# MEASUREMENT OF CHLORINE DISINFECTION

## SCIENCE OF DISINFECTION RESIDUAL WORKSHOP
## PHILADELPHIA WATER AND PAAWWA
## NOVEMBER 24, 2015

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# CHLORINE CHEMISTRY IN DRINKING WATER SYSTEMS

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# OVERVIEW OF CHLORINE CHEMISTRY IN WATER TREATMENT

- When chlorine is added to water at a pH greater than 4, hypochlorous acid (HOCl) is formed as illustrated by the following empirical equation:

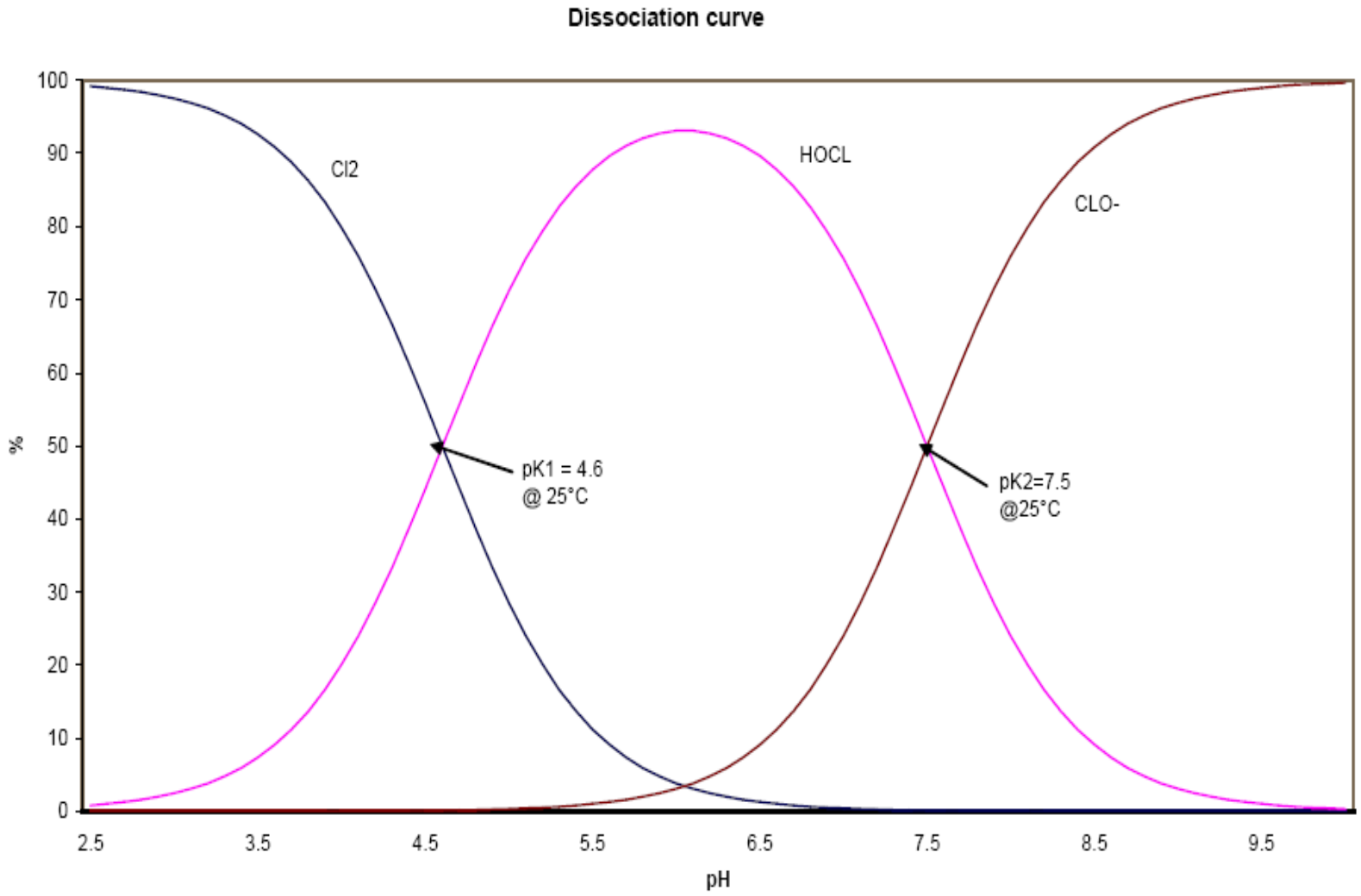
$$Cl_2 + H_2O \Longleftrightarrow HOCl + H^+ + Cl^-$$

- As the pH increases above 4, the hypochlorous acid will dissociate to form the hypochlorite ion ($OCl^-$):

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

- $Cl_2$, HOCl, and $OCl^-$ is known as “Free Available Chlorine” (FC)

# DISSOCIATION OF CHLORINE AS A FUNCTION OF PH



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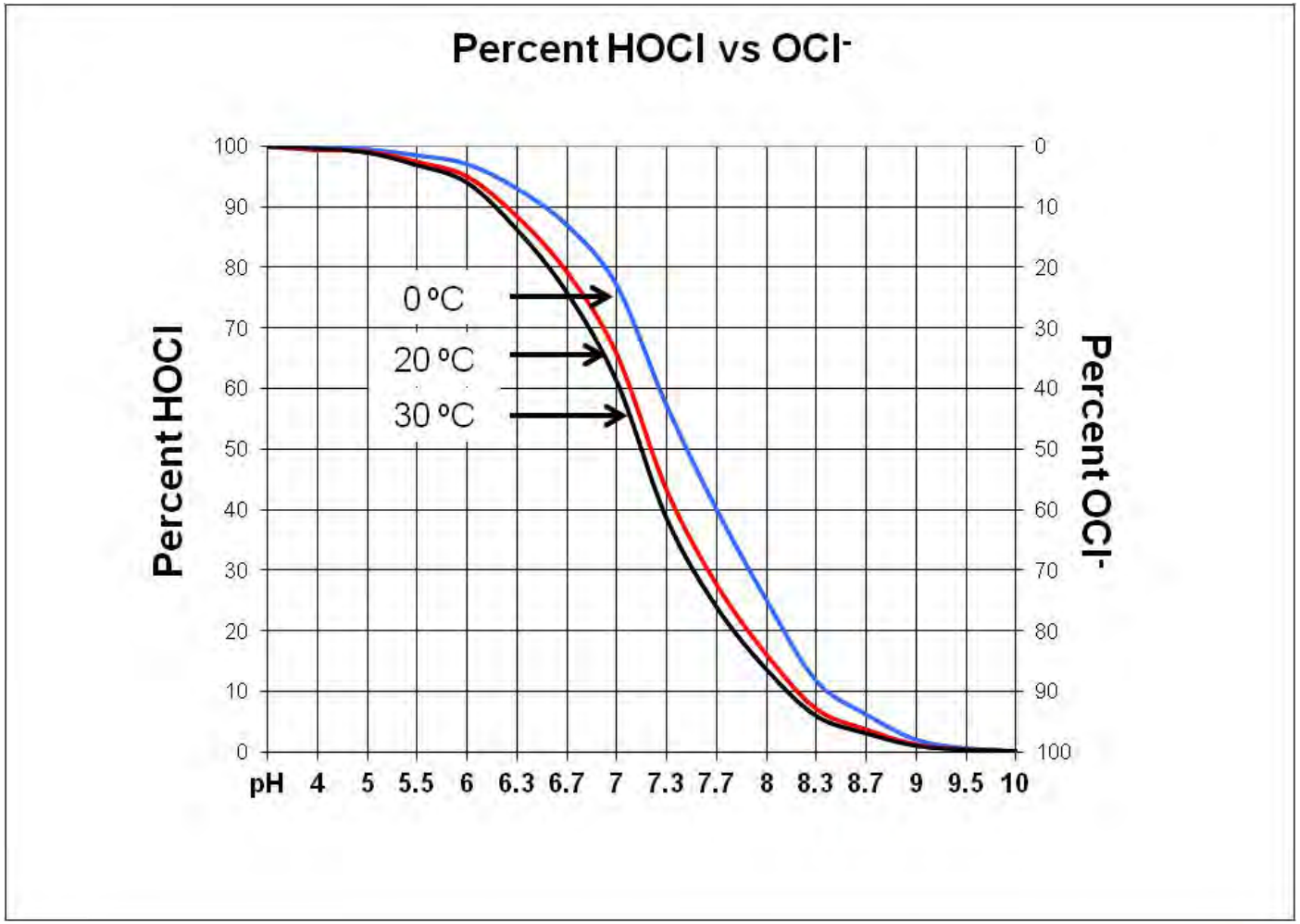
# PERCENT OF HOCL AND OCL$^-$ AS A FUNCTION OF PH AND TEMPERATURE



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# DISINFECTION VALUE OF FREE CHLORINE SPECIES

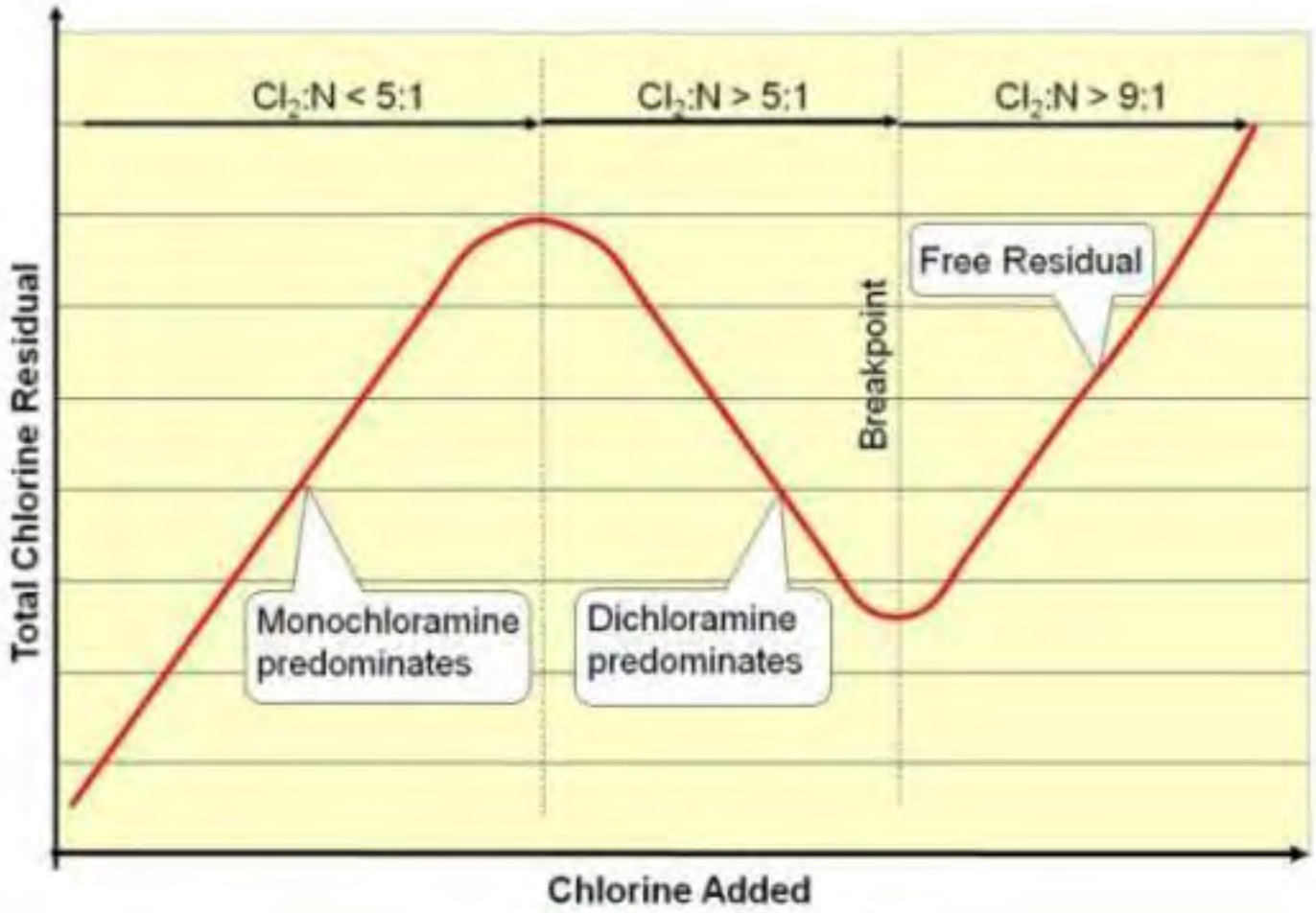
- Hypochlorous acid (HOCl)
  - 1.4 electron volts (ev)

- Hypochlorite ion ($OCl^-$)
  - 0.9 electron volts (ev)

# REACTION OF CHLORINE WITH NITROGEN COMPOUNDS

- $HOCl + NH_3 \Longleftrightarrow NH_2Cl + H_2O$ (Monochloramine)
- $HOCl + NH_2Cl \Longleftrightarrow NHCl_2 + H_2O$ (Dichloramine)
- $HOCl + NHCl_2 \Longleftrightarrow NCl_3 + H_2O$ (Trichloramine)
- $HOCl + NCl_3 \Longleftrightarrow HOCl + *$ (Destruction of $NCl_3$)
- Mono, di, tri, and organic chloramines are known as Total Chlorine (TC)

# DISTRIBUTION AS A FUNCTION OF MOLAR RATIOS



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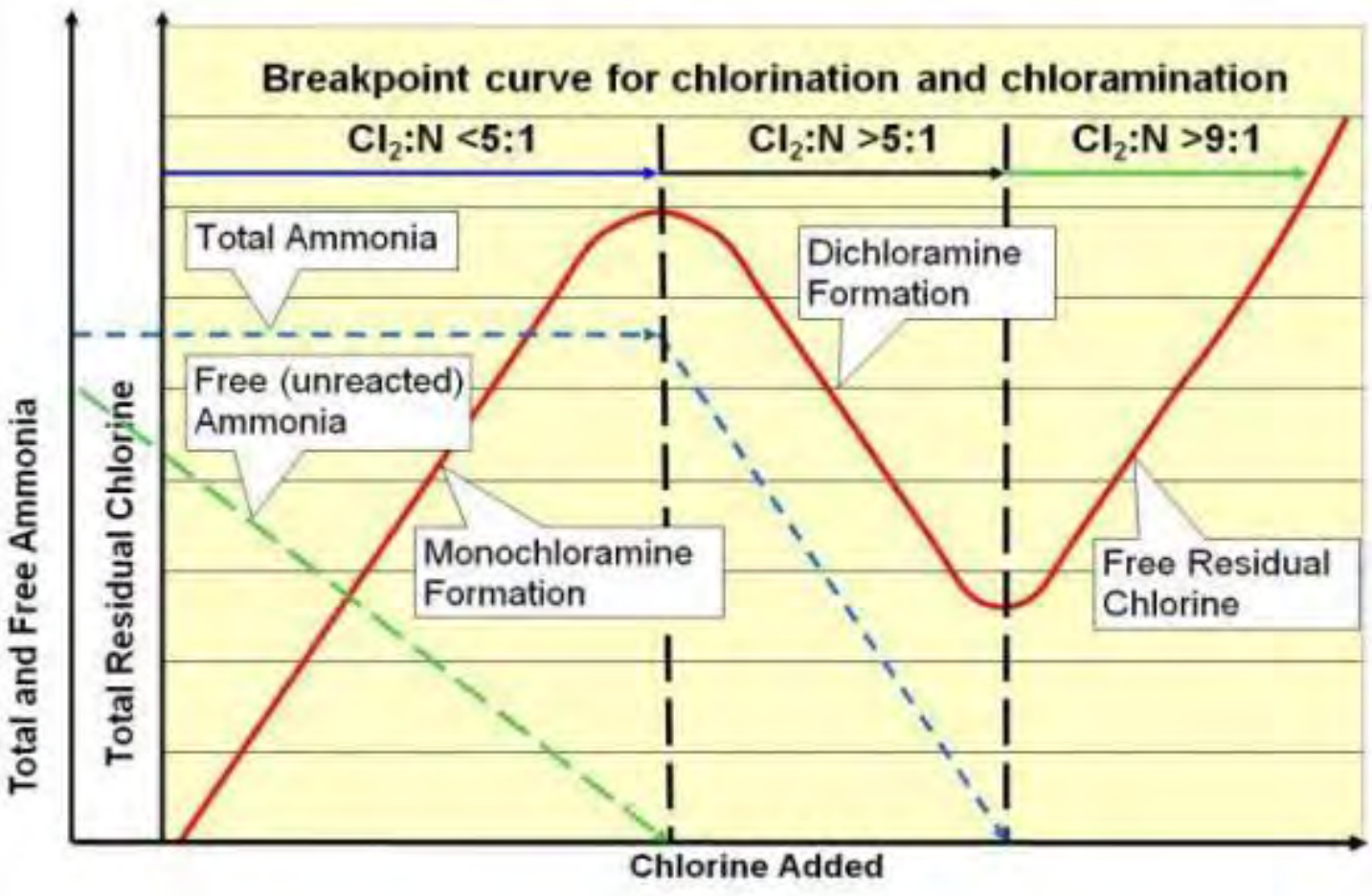
# BREAK TRHOUGH CURVE WITH AMMONIA



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# DISINFECTION VALUE OF CHLORAMINATED SPECIES

- Monochloramine ($NH_2Cl$)
  - 0.81 electron volts (ev)
- Dichloramine($NHCl_2$)
  - < Monochloramine
- Trichloramine ($NCl_3$)
  - < Dichloramine
- Organic chloramines
  - None

# MEASUREMENT OF CHLORINE IN TREATED DRINKING WATER

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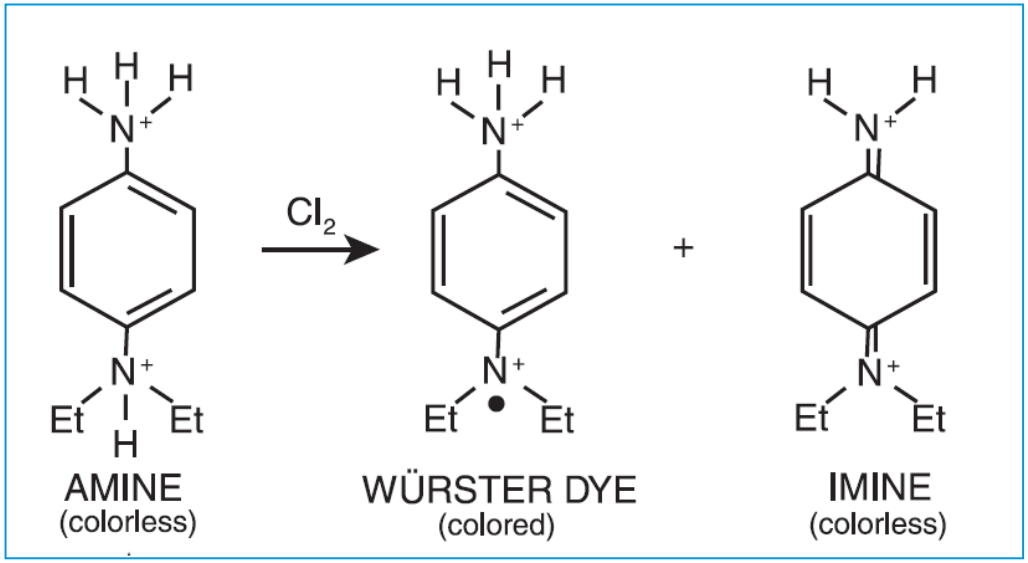
# TYPICAL EPA APPROVED CHLORINE CHEMISTRY MEASUREMENT TECHNOLOGIES

- DPD Colorimetry
  - Chlorine oxidizes DPD to form a pink color
  - SM 4500-CL G

- Amperometric Titration
  - Amperometric titration measures the current change as a function of titrant added
  - SM 4500-CL D & E

- Amperometric
  - Reduction of chlorine using an applied voltage followed by measurement of consumed electrons
  - EPA Method 334.0

- **Free and Total Chlorine Chemistry**
  - N, N-diethyl-p-phenylenediamine (DPD)
  - Buffer
  - Potassium Iodide
  - Ascorbic Acid



# CHLORINE METHOD SELECTION (AMPEROMETRIC)

| Method | Advantages | Disadvantages |
|---|---|---|
| • EPA Method 330.1<br>– Online F&TC | • Reagentless | • Fe and Mn interferences<br>• Frequent Calibration required with gold standard<br>• Doesn't work well in unstable water (pH and temperature |

# CHLORINE METHOD SELECTION (DPD)

| Method | Advantages | Disadvantages |
|---|---|---|
| • SM4500-CL G<br>– Hach Method 8021 (FC) PP<br>– Hach Method 8167 (TC) PP | • Gold Standard | • Fe and Mn interference<br>• Waste Stream |
| • SM4500-CL G<br>– DPD Pump F&TC | • Gold Standard | • Fe and Mn interference<br>• Waste stream |
| • Hach Method 10260<br>– SL1000 F&TC | • Gold Standard<br>• Portability | • Fe and Mn Interference |

# CHLORINE METHOD SELECTION (INDOPHENOL)

| Method | Advantages | Disadvantages |
|---|---|---|
| • Hach Method 10241 (Indophenol Chlorine) | • Free from Fe and Mn interferences<br>• Equivalent to gold standard in performance | • Only for FC |

# ONLINE DPD FREE AND TOTAL CHLORINE

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# ONLINE AMPEROMETRIC




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# ONLINE AMMONIA AND MONOCHLORAMINE




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# AMPEROMETRIC TITRATION



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# POCKET COLORIMETER POWDER PILLOWS





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# SL1000 PORTABLE PARALLEL ANALYSIS




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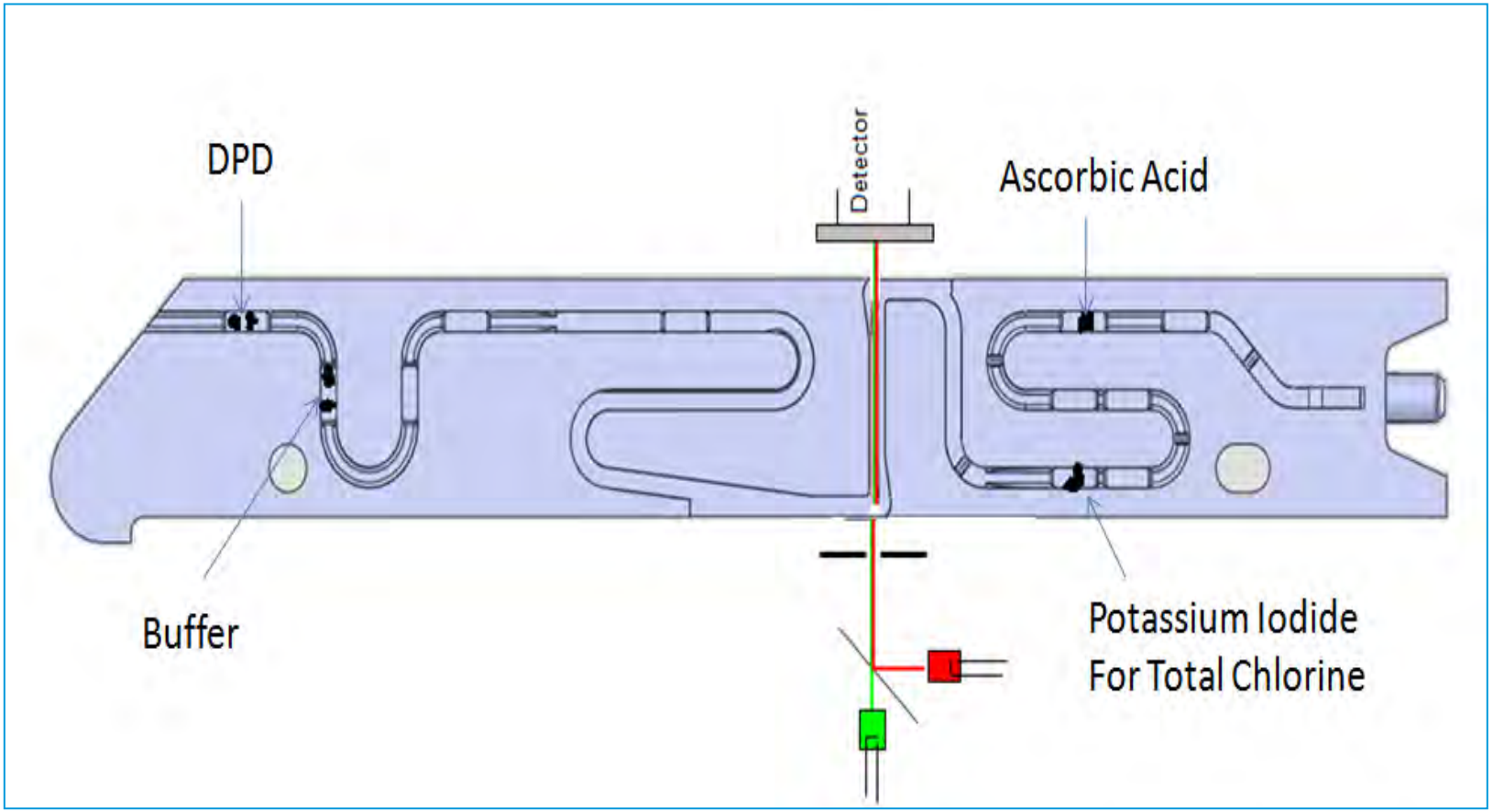
# PARALLEL PORTABLE ANALYSIS



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# THANK YOU