

Basic Chlorine Chemistry and Chlorine Monitoring

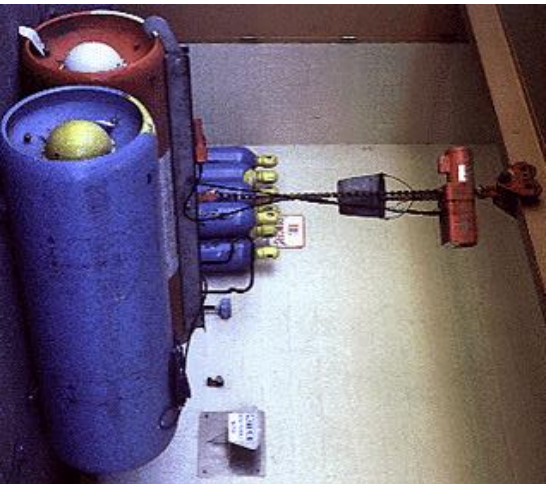
Ted Simmons

RSM for Southern Ohio
Hach Company



Be Right™

Sources of Chlorine



Gaseous
Chlorine



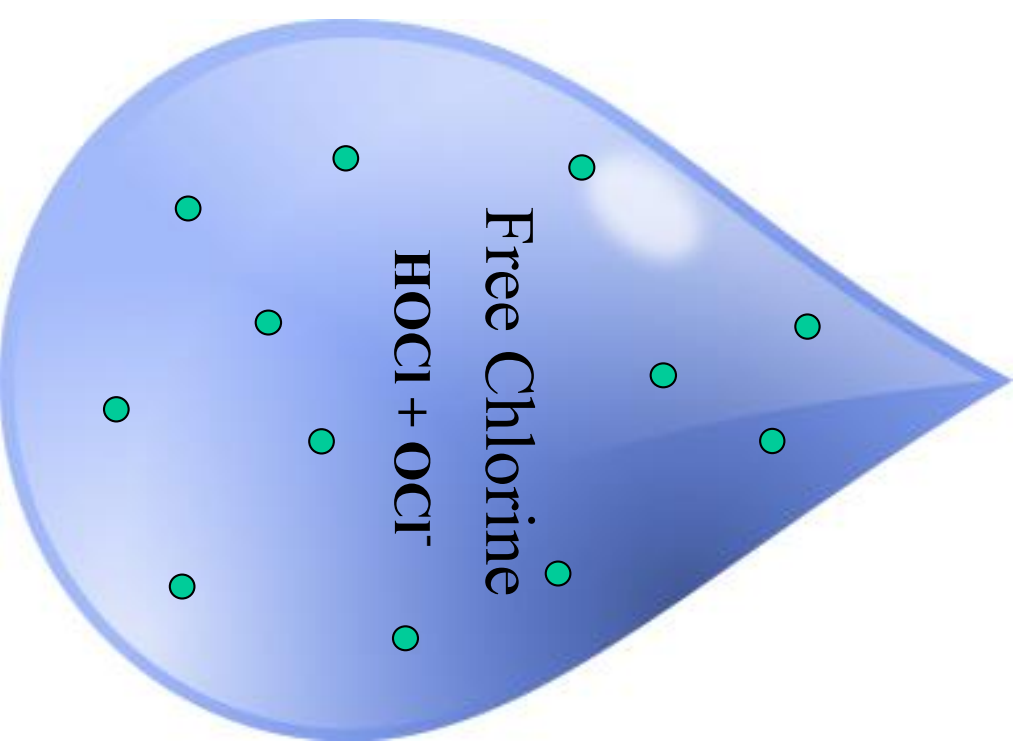
Liquid
Sodium
Hypochlorite



Tablet
Calcium
Hypochlorite

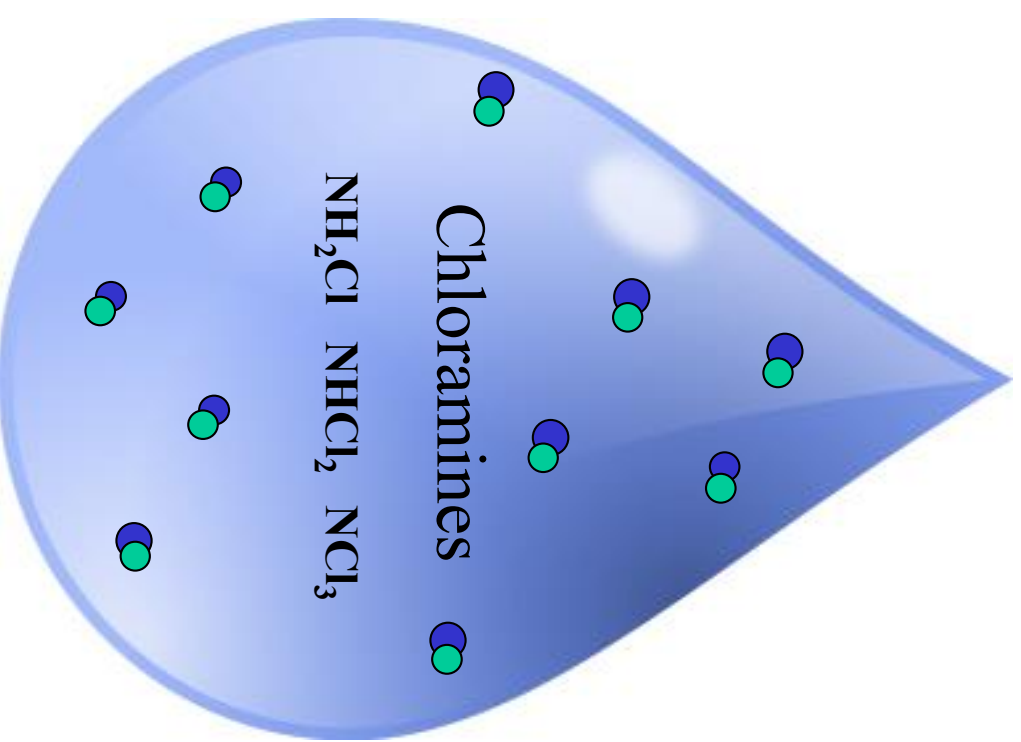
Free Chlorine

- Chlorine existing in water as Hypochlorous acid (HOCl) or the hypochlorite ion (OCl⁻)
- Chlorine that has not combined with ammonia or nitrogen compounds



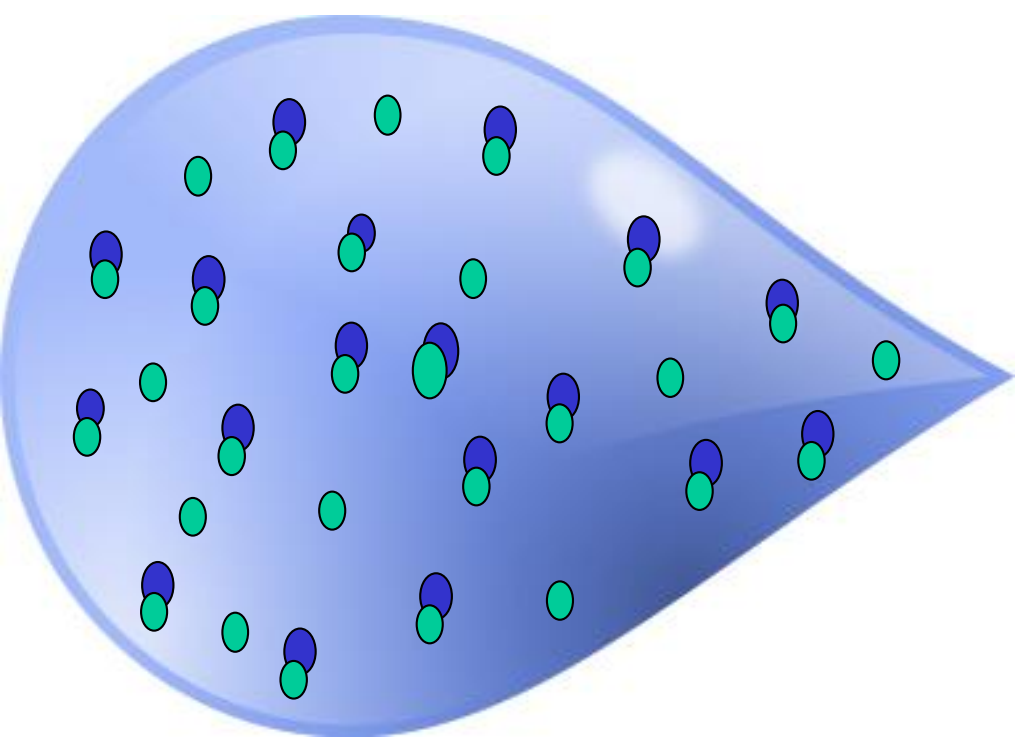
Combined Chlorine

- Chlorine (HOCl and OCl-) reacts with ammonia to form chloramines
- The predominate species are
 - monochloramine
 - dichloramine.
- Less dominant species
 - trichloramine or nitrogen trichloride



Total Chlorine

- Combination of Free and Combined Chlorine



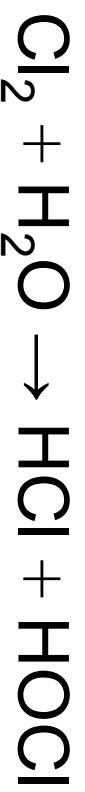
Free Chlorine vs. Chloramines

	Free Chlorine	Chloramines
Oxidation Strength	Strong	Weak
Volatility	More	Less
Required Dosage	Low	High
DBPs	Yes	No

Free Chlorine

Quick Chemistry Lesson

- When gaseous chlorine is added to water the following reaction occurs



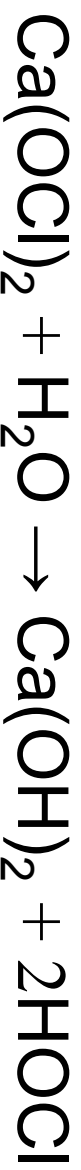
pH ↓

- When Sodium hypochlorite is added to water the following reaction occurs



pH ↓

- When Calcium hypochlorite is added to water the following reaction occurs



pH ↓

Free Chlorine

Dissociation in Water

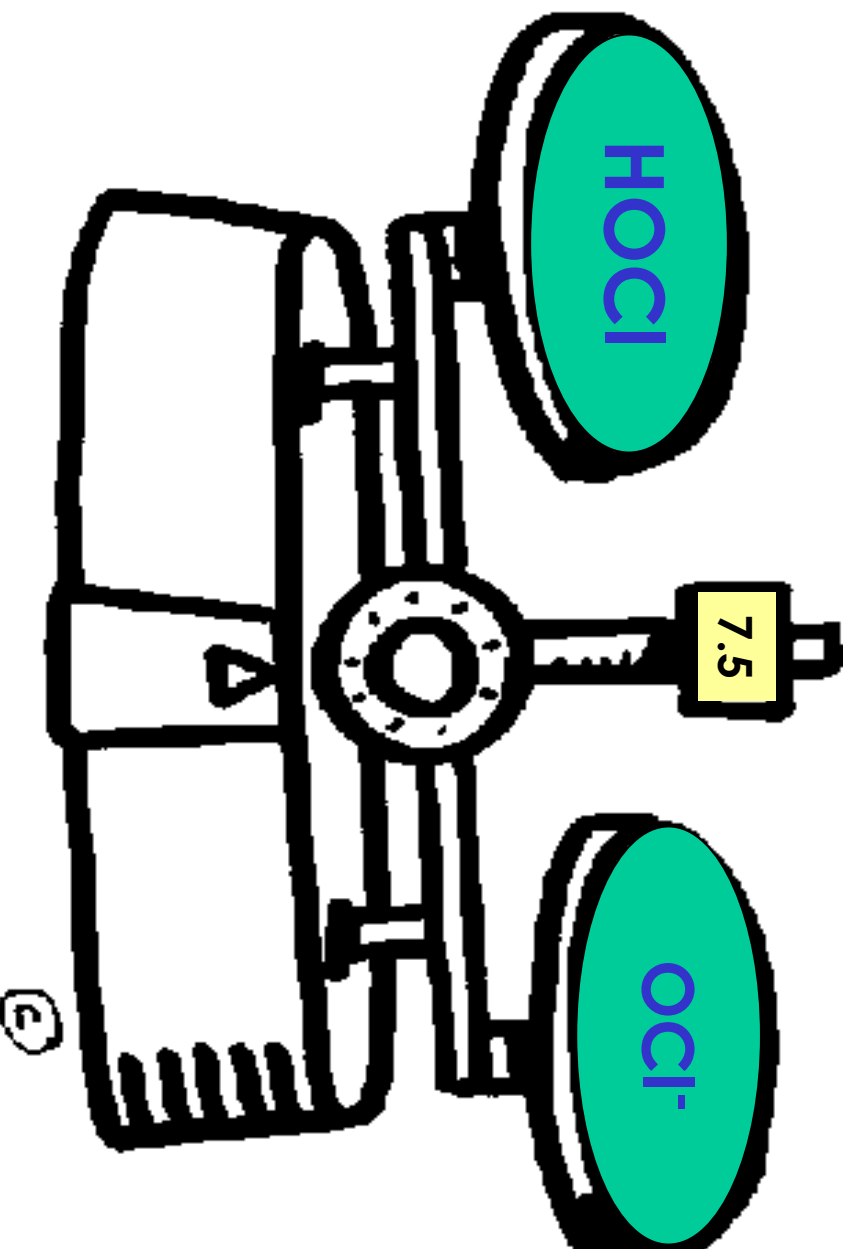
- Hypochlorous acid further dissociates depending on pH and temperature



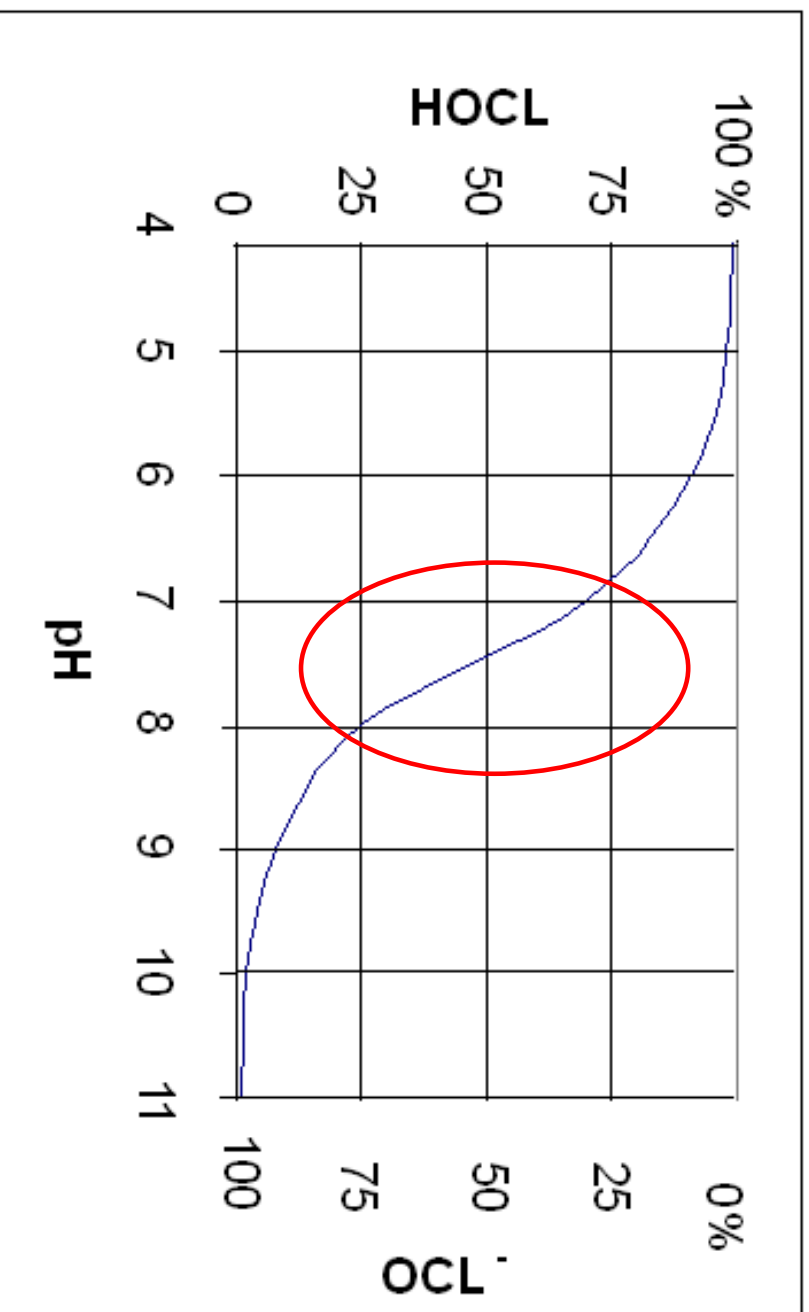
- Hypochlorous acid (HOCl) is up to 100 times more efficient as a disinfectant than the hypochlorite ion (ClO^-)

HOCl is the most effective disinfectant form of chlorine

- <math>pH < 7.5</math> - free chlorine is predominately in the HOCl form.
- >math>pH > 7.5</math> - free chlorine is primarily in the OCl⁻ form.



Dissociation Curve



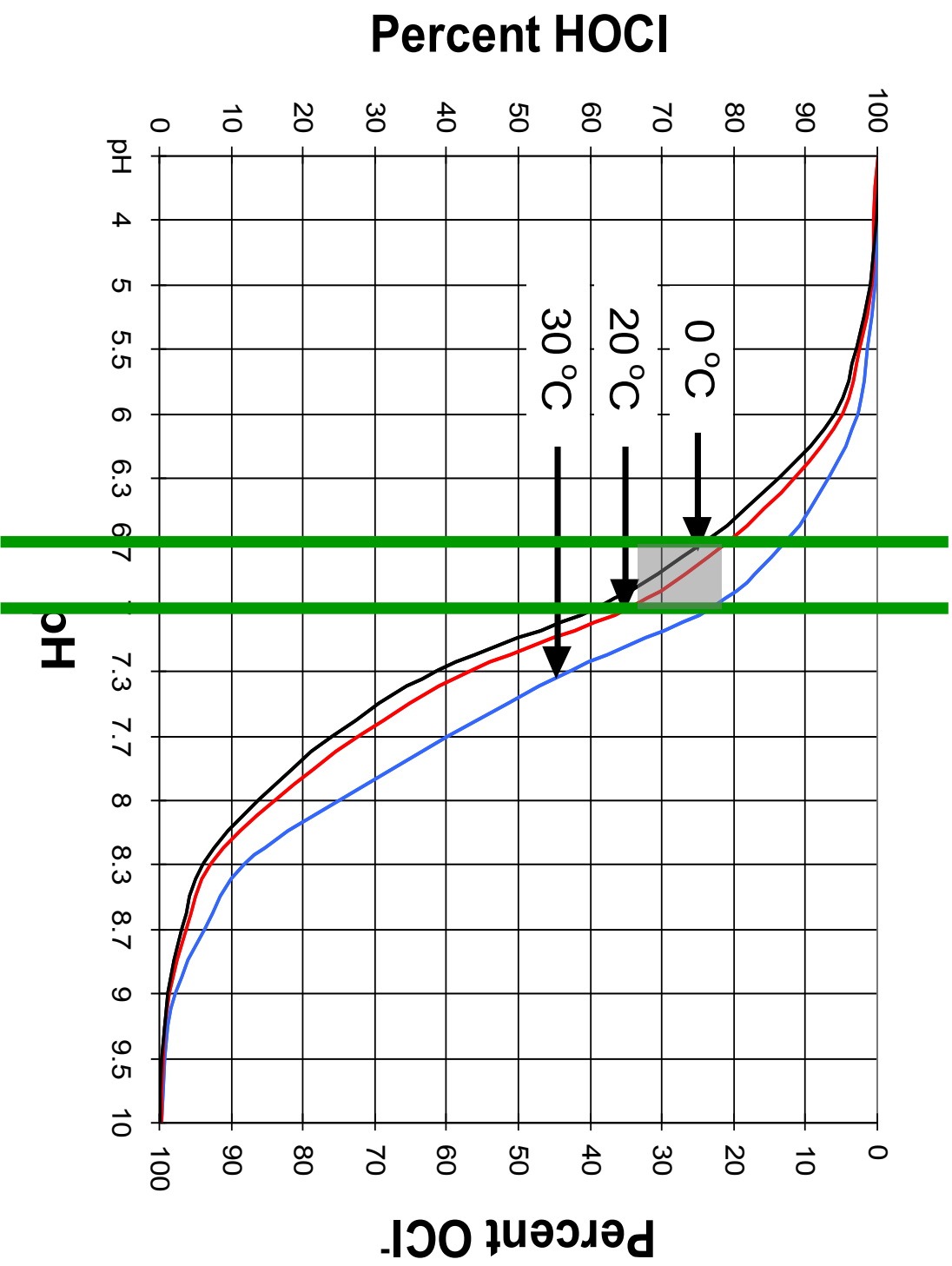
How Does Temperature and

pH changes affect chlorine measurements?

- Amperometric analyzers measure HOCL
- HOCL concentration is dependent on temperature and pH
- The following slides show the affects of temperature and pH changes on the HOCL concentration which in turn affects analyzer drift.

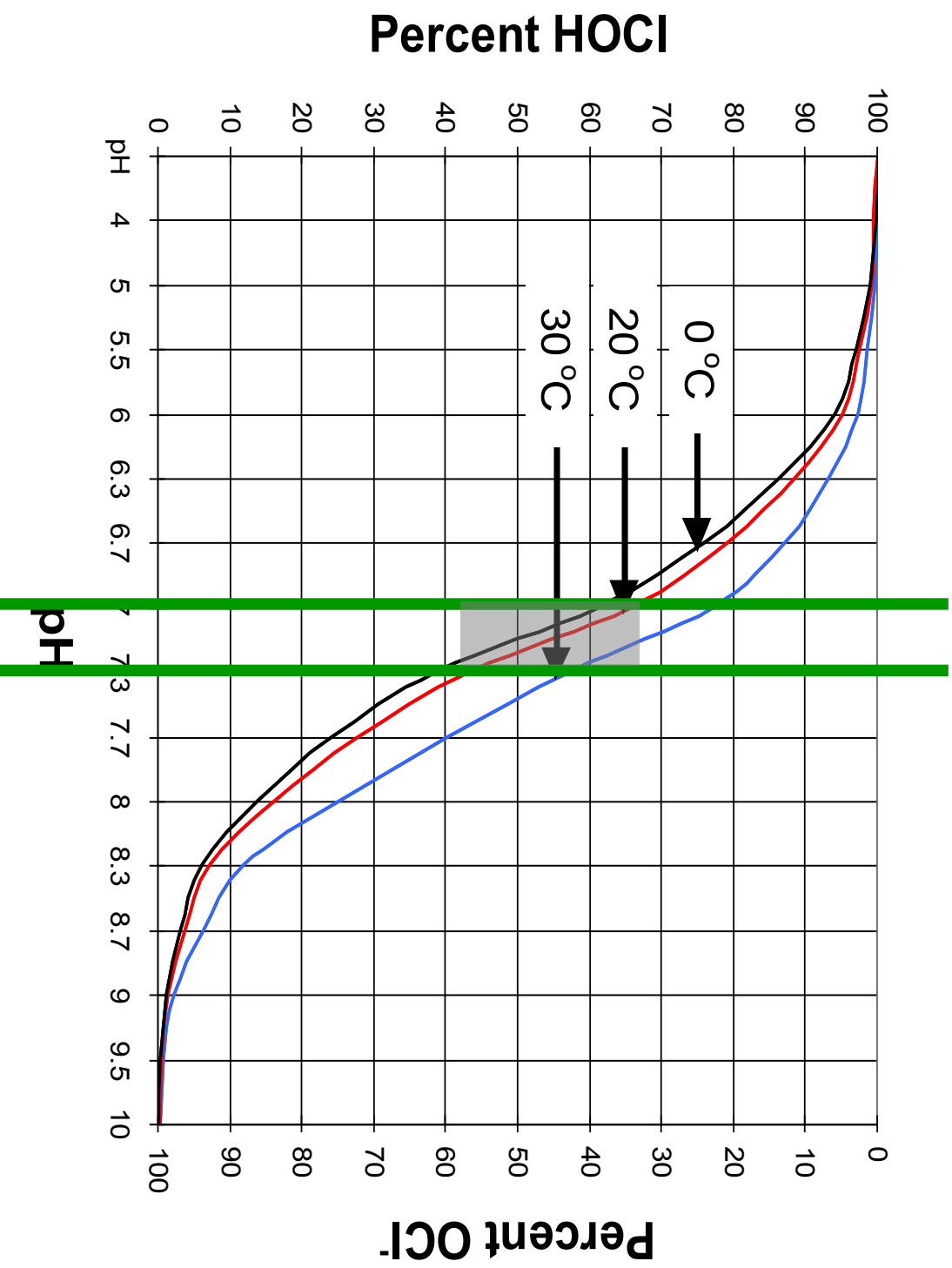
HOCl vs. OCl⁻

pH from 6.7 to 7.0 = 10% change in HOCl concentration



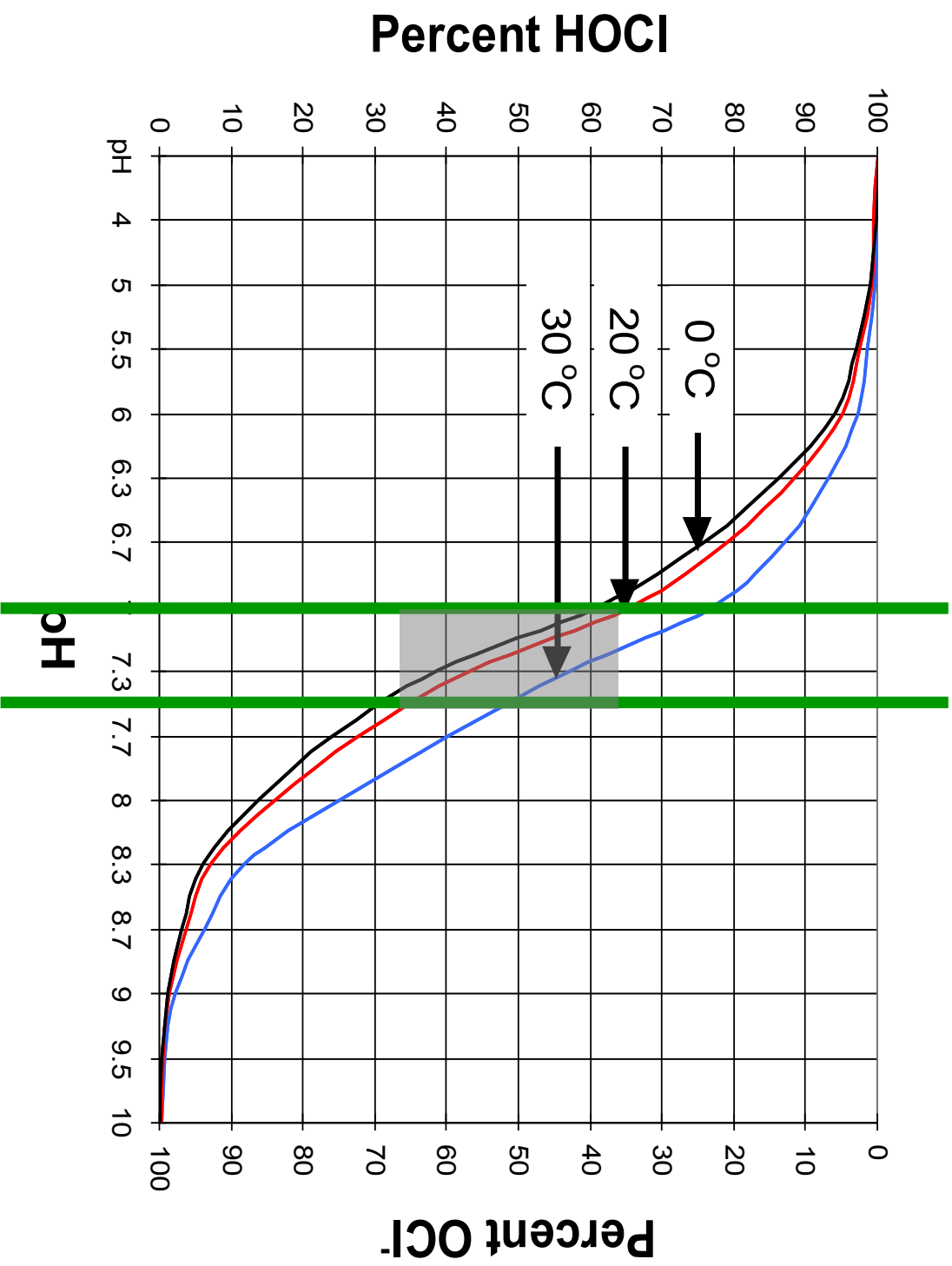
HOCl vs. OCl⁻

pH from 7.0 to 7.3 = 25% change in HOCl concentration



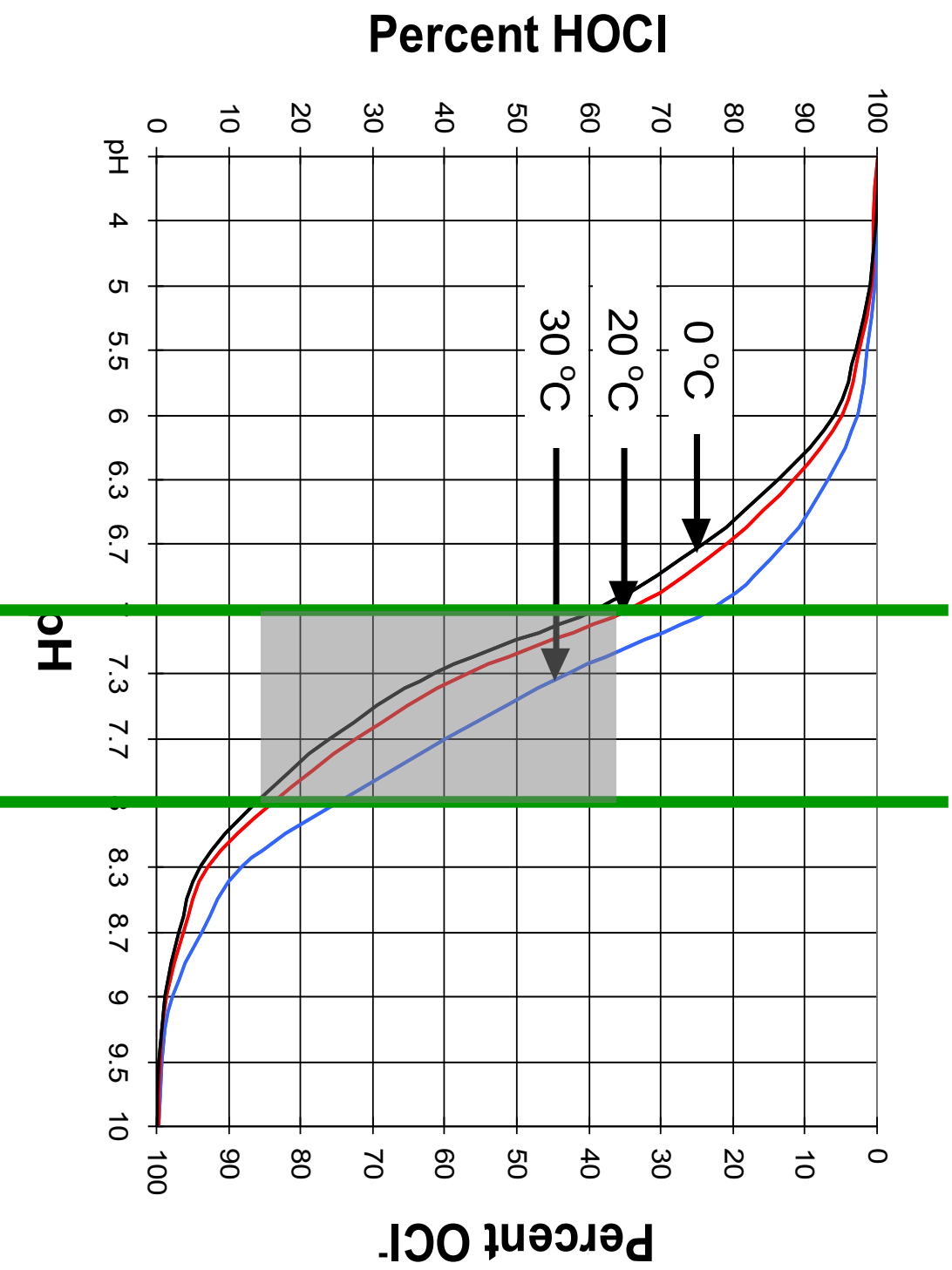
HOCl vs. OCl⁻

pH from 7.0 to 7.5 = 30% change in HOCl concentration



HOCl vs. OCl⁻

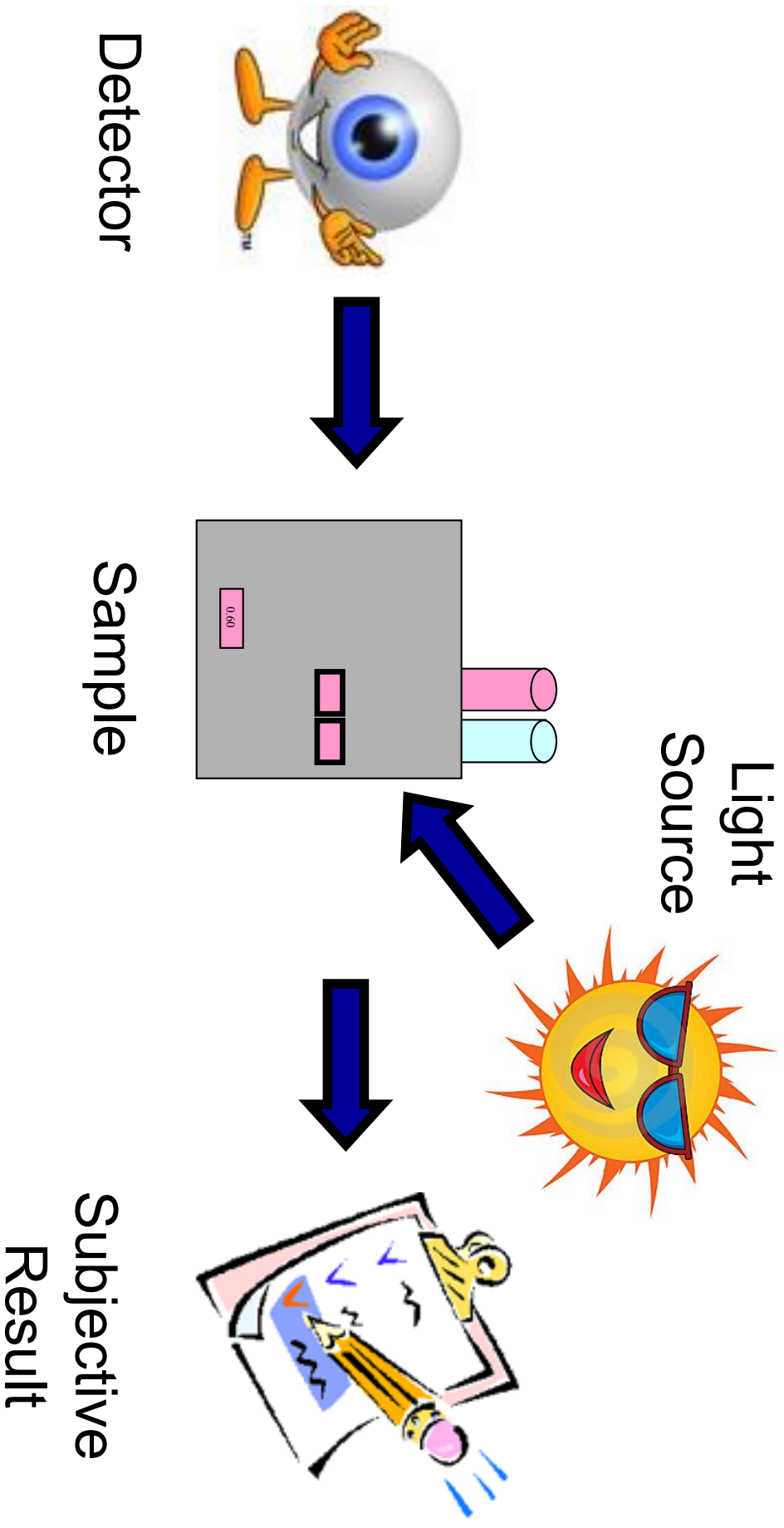
pH from 7.0 to 8.0 = 50% change in HOCl concentration



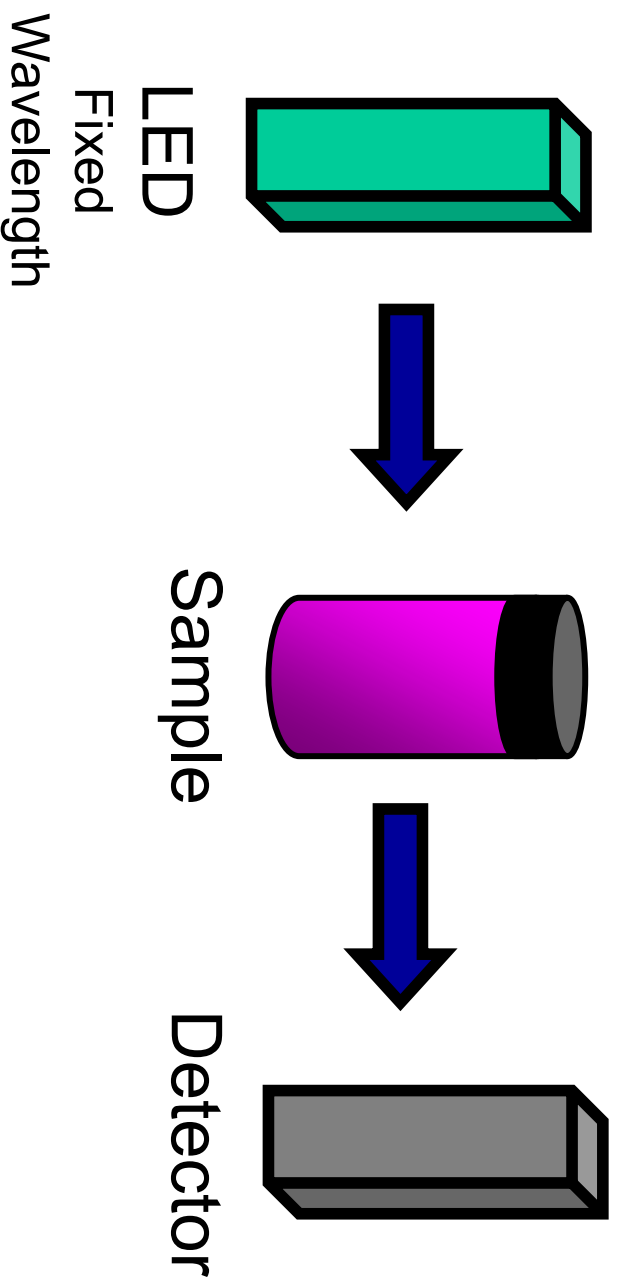
Grab Sample Analysis



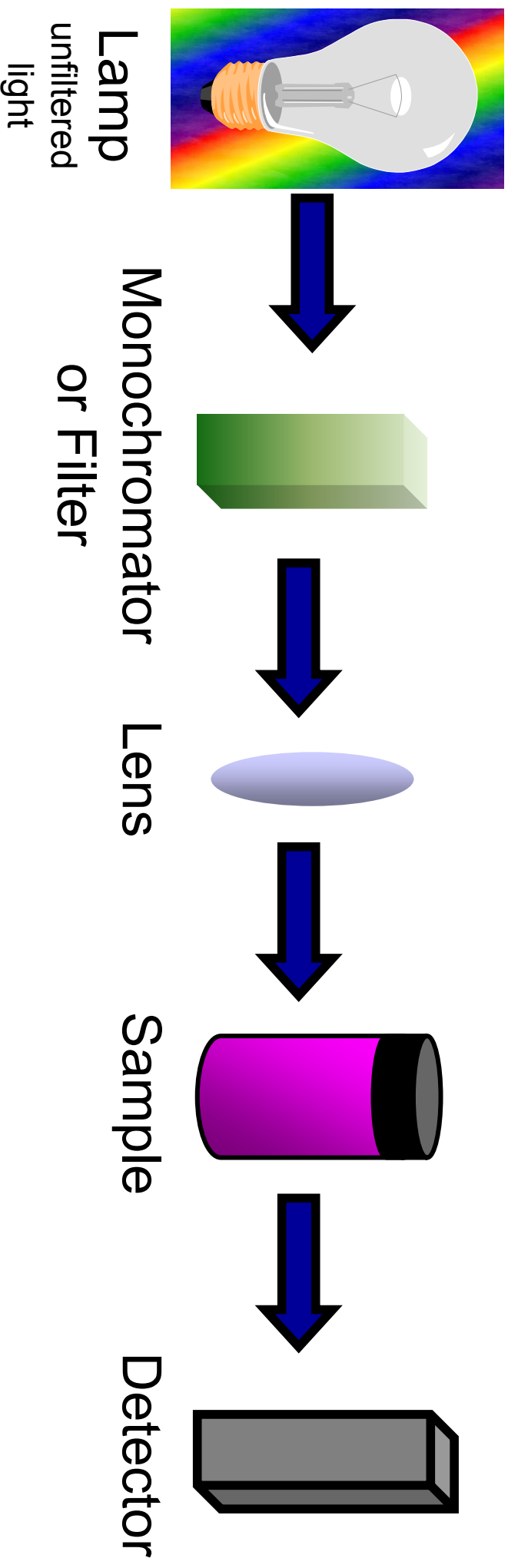
Basic Color Comparator



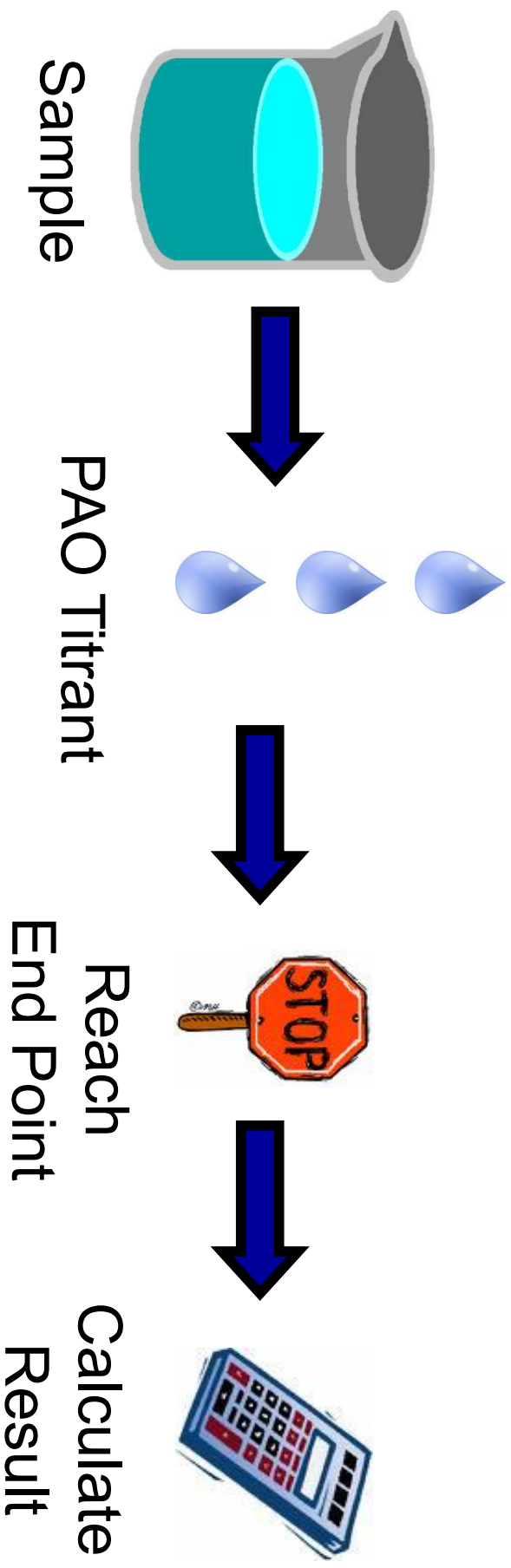
Basic Colorimeter



Basic Spectrophotometer



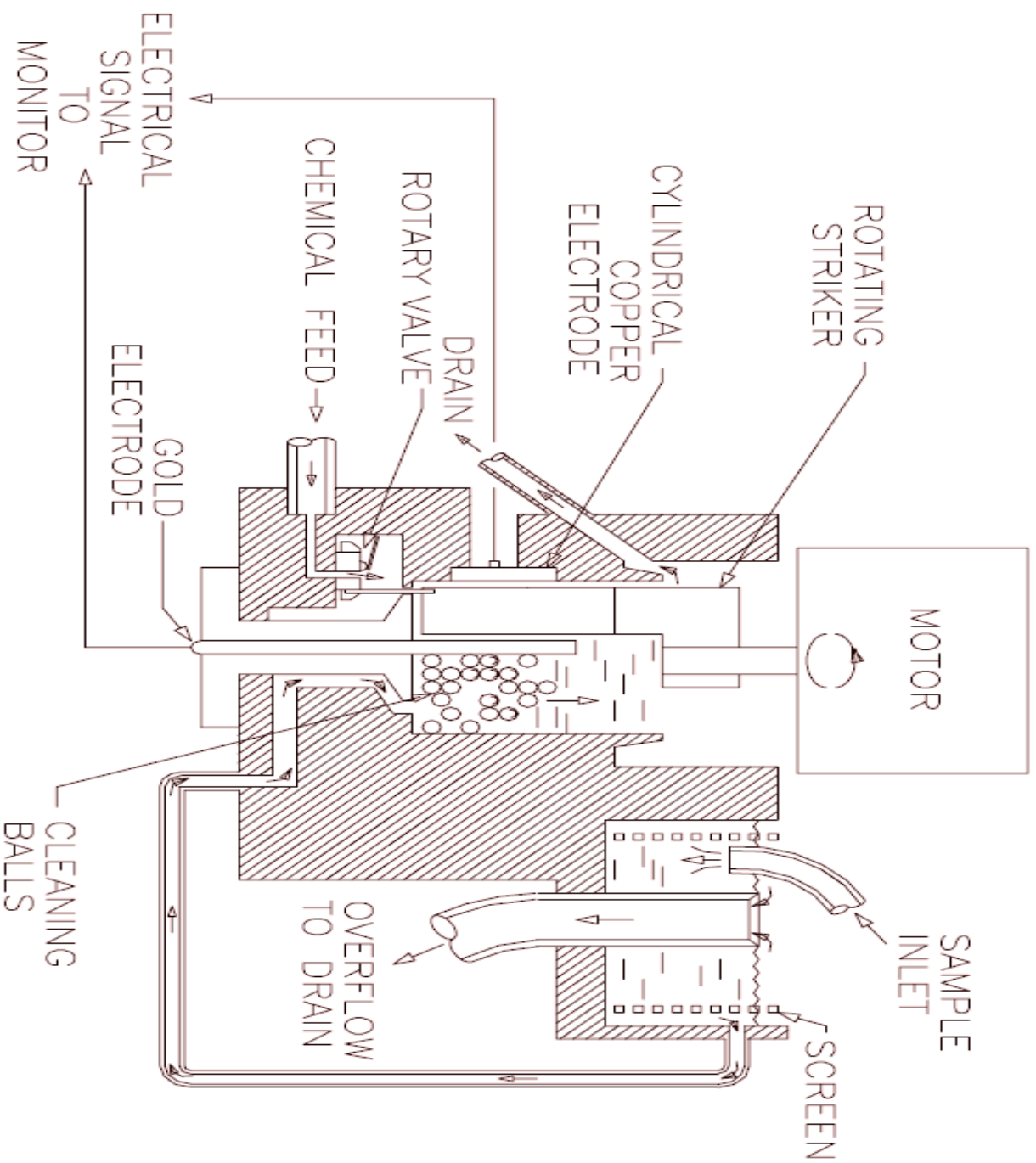
Basic Titration



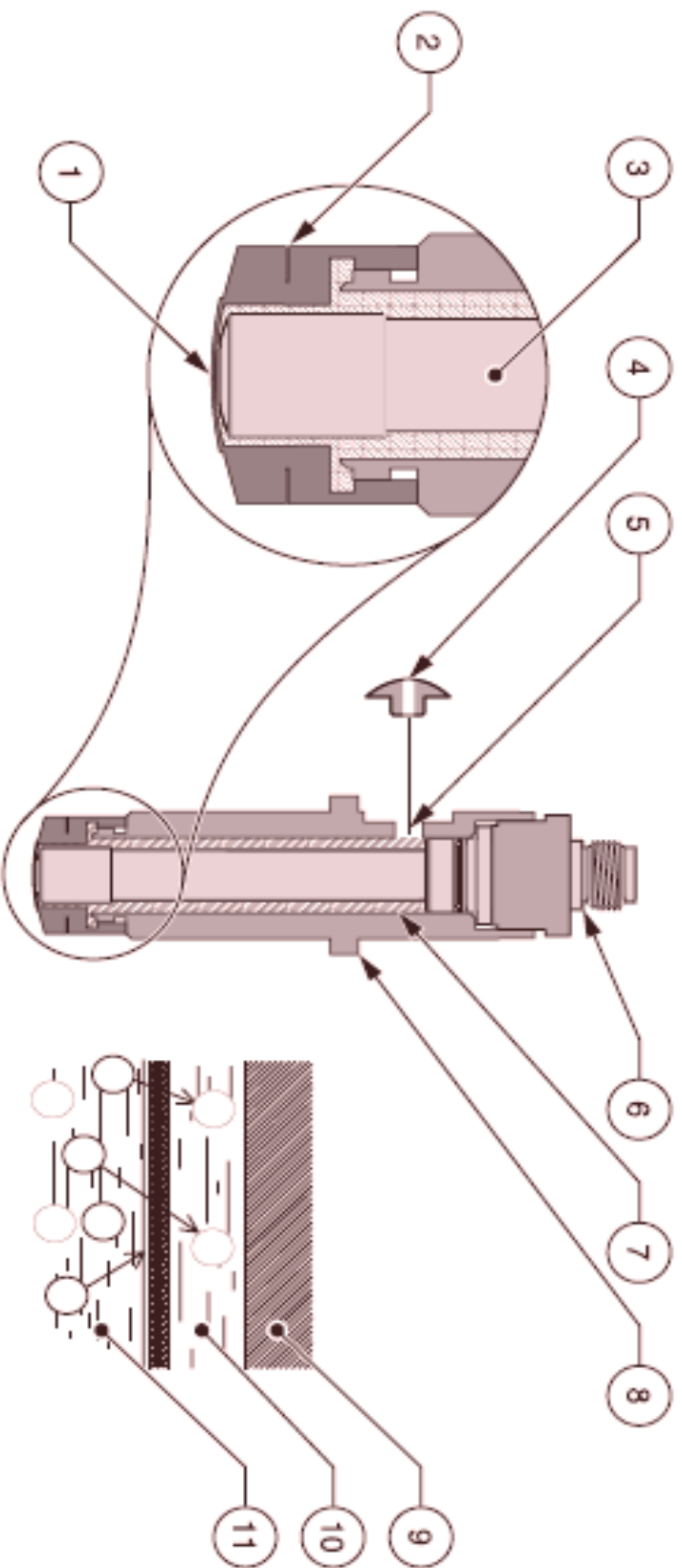
Online Chlorine Monitoring



Amperometric Open Cell Analyzer

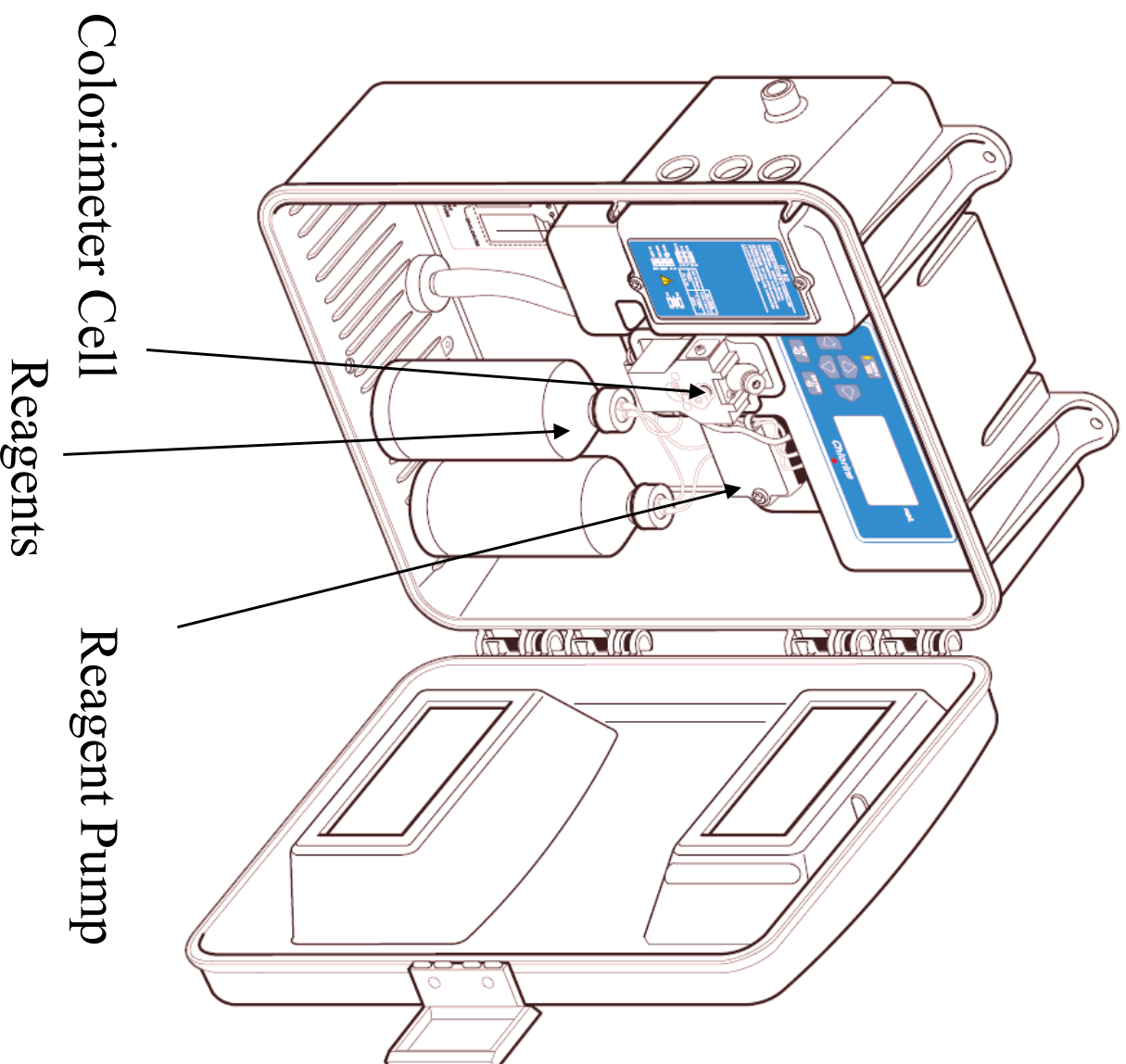


Amperometric Probe Analyzer



1	Membrane	7	Electrolyte
2	Membrane Holder	8	Probe Body
3	Anode	9	Cathode
4	Electrolyte Filling Plug ¹	10	Membrane/Interface Sample
5	Electrolyte Filling Hole	11	Sample
6	Assembled Electrode		

DPD Colorimetric Method



Comparing Methods

	DPD	Amperometric Open Cell	Amperometric Probe
Calibration	No	Yes	Yes
Affected by pH & Temp	No	Yes	Yes
pH Comp	Not required	Requires reagent	Requires pH probe
Temp Comp	Not required	Yes	Yes
Reagents	Yes	Depends on pH	Depends on pH
Moving parts	Yes	Yes	No (yes if reagent is uses)
Maintenance	Reagent change (5 min/month) Tubing Change (15 min 1-2x per year)	Calibration (15 min 2x per month) Reagent Change (5 min 2-4x per month)	Calibration (15 min 2x per month) Membrane Change (15 min 2-4x per year)

Amperometric Analyzers Application Considerations



Air



Iron and/or Manganese

What have we learned?



Total chlorine is more volatile than free chlorine, but is a stronger oxidizer

True or False

Total chlorine is more volatile than free chlorine, but is a stronger oxidizer

False

In drinking water, total chlorine is formed when _____ is added to the water prior to entering the distribution system

In drinking water, total chlorine is formed when _____ is added to the water prior to entering the distribution system

ammonia

Chlorine is added to water in the form of _____, _____ and _____.

Chlorine is added to water in the
form of _____, _____ and _____.

gas, liquid and solid

A basic colorimeter typically is
capable of producing how many
wavelengths

A basic colorimeter typically is
capable of producing how many
wavelengths

one

Amperometric chlorine probes
measure HOCl, OCl⁻ or both

Amperometric chlorine probes
measure HOCl, OCl⁻ or both

HOCl

DPD chlorine analyzers measure
 HOCl , OCl^- or both

DPD chlorine analyzers measure

HOCl , OCl^- or both

both

Amperometric probe chlorine analyzers are more accurate when the pH of the sample is below _____ and is _____

Amperometric probe chlorine analyzers are more accurate when the pH of the sample is below _____ and is _____

7.5 and is stable

Thank You

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