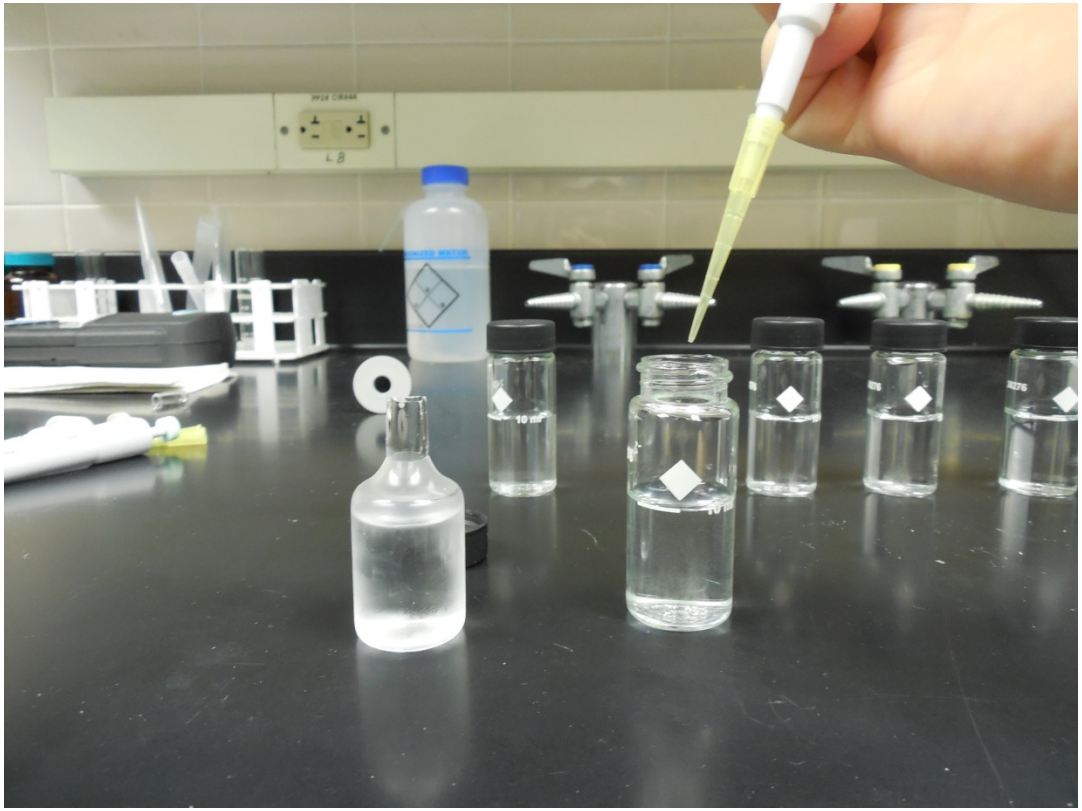
Volumes added:

0.03 ml

0.10 ml

0.20 ml

0.30 ml



Chlorine Standard Addition and Check

Place the blank into the unit – the diamond on the vial should face toward the user.

Place the cap back on, and press “0”

Remove the blank and place the first standard into the unit. Cap and press the read button.

Record this value

Repeat with the other standards.

Chlorine Standards - Math

- Expected Values:
  - 0.03 ml: (0.03 / (0.03 + 10)) x 65.0 mg/L
  - 0.10 ml: (0.10 / (0.10 + 10)) x 65.0 mg/L
  - 0.20 ml: (0.20 / (0.20 + 10)) x 65.0 mg/L
  - 0.30 ml: (0.30 / (0.30 + 10)) x 65.0 mg/L

- 0.19 mg/L, 0.64 mg/L, 1.27 mg/L, 1.89 mg/L

Chlorine Standards - Math

- EPA 334.0 states +/- 15% of expected values to pass. ((True – Expected) / Expected) x 100%

- So:
  - ((0.18 mg/L – 0.19 mg/L) / 0.19 mg/L) x 100%
  - ((0.64 mg/L – 0.64 mg/L) / 0.64 mg/L) x 100%
  - ((1.29 mg/L – 1.27 mg/L) / 1.27 mg/L) x 100%
  - ((1.77 mg/L – 1.89 mg/L) / 1.89 mg/L) x 100%

Chlorine Standards - Math

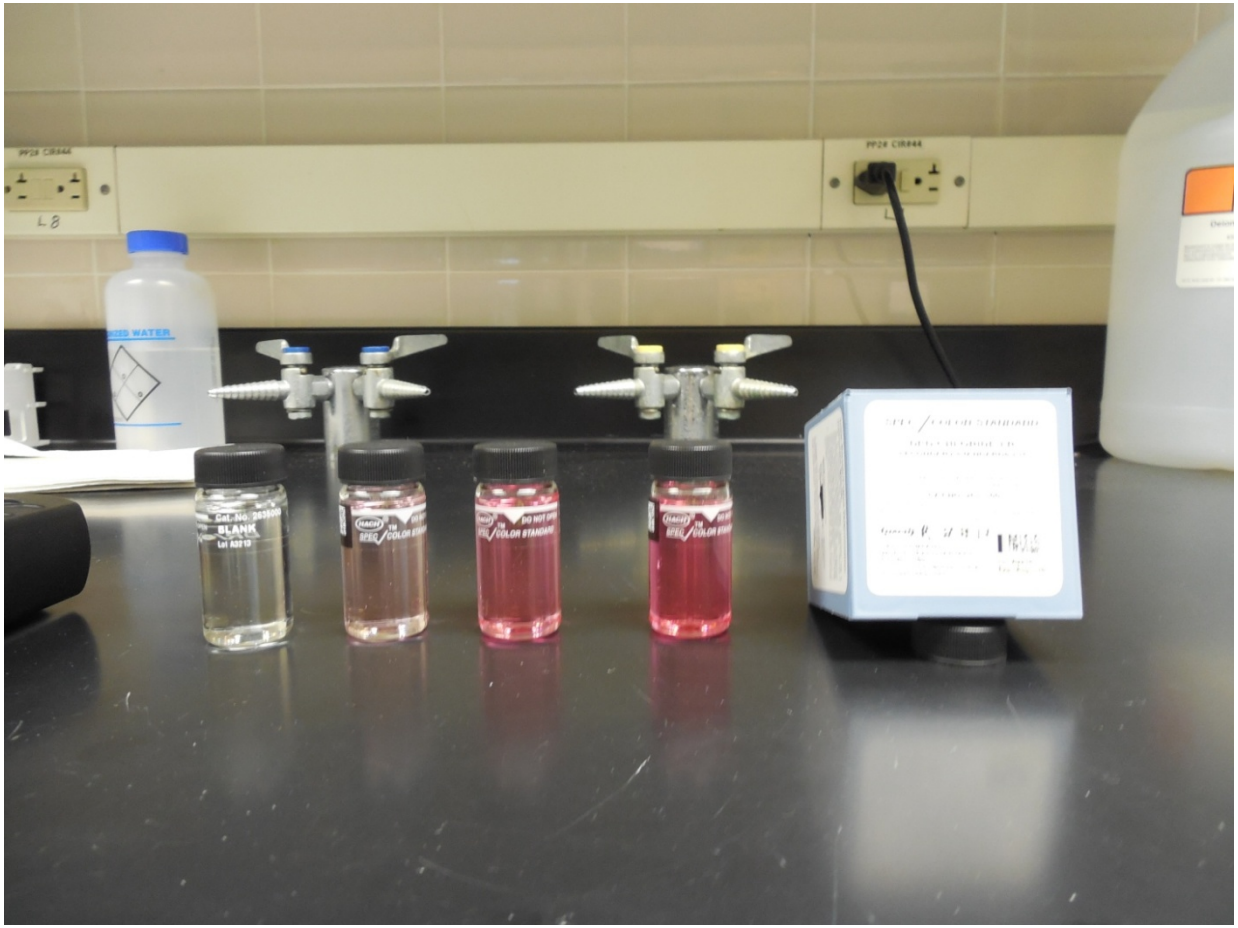
- 0.03 ml: -5.3 % ----PASS
- 0.10 ml: 0.0 % ----PASS
- 0.20 ml: 1.6 % ----PASS
- 0.30 ml: -6.3 % ----PASS

- This unit passes calibration check

Secondary Standards

- Secondary Gel Standards
  - These provide a quick check of instrument performance/accuracy.
  - They do not check reagent, glassware, or analyst performance
  - Should perform a check at least quarterly
  - DO NOT calibrate the instrument with these.
  - Acceptable ranges are stated with paperwork included with the standards
  - Secondary standards must be verified before use and any time an initial calibration is performed.

DPD Colorimetric Method – Calibration Checks



Chlorine Standards

- **Specification Check Standards (Secondary Standards)**
  - Gel standards that simulate specific chlorine values
  - Used as a quality control check (verifies correct instrument operation).
  - Used to verify instrument performance/accuracy has not changed from initial performance evaluation.
  - Cannot be used to calibrate an instrument.

Note: *Before proceeding, make sure the instrument is in the low* ***(LR)*** *range channel. See Switching Ranges on page 2—4.*

Using the Spec√ Standards

1. Place the colorless Spec√ blank into the cell holder with the alignment mark facing the keypad. Tightly cover the cell with the instrument cap.
2. Press **ZERO**. The display will show "0.00".
3. Place the STD 1 cell into the cell holder. Tightly cover the cell with the instrument cap.
4. Press **READ/ENTER**. Record the concentration measurement.
5. Repeat steps 3 and 4 with cells labeled STD 2 and STD 3.
6. Compare these measurements with previous measurements to verify the instrument is performing consistently. (If these are the first measurements, record them for comparison with later measurements.)

Note: *If the instrument is user-calibrated, initial standard measurements of the Spec√ Standards will need to be performed again for the user calibration.*

Spec√™ Secondary Standards for DPD Chlorine

Note: *Due to improvements in the optical system of the Pocket Colorimeter™ II, the tolerance ranges and values on the Certificate of Analysis of previously purchased Spec√ standards may no longer be valid. Obtain a new set of standards, or use the Pocket Colorimeter II to assign new values to existing standards.*

The DPD Chlorine Spec√ Secondary Standards are available to quickly check the repeatability of the Pocket Colorimeter™ II instrument (see OPTIONAL REAGENTS on page 1—51).

After initial measurements for the Spec√ standards are collected in the low range (LR) channel, the standards can be re-checked as often as desired to ensure the instrument is working consistently.

The standards do not ensure reagent quality nor do they ensure the accuracy of the test results. Analysis of real standard solutions using the kit reagents is required to verify the accuracy of the entire Pocket Colorimeter system. The Spec√ Standards should *NEVER* be used to calibrate the instrument. The certificate of analysis lists the expected value and tolerance for each Spec√ Standard.

SPEC√ SECONDARY STANDARDS
DPD CHLORINE

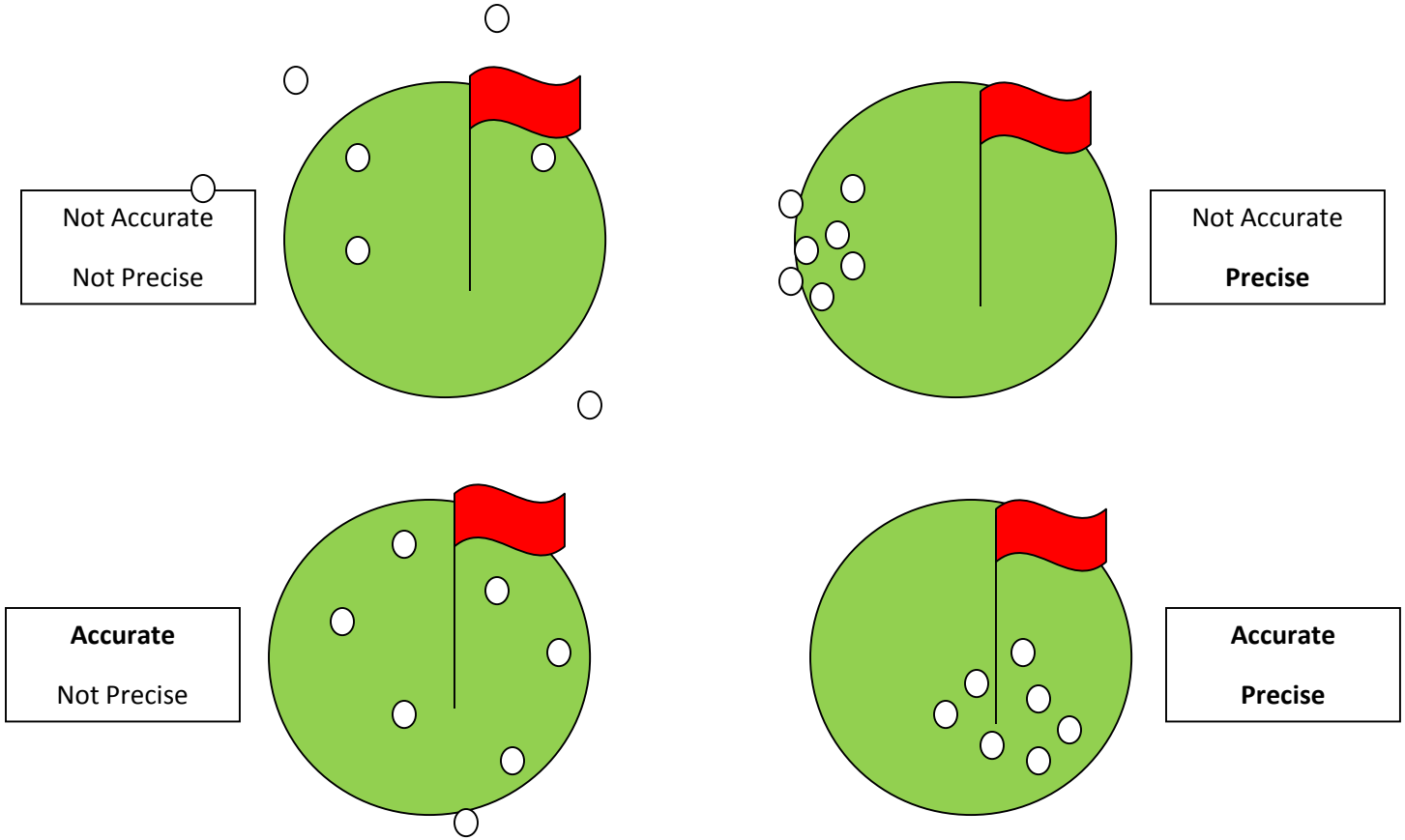
Certificate of Analysis
and
Record of Performance Verification

SECONDARY STANDARDS EXERCISE

Initial Demonstration of Capability (IDOC)

- Each analyst must demonstrate that they can properly perform the procedure and produce accurate and reliable results.
- Subsequently done with any significant changes (new instruments, new operators, new standards, new/revised methods).
- Measure their accuracy and precision. Accuracy and precision are best explained with a picture…

Accuracy vs. Precision



IDOC Procedure

- Prepare a chlorine standard solution.
- The standard should be near the expected values of water samples that will be read
- Have the analyst run the blank and five (5) samples immediately after prep (<15 minutes)
- Record these values

IDOC Procedure

- Calculate the average of the readings:
  - Add the five readings and divide by five (5)
  - Result must be +/- 15% of the expected value
- Calculate the relative standard deviation
  - Use a spreadsheet to calculate the standard deviation.
  - For relative standard deviation: divide the *standard deviation* by the average of the values and multiply times 100%.
  - Must be <= 15% for analyst to pass

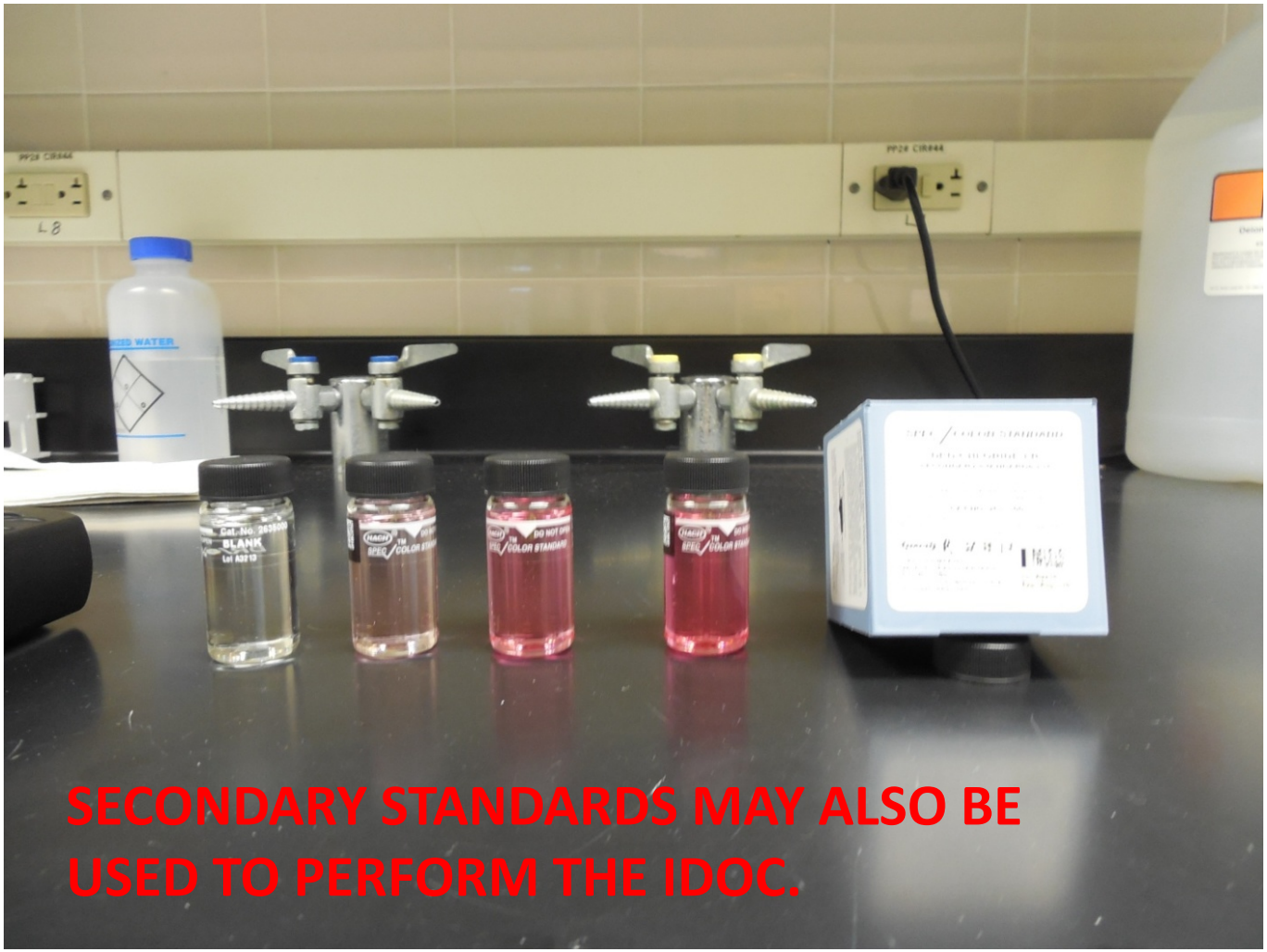
Example

- 1.00 mg/L standard used;
- Analyst readings of: 0.92, 1.01, 0.98, 1.12, 0.89 mg/L

- Average = (0.92+1.01+0.98+1.12+0.89) / 5 = 0.98
- % Difference (0.98-1.00) / 1.00 x 100% = **2%**

- Relative Standard Deviation = (0.090/0.98) x 100%
- RSD = **9.2%**

DPD Colorimetric Method – (IDOC)



SECONDARY STANDARDS MAY ALSO BE USED TO PERFORM THE IDOC.

DPD Colorimetric Method SOP

- A good SOP will make it so any competent person could come in and perform the procedure.

- It is not intended for persons such as your Mayor, Superintendent, Public Works Director, janitor. Unless they happen to be a water operator..?

Why Do I Need an SOP?

- Creates consistency when a process is performed.
- Provides a format that is easy to follow.
- Reduces the possibilities of human error.
- Provides guidelines for operators/samplers to follow.
- Ensures data is Legally Defensible.

Cl2 DPD SOP – Suggested Components

- What are we testing for?
  - Free Chlorine Residual vs. Total Chlorine Residual
- Why are we testing for it?
  - Performance? Regulatory?
- Who is performing the tests?
  - Do not allow non-trained personnel perform the test and report the results.

Cl2 DPD SOP – Key Components

- Required Materials (Equipment and Supplies)
- Actual Test Procedure (Analytical Methods)
- Sample Collection (Sample Handling/Collection Procedures)
- Analyst Training and Performance
- Quality Control Measures
- Frequency of QC Measures
- Traceability of Measurements
- Reporting of Results

DPD Colorimetric Method - Materials

- Instrument (SM 21):
  - Colorimetric, wavelength 490 to 530 nm
  - Light path of 1 cm or longer

- Glassware (SM 21, HACH):
  - Use clean sample vials
  - Use separate ones for FREE and TOTAL chlorine (Prevents iodide contamination in free chlorine measurements)

DPD Colorimetric Method - Materials

- DPD
  - Available in multiple delivery platforms:
    - Pillow Packs
    - Accu-vials
    - Test-n-tube
    - Liquid
    - Powder
      - Automatic Dispensers
      - Scoops

DPD Colorimetric Method - Materials

- Chlorine Standard Ampules
  - Used for creating chlorine standards
  - Other standards may be available from other sources
- Distilled or Deionized Water
  - Rinsing glassware
- Bleach/Hypochlorite
  - Disinfection of Sample Vials

DPD Colorimetric Method - Materials

- Take care to select DPD for the type of chlorine residual you are measuring (free vs. total)
- Log in and record information DPD when received
  - Date of Receipt
  - Product # and Lot #
  - Expiration Date
  - Date Opened
- LABEL the DPD with expiration date

Analytical Procedures

Approved Methods

For Free and Combined Chlorine

Method	SM Reference
• Amperometric Titration Method	4500-Cl D
• Low Level Amperometric Titration	4500-Cl E
• DPD Ferrous Titrimetric Method	4500-Cl F
• **DPD Colorimetric Method**	**4500-Cl G**
• Syringaldazine (FACTS) Method	4500-Cl H

– **Be aware of details associated with**:

- Low Range vs. High Range
- Total Chlorine vs. Free Chlorine

DPD Colorimetric Method
Key Components

- Sample Collection (Sample Handling/ Collection Procedures). References instrument manual and training materials.

- Analyst Training and Performance. May be accomplished through DOH training and annual chlorine proficiency testing.

DPD Colorimetric Method Quality Control Measures and Frequencies

- Use of Primary and Secondary Standards
- Initial Determination of Capability (IDOC)
- Instrument Calibration - Verification
- Implementation of SOP
- Others

- Frequency of QC Measures should be identified in the SOP.

Initial Demonstration of Capability (IDOC)

- Simple procedure that shows each sampler/ operator is capable of performing analysis.
- Ensures accuracy of your colorimeter.
- SOP should include the procedure for performing the IDOC. (Step by step instructions – should be sign by analyst & witness).

DPD Colorimetric Method Quality Control Measures and Frequencies

- Routine Calibration Verification Standard –

  - Performed prior to collecting a chlorine residual for compliance

    -- Before leaving the office or plant for the day.
    (secondary gel standards are temperature sensitive)

    -- Prior to sampling & again after final sample analysis of the day. (more defensible especially for systems collecting a large number of samples)

DPD Colorimetric Method Quality Control Measures and Frequencies

- Routine Calibration Verification Standard –
  - Ensures your Colorimeter is reading within range.
  - Rule of Thumb. Use standard that is ½ the expected chlorine residual.
  - Reading should be $\leq$ 15% of known concentration
  - Notice trending toward $\geq$ 15%

DPD Colorimetric Method
Key Components

- **Recordkeeping**

  - **Describe your internal procedures for recordkeeping**.

    May include:

    -- Writing results on chain of custody forms

    -- Maintaining a log of results & date analyzed

    -- Creating a spreadsheet

DPD Colorimetric Method
Key Components

- **Reporting of Results**

  - Describe your internal procedures for reporting data.
    -- Compliance Data
    -- Operational Data
  - Report Frequency – Routine Monitoring Data.
    -- Daily (contact time, minimum residual at entry point)
    -- ASAP (failure to meet contact time, on-line analyzer fails)
    -- 3 months (sampling logs to verify plant in compliance)

DPD Colorimetric Method

Traceability of Measurement

- When you obtain your standards and reagents, make sure you also get the associated Certificate of Analysis from the supplier.

- Also make sure you have up to date Safety Data Sheets for materials being used also. DPD is toxic. Refer to MSDS.

Options

- The costs may make these tests prohibitive for small systems.
- A local larger system may be willing to perform verification on your portable units
- Work with your local public health official to find a solution.

SOP Summary

- The SOP can be as simple as you want it.
- Make sure it works – have someone read it and perform the task
- Keep a revision # and approval date on each SOP.
  - Helps ensure someone does not use an old SOP that may be floating around still…..
- Review them periodically (annually is preferred)
- Each sampler/operator should read the SOP and sign/date. Copies should be kept on file,

WHY IS THIS IMPORTANT?

- Chlorine Residual results must be obtained in a manner consistent with Laboratory Methods?
- Holding Time for Chlorine testing is immediately.
- Field Colorimeters developed to comply with Method 4500-Cl G are acceptable for compliance reporting.
- Legal defensibility.

What I Need to Do?

- Utilize **EPA Approved Colorimeter(s)** that meet Method 4500 Cl G criteria.

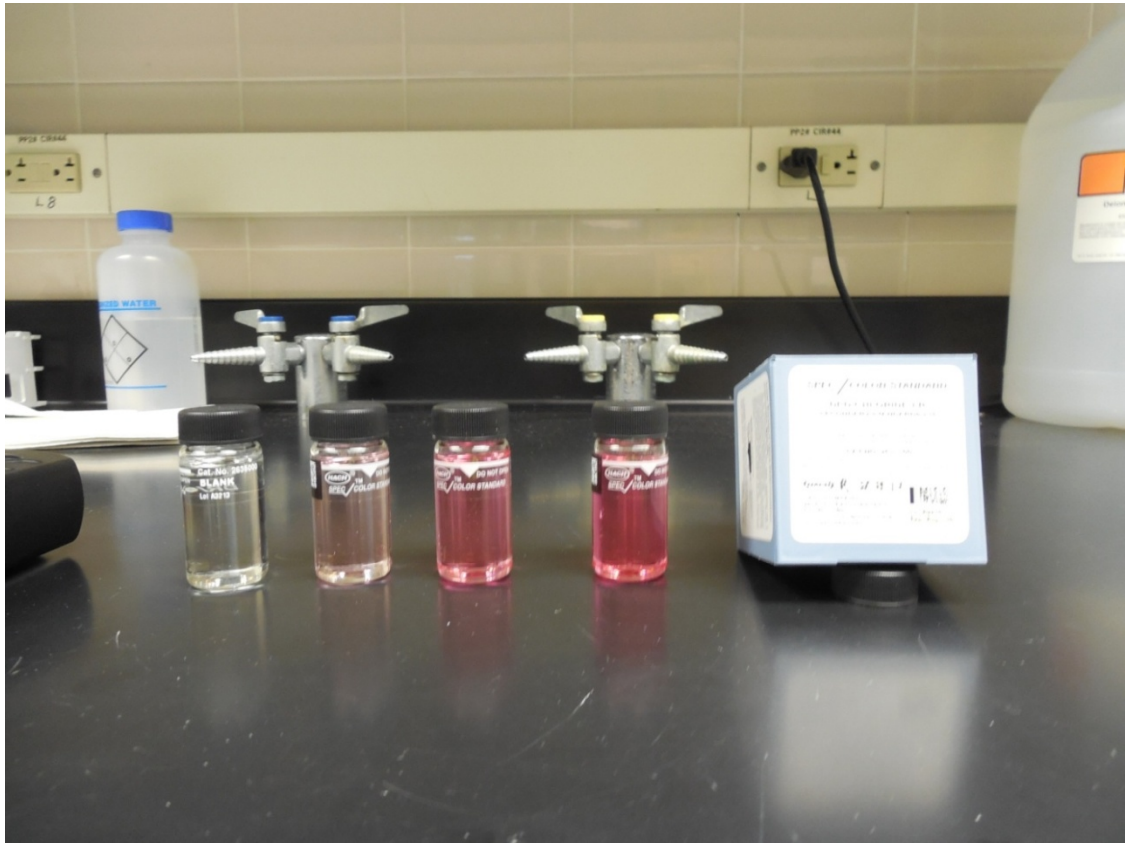
  - Wavelength must be 490-530nm with light path > 1 cm

  (SM 4500-Cl G 2.a.2)
- Develop and implement a **Standard Operating Procedure (SOP)**.
- Perform an **Initial Demonstration of Capability (IDOC)**.
- Utilize **Secondary Standards** to verify the calibration of your Colorimeter.
- **Be prepared to defend your data!!**

PROPOSED REVISED CHLORINE PROFICIENCY TEST

- **PART 1: Standards Measurement Stations**
- **PART 2: Troubleshooting Your Instrument**
- **PART 3: Testing Unknown Water Samples**

PART 1: Standard Measurements
Check of Instrument Performance



USE OF SECONDARY GEL STANDARDS (LR, MR, HR)

PART 2: Troubleshooting Your Instrument

POSSIBLE PROBLEMS:

- Solids in Water Sample
- Sample Vial Dirty (outside/inside)
- Proper Sample Volume
- Dirty optics
- Moisture within optics
- Fogging of vial (cold sample water)
- Correct orientation of vial markings
- Reagent shelf life
- Instrument battery life
- Instrument accuracy
- Others

PART 3: Testing Unknown Water Samples

Conduct Chlorine Residual Testing on a series of unknown samples. Unknown Samples may be Low Range, High Range, nd/or Out-of-Range..

Chlorine Proficiency Testing will be conducted later this year (2017) and annually thereafter.

- QUESTIONS & ANSWERS
- TRAINING EVALUATION
- RTCR/GWR Sampling Training &
  Chemical Compliance Monitoring Training