Digital Chlorine Meter Operation and Troubleshooting

Clean and Safe Drinking Water Workshop 2010 Gander, NL

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OUTLINE

- Chlorine Chemistry
- Various Testing Devices
- Colorimetry and Reagents Explained
- Pocket Colorimeter I and II Overview
- Low Range Free Chlorine Test

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OUTLINE

- Low Range Total Chlorine and High Range Testing Differences
- Result and Unit Verification
- Error Messages and Troubleshooting

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Chlorine Chemistry

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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 Hypochlorite:

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

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 exists predominantly in the OCl^- form

Chlorine Chemistry & Disinfection Efficiency:

Free Chlorination:

$Cl_2 + H_2O \longrightarrow HOCl + OCl^-$ *(strongest)*

Chloramination:

$NHCl_2 + HOCl \longrightarrow H_2O + NCl_3$

$NH_2Cl + HOCl \longrightarrow H_20 + NHCl_2$

$NH_3 + HOCl \longrightarrow H_20 + NH_2Cl$

decreasing disinfection efficiency

Organic Amines:

Org N + HOCl $\longrightarrow$ OrgN-Cl *(~none)*

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Various Options for Manually Measuring Chlorine in Water

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Measuring Devices

Test Strips

- Easiest to Use
- Not very accurate
- DPD pillow instead

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Measuring Devices

Colour Comparison Kit

- Accurate to 0.1mg/L
- Affected by light
- Operators see different readings

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Measuring Devices

Titrations (Digital Amperometic Analysis)

- Very Accurate, (ppb)
- Relatively Expensive
- Effluent Discharge to sensitive areas

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Measuring Devices

Digital Colorimetry

- Accurate to 0.01mg/L
- Easy to use
- Waterproof
- Low cost per unit test

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How do Colorimeters Read a Sample?

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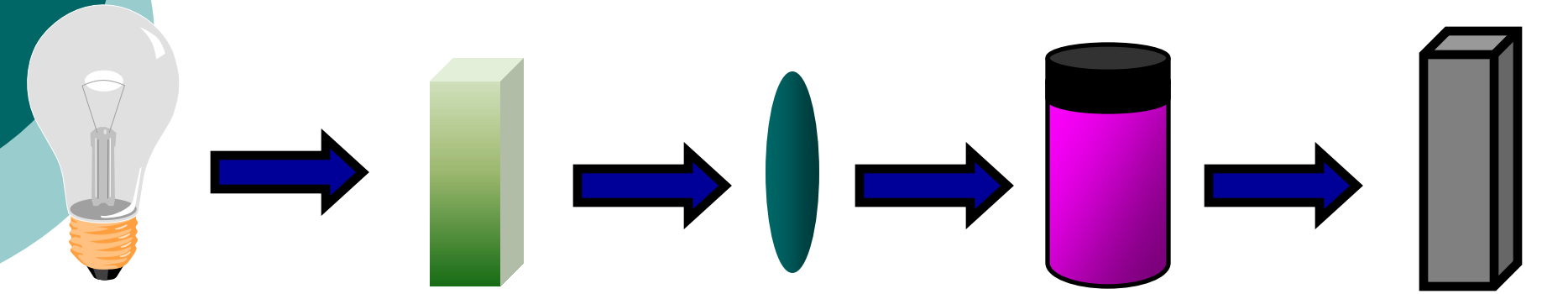
Basic Colorimeter



Lamp

Monochromator or Filter

Lens

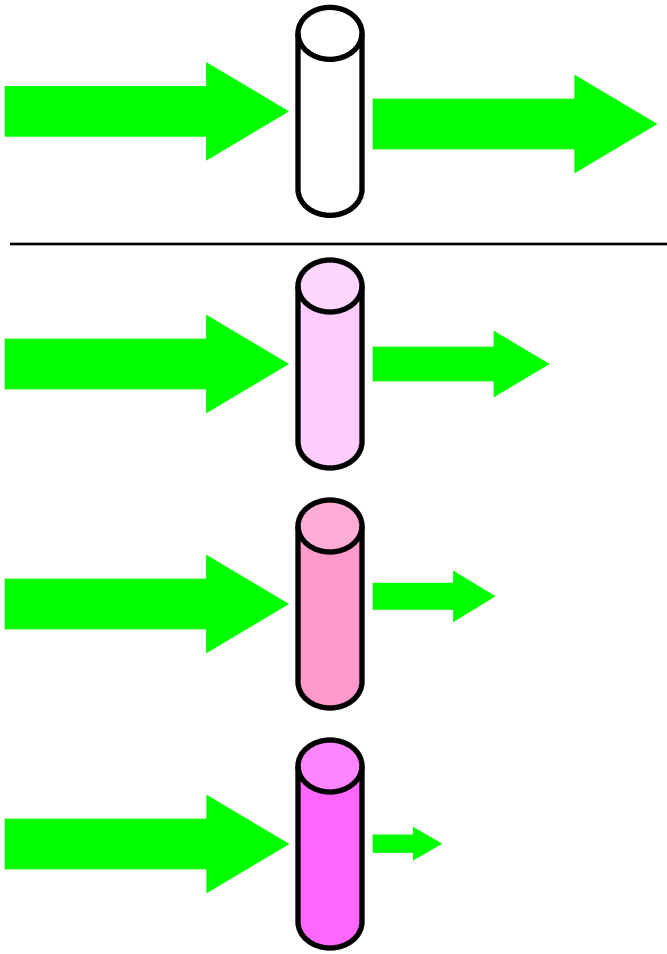
Sample

Detector

Colorimetry Explained

- (ZERO) Measure the amount of light passing through the untreated sample.
- (READ) Measure the amount of light passing through the reacted sample.
- Convert the difference in transmitted light into a concentration, using the built-in calibration curve.

Light Source



Detector

% Transmittance		Absorbance
100	"ZERO"	0.00
60	"READ"	0.22
40	"READ"	0.40
10	"READ"	1.00

(Abs = -log T)

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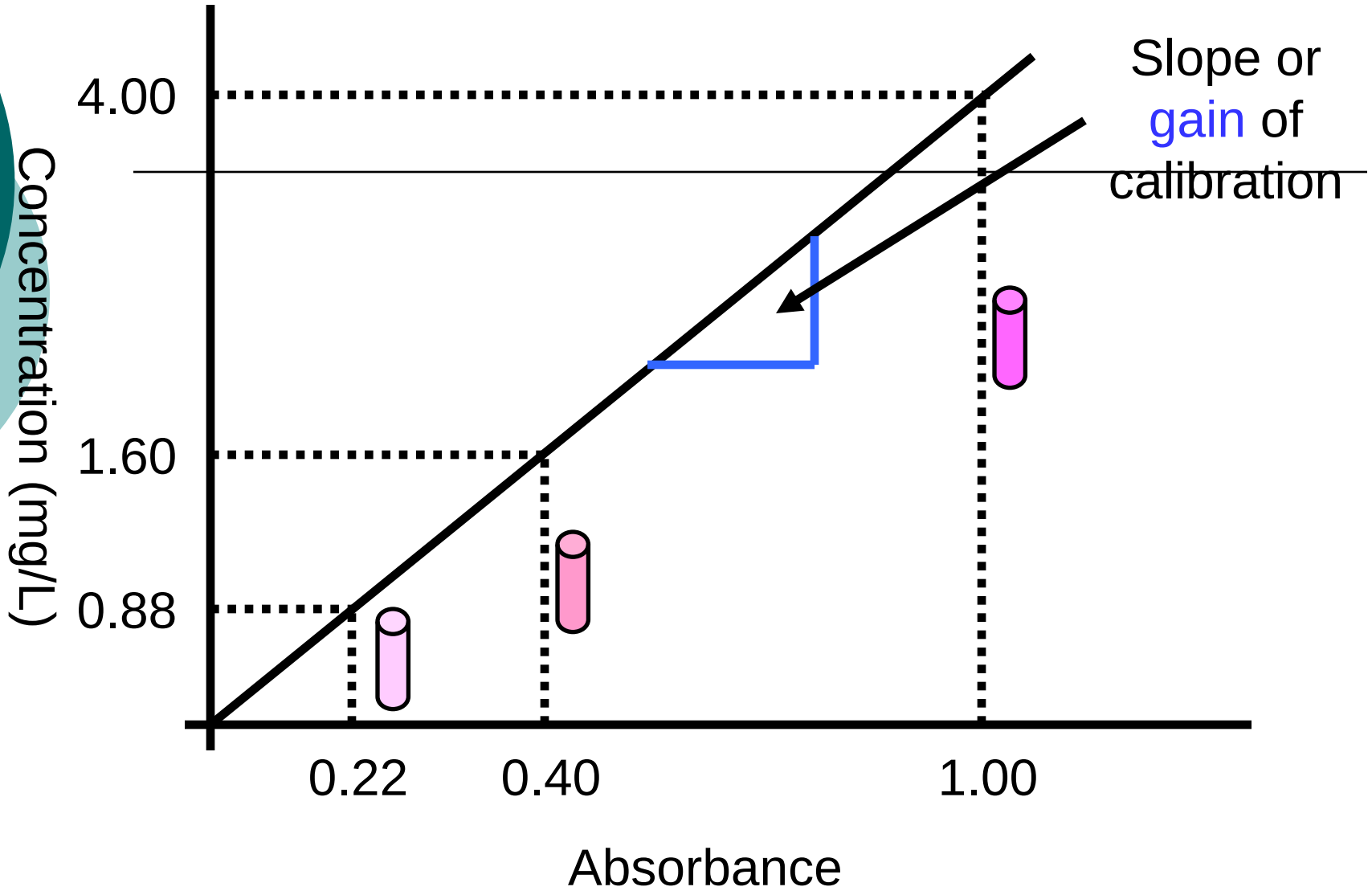

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Reagents

- Convenient reagent packaging
  - Permachem foil pouches
    - Originally “Powder Pillows”
  - AccuVac vials
  - SwifTest(TM) Dispenser

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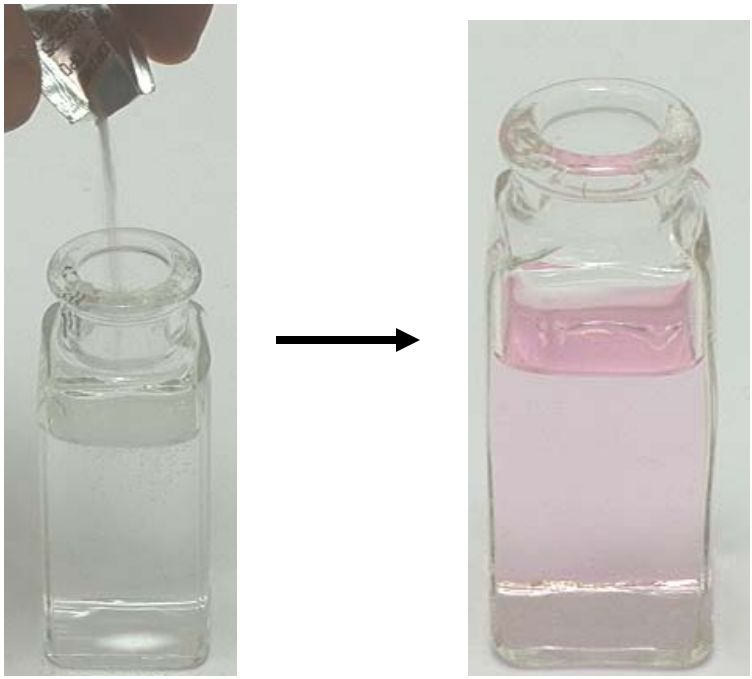
What do the Reagents Do?

Reagents + Sample

↓

Colored Complex



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How to Make Menu Changes on Pocket Colorimeters

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Pocket Colorimeter I

Two Ranges LO = 0-2.00,
HI = 0-4.5 mg/L

- Switching Ranges
- Retrieving Factory Default Calibration

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Pocket Colorimeter I

Switching Ranges

- Hold ZERO and READ key, after 1 sec release ZERO key
- HI or LO will show range instrument is in
- Repeat above steps to switch ranges

Pocket Colorimeter I

Retrieving Factory Default Calibration

- Hold ZERO and READ for 3 secs
- CAL then flashing 0 is displayed
- Press READ and hold for 2 secs until dFL is displayed

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Pocket Colorimeter II

Two Ranges LO = 0-2.00, HI = 0-8.0 mg/L

- Switching Ranges
- Retrieving Factory Default Calibration

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Pocket Colorimeter II

Switching Ranges

- Press MENU key
- Display will show SEL
- Use READ key to toggle between LR and HR
- Press MENU key to accept

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Pocket Colorimeter II

Retrieving Factory Default Calibration

- Hold MENU key until USER then CAL appears
- Press ZERO to find dFL
- Press READ to restore factory calibration

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How To Run a Proper Test For Low Range Free Chlorine

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Good laboratory Practice

- **Measuring Hints**
  - Analyze immediately after collection
  - Avoid Plastic containers
  - Dedicate 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.

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Good laboratory Practice

- **Measuring Hints**
  - 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.)
    - Thorough rinsing after each use allows for only occasional pre-treatment.
    - Air dry the sample cells and sampling containers.

Good laboratory Practice

- **Measuring Hints**
  - If sample turns yellow or shows a flash of pink then goes colorless, dilute the sample and repeat the test.
  - Multiply the result by the dilution factor.

Sample Collection, Storage and Preservation

- Collect sample by allowing water to flow for at least 3 - 5 minutes
- If collecting bulk sample, allow container to overflow with the sample several times
- Cap the sample container so there is no headspace
- If transport is absolutely necessary (which is not recommended), chill the sample to 4 degrees C and analyze as quickly as possible.

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Sampling and Sample Preservation

- The sample is usually the greatest limiting factor in obtaining a true or representative result.

The analysis is only as good as the sample

Running the Test

- Following the proper sampling techniques, fill the GLASS cell to the 10mL mark and cap it
- Dry outside of cell with a wipe
- Place cell in holder (diamond forward), cover with the instrument cap and hit ZERO
- 0.00 will be displayed, remove cell

Running the Test

- Add a 10mL DPD Free reagent to the sample, as indicated in the procedure, cap and gently invert for 20 secs

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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 $\longrightarrow$ magenta colored compound.
- Reaction time of $\leq$ 1:00 minute --- No Longer

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Running the Test

- Place cell in holder, cover with instrument cap and hit READ
- The free chlorine result will be displayed in mg/L chlorine

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Low Range Total Chlorine and High Range Tests

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Reaction Chemistry
Total Chlorine

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

  Free Chlorine + Chloramines + KI + DPD ⟶ magenta-colored compound.

- Reaction time ≥ 3:00 minutes Not longer than 6 minutes

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High Range Tests

- Put PCI or PCII into HR mode
- Use PLASTIC cells and 2 X 10mL DPD reagents
- PCI uses 10mL of sample
- PCII uses 5mL of sample
- Short pathway faces front to back

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Low Range Total and High Range Tests

- Procedure is the same for all tests
- Only changes are cells, sample volume (PCII), reagent addition (2 pillows), cell orientation
- Free – Within 1 min
- Total – Between 3 and 6 min

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How Do I Know if my Results are Correct?

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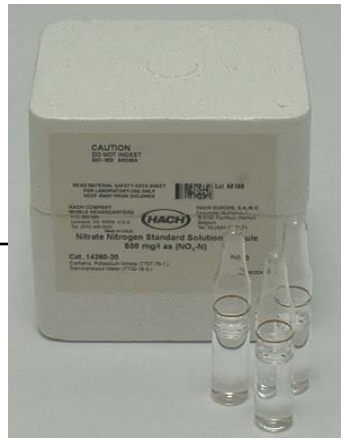
Use of Standards

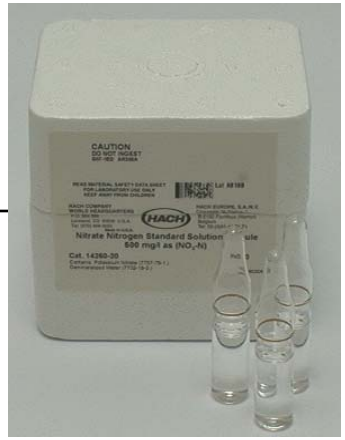
- What is a standard?
  - Primary Standard is a solution of D.I. water containing a known amount of a specific substance
  - Secondary Standards (SpecCheck)

Use of Standards



- Primary Chlorine Standard
  - Primary Standard used with PC comes as a higher concentration (typically from 25-30mg/L)
  - Standards are manufactured highly concentrated as weaker chlorine solutions are not stable for long periods
  - Primary standards can be used for calibration verification, instrument performance, operator technique, interfering substances

Use of Standards



- Primary Standard Additions
  - Smaller volumes of highly concentrated solutions
  - Identifying interferences and percent recovery
  - Is my sample compatible with the test?
  - Use to prepare a known concentration for any purpose.

Use of Standards

- Secondary SpecCheck Standards
  - Gel standards that simulate specific chlorine values (Secondary Standards)
  - Used as a calibration check only
  - Cannot be used to calibrate an instrument

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Errors and Troubleshooting

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Common Errors and Interferences

- E1, E2 and E3 Errors
  - Verify instrument cap is seated correctly and re-zero
  - Check to make sure LED lights up when READ is pressed
  - Change batteries
  - E2 on PCI often means interference filter should be replaced – no longer any available

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Common Errors and Interferences

- All other “E” Errors
  - Factory default calibration curve has been changed
  - Follow procedure to retrieve factory calibration
  - If error persists, unit requires servicing

Common Errors and Interferences

- Flashing Values
  - Flashing 0.00 – Check cap/re-zero
  - Flashing number above stated range – Check for light blockage and/or dilute then retest
  - Flashing square on PCII – instrument has not been zeroed properly

Common Errors and Interferences

- Common Interferences - Manganese
  - Add 3 drops of Potassium Iodide, mix and wait one minute
  - Add 3 drops of Sodium Arsenite mix a run test as per procedure
  - Subtract this result from original analysis to obtain correct chlorine concentration

Common Errors and Interferences

- Common Interferences - Monochloramine
  - See a gradual drift towards higher readings.
  - Try to analyze sample as soon as possible after adding reagent
  - 3.0 mg/L monochlor will increase chlorine result by 0.1mg/L after 1 min

Common Errors and Interferences

- Common Interferences – All other oxidants
  - Oxidants such as bromine, ozone and iodine will cause false positives for chlorine readings

Common Errors and Interferences

- Other Possible Interference Solutions
  - FreeChlor F Reagent Solution used to determine free chlorine in the presence of manganese, chloramines and other oxidants.
  - At moment, can only be used with Monochloramine test

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QUESTIONS????????

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