Chlorine, Chlorination, Chlorine Measurement

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Hach Company

Disinfection

- To kill or inactivate organisms capable of causing disease
- Typically viewed as use of a chemical such as chlorine, chlorine dioxide, iodine, chloramines, ozone

Practical Disinfection

- As a practical matter, the entire water process should be viewed as part of the disinfection process.
- Chemical disinfectants complement and are complemented by the other processes

Disinfection Considerations

- Effectiveness of disinfection is influenced by:
  - pH
  - Temperature
  - Contact time
  - Type and population of organism
  - Type and concentration of disinfectant
  - Chemical and physical character of the water

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Chlorine

- A chemical element - identified in 1774 by Scheele. Atomic No.17. Atomic mass 35.5
- Chlorine from the Greek *Chloros*, meaning greenish yellow
- First used to deodorize sewers in London in the 1830's (germ theory of disease was not expressed until almost 50 years later)
- Classified by USDOT as non-flammable, compressed gas

Uses of Chlorine

- Water
  - Disinfection
  - Enhanced coagulation
  - Taste and odor control
- Industrial Water
  - Control slime
  - Control/destroy phenols and cyanide
- Wastewater
  - Disinfection
  - Odor control
  - Reduce BOD
  - Control filter flies
  - Control ponding on trickling filters

Chemical Properties of Chlorine

- Highly reactive, never found free (Cl) in nature. Always found combined with other elements or itself (Cl_2)
- Non-flammable, non-explosive
- Supports combustion of many substances
- Usually forms univalent compounds, NaCl, but may exist as -1, +1, +3, +5 or +7
- Slightly soluble in water, reacts to form hydrochloric and hypochlorous acids

Chemical Properties (cont.)

- Reaction with metals is dependent upon temperature and presence of moisture. Dry, clean metals (Cu, Pb, Ni, Pt, Ag, steel) below 121 ^{o}C (250 ^{o}F) are resistant to chlorine
- Violent (explosive) reaction with organic compounds - diesel fuel, vegetable matter
- Reacts with many inorganic elements and compounds - KCl, $CaCl_2$

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Physical Properties of Chlorine

- Boiling Point - -34 ^{o}C (-29.29 ^{o}F)
- Melting Point - -100 ^{o}C (-150 ^{o}F)
- One volume of liquid will become 457.6 volumes of gas at STP (high expansion rate)
- Cl_2 gas is 2.48 times the density of air
- Liquid Cl_2 (compressed gas) is 1.468 times the density of water (at 4 ^{o}C/39 ^{o}F)

Chlorine Terminology

- Chlorine - A chemical element
- Liquid chlorine - liquefied compressed gas
- Dry chlorine - chlorine gas or liquid containing < 150 mg/l of water
- Moist (wet) chlorine - chlorine gas or liquid containing > 150 mg/l of water
- Chlorine solution - solution of chlorine and water ($HOCl$, OCl^-)
- Liquid bleach - solution of sodium hypochlorite

Reaction with Water

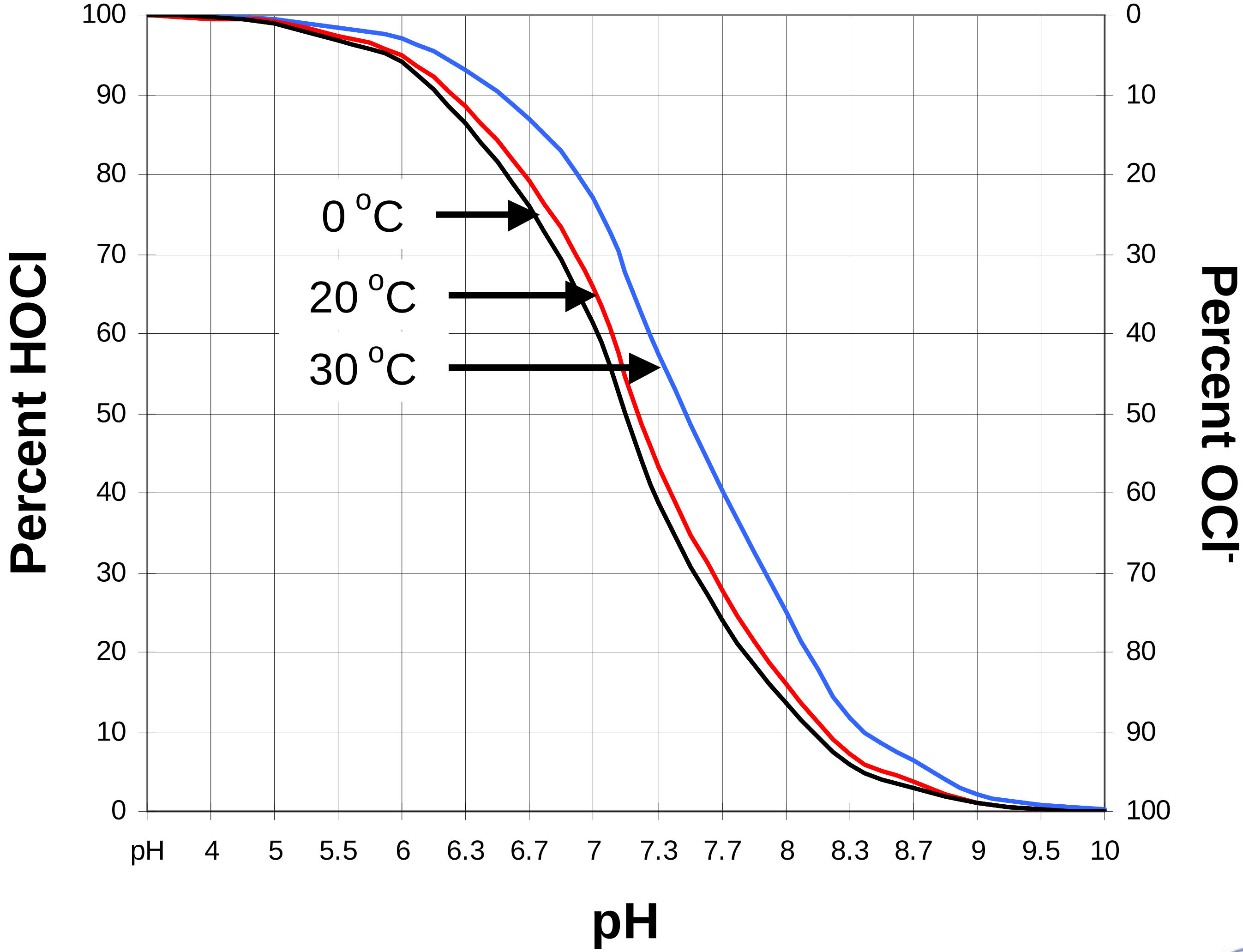
- Forms hydrochloric (HCl) and hypochlorous (HOCl) acids:

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

- Reaction is reversible. Above pH 4, reaction is to the right
- HOCl dissociates to the hydrogen ion and hypochlorite ion (OCl^-) varying with temperature and pH

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

HOCl vs. OCl^-



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Free Available Chlorine

- Chlorine existing in water as hypochlorous acid ($HOCl$) or the hypochlorite ion (OCl^-) is defined as free available chlorine

Hypochlorite Salts

- Salts used for chlorination include
  - Lithium hypochlorite $LiOCl$

    $$LiOCl + H_20 \longrightarrow Li^+ + HOCl + OH^-$$

  - Sodium hypochlorite $NaOCl$

    $$NaOCl + H_20 \longrightarrow Na^+ + HOCl + OH^-$$

  - Calcium hypochlorite $Ca(OCl)_2$

    $$Ca(OCl)_2 + 2H_20 \longrightarrow Ca^{2+} + 2HOCl + 2OH^-$$

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Combined Chlorine

- Chlorine (HOCl and OCl^-) reacts with ammonia to form chloramines, commonly referred to as 'combined chlorine'
- The predominate species are monochloramine and dichloramine. A small fraction is trichloramine or nitrogen trichloride

Chloramine Formation

- Monochloramine - NH_2Cl

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

- Dichloramine - $NHCl_2$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$$

- Tricholoramine (Nitrogen Trichloride) - NCl_3

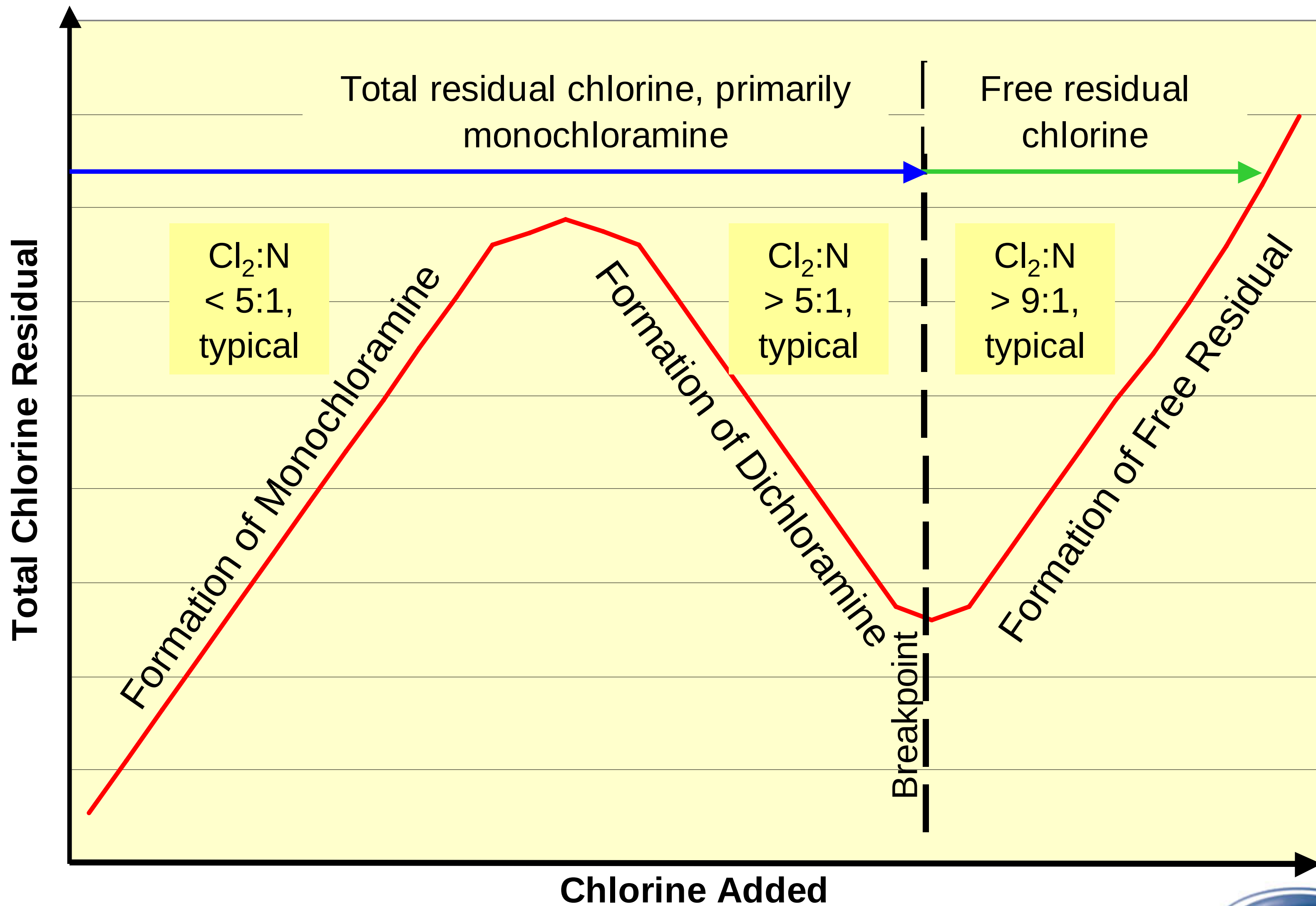
$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$$

- Chloramines are not as effective disinfectants as free chlorine

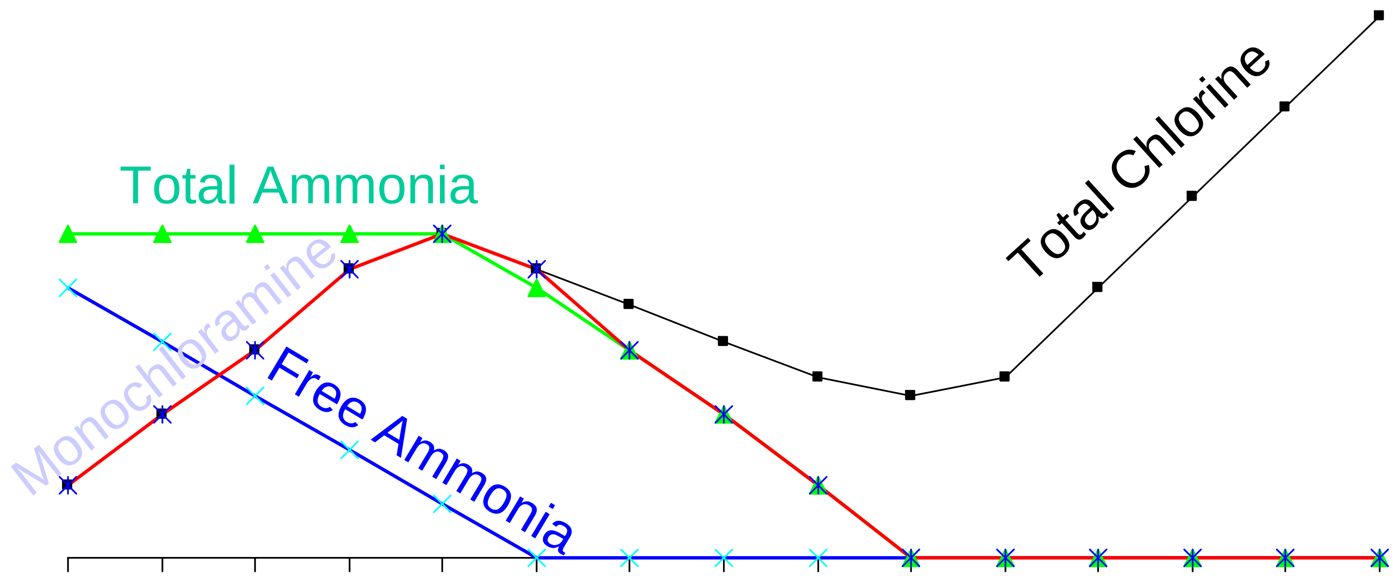
Definition of Unreacted Ammonia

- Ammonia in solution as
  - NH_3 Free ammonia gas dissolved in water or;
  - NH_4^- The ammonium ion

Breakpoint Curve



* Know where you are!
* Know what species you are making!



Breakpoint Curve Considerations

- Shape of the curve is dependent upon
  - amount of ammonia and other chlorine demand substances in the water
  - temperature
  - pH
  - contact time
- Most effective disinfection, least taste and odor occurs with free residual chlorine
- Free chlorine may lead to formation of DBP

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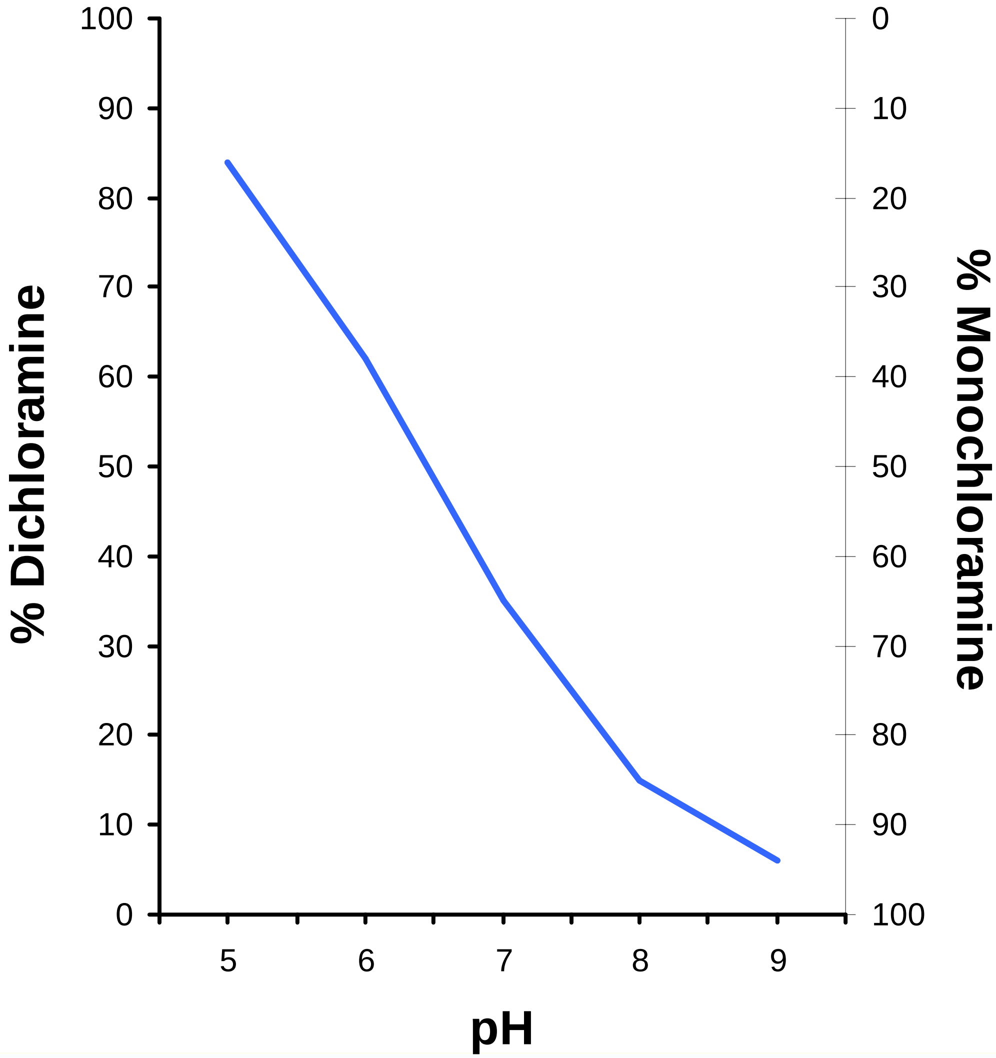
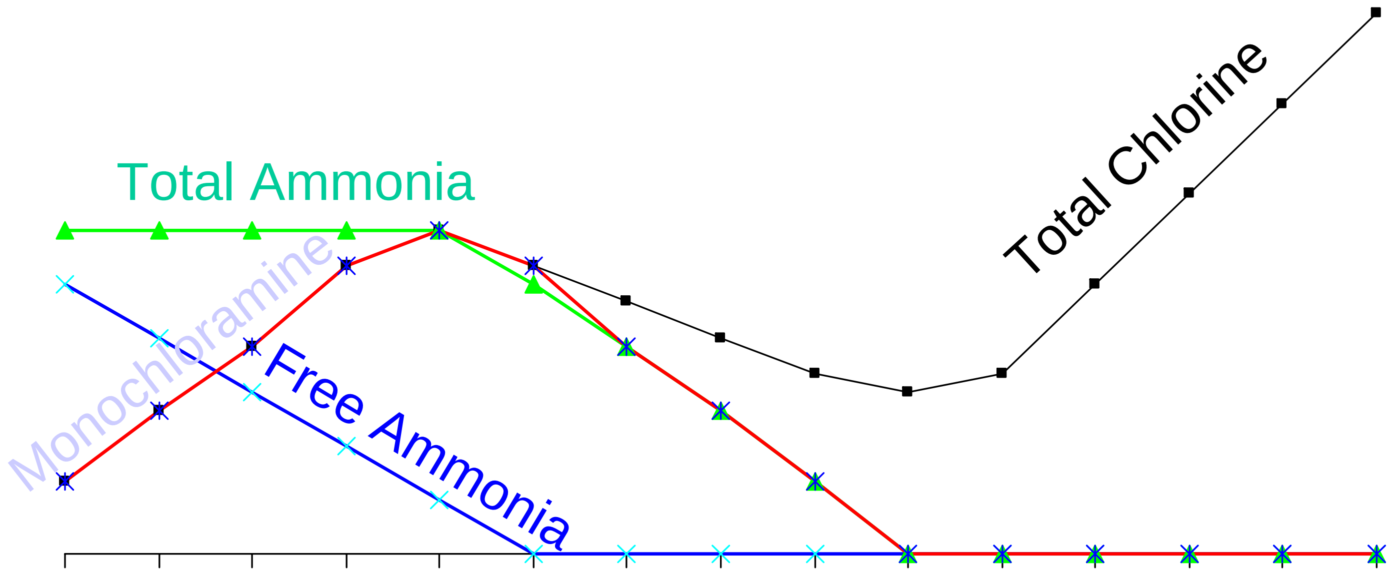
Effect of pH on Chloramine Species



- Distribution of chloramine species is effected by:
  - pH
  - Ammonia concentration (see breakpoint curve)

The APA6000™ Can Help

- Know where you are!
- Know what species you are making!



Chloramines

- Less effective disinfection than free chlorine. HOCl is 25X more effective biocide
- Chloramines require longer contact time and/or greater concentration than free chlorine.
- Possible taste and odor (dichloramine)
- More stable than free chlorine (long distribution systems)
- Generally do not produce DBP (NH_2Cl may form DBP, but are not as hazardous)

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Chloramination

- Chloramination: Purposeful use of chlorine and ammonia to form monochloramine.
  - Minimizes formation of chlorinated organics
  - Ammonia to chlorine Ratio is controlled to favor formation of monochloramine, typically 5:1 Cl_2:N
- Total residual chlorine test: All free and combined chlorine species

Advantages of The APA6000TM

- Specifically measures monochloramine
- Provides measurement for total and free ammonia
- Single analyzer to optimize chloramination
- Auto-calibrations and sample sequencing

Interference's

Species	Conc (mg/L)	Interference	Species	Conc (mg/L)	Interference
Al	10	None	ClO_3^{1-}	10	None
B	10	None	ClO_2^{1-}	10	None
Cr	10	None	NO_3^{3-}	10	None
Fe	10	None	F^-	10	None
Pb	10	None	CO_3^{2-}	10	None
Mg	10	None	PO_4^{3-}	10	None
Mn	10	None	Cl^-	10	None
Ni	10	None	H_2O_2	0.03%v/v	None
Na	10	None	O_3	~20 ppm/min	+
Zn	10	None	Cysteine	3	None
SO_4^{2-}	10	None	Tyrosine	3	None
			Diethylamine	3	None

Only Ozone!

Dechlorination

- After super chlorination or before discharge from a treatment process to a stream or lake
  - Sulfur Dioxide - SO_2
  - Sodium Bisulfite - $NaHSO_3$
  - Sodium Sulfite - Na_2SO_3
  - Sodium Thiosulfate - $Na_2S_2O_3$
  - Activated Carbon - C

Dechlorination with Sulfur Dioxide

- Sulfur dioxide forms sulfurous acid with water: $SO_2 + H_2O \longrightarrow H_2SO_3$, then
- $H_2SO_3 + HOCl \longrightarrow HCl + H_2SO_4$
- $H_2SO_3 + NH_2Cl + H_2O \longrightarrow NH_4Cl + H_2SO_4$
- $H_2SO_3 + NHCl_2 + 2H_2O \longrightarrow NH_4Cl + HCl + 2H_2SO_4$
- $H_2SO_3 + NCl_3 + 3H_2O \longrightarrow NH_4Cl + 2HCl + 3H_2SO_4$

Analytical Methods for Chlorine and Chloramine

- DPD Colorimetric and Titration
- Amperometric Titration
- Monochlor-F Chloramine
- Iodometric Titration
- Orthotolidine
- Syringaldazine (FACTS)
- Potentiometric electrode

Comparison of Methods

Method	Range mg/l	Detection Level	%RSD	Use	Skill
DPD colorimetric	0-5	0.005	1-2	F & T	1
Ultra low-range DPD colorimetric	0-0.500	0.002	5-6	T	2
DPD titration	0-3	0.018	2-7	F & T	2
Iodometric	Up to 4%	1	NR	Total Oxidants	2
Amperometric Titration - Forward	Up to 10	0.015	1-2	F & T	3
-Back	0.006-1	0.006	15	T	3
Electrode	0-1	0.05	10	Total Oxidants	2
Monochlor-F W WW	0-4.5 0-10	0.09	2	Mono-chloramine	1

Skill Level: 1= Minimal training; 3 = Experienced

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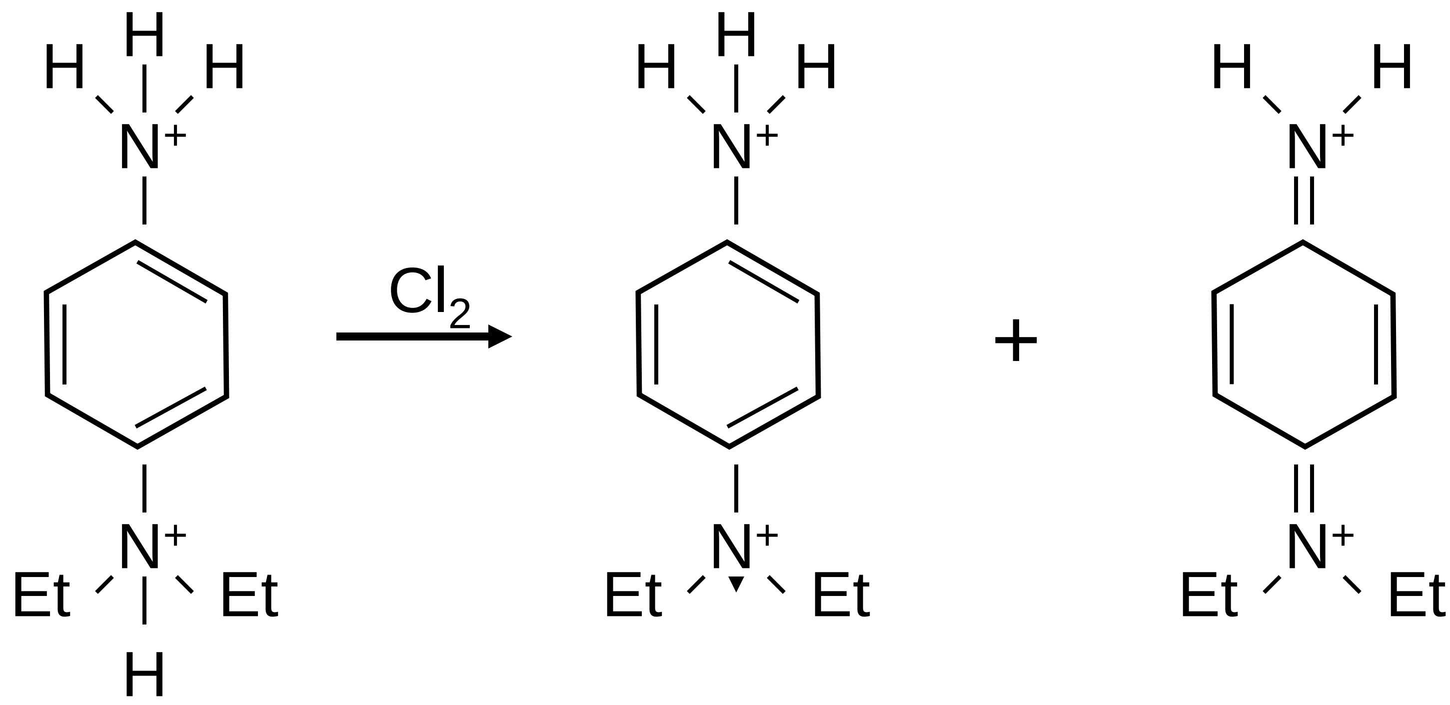
DPD Colorimetric Method

- Introduced by Palin in 1957
- Chlorine oxidizes DPD (N,N-diethyl-p-phenylenediamine) creating two reaction products
  - At near neutral pH, the primary oxidation product is a Würster dye (magenta color)
  - DPD can be further oxidized to the relatively unstable imine compound (colorless)

DPD-Chlorine Reaction Products



AMINE
(colorless)

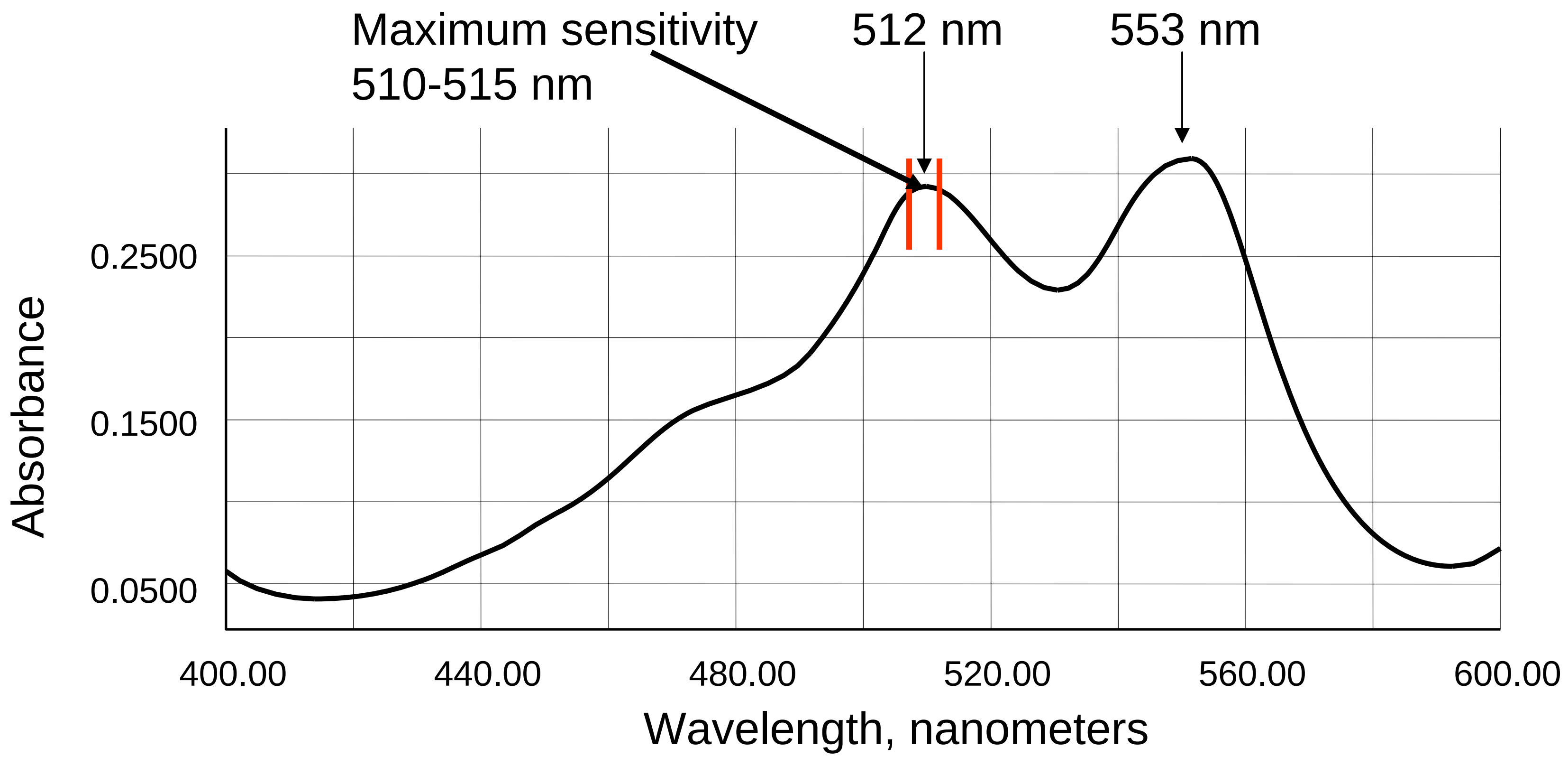
WÜRSTER DYE
(magenta colored)

IMINE
(colorless)

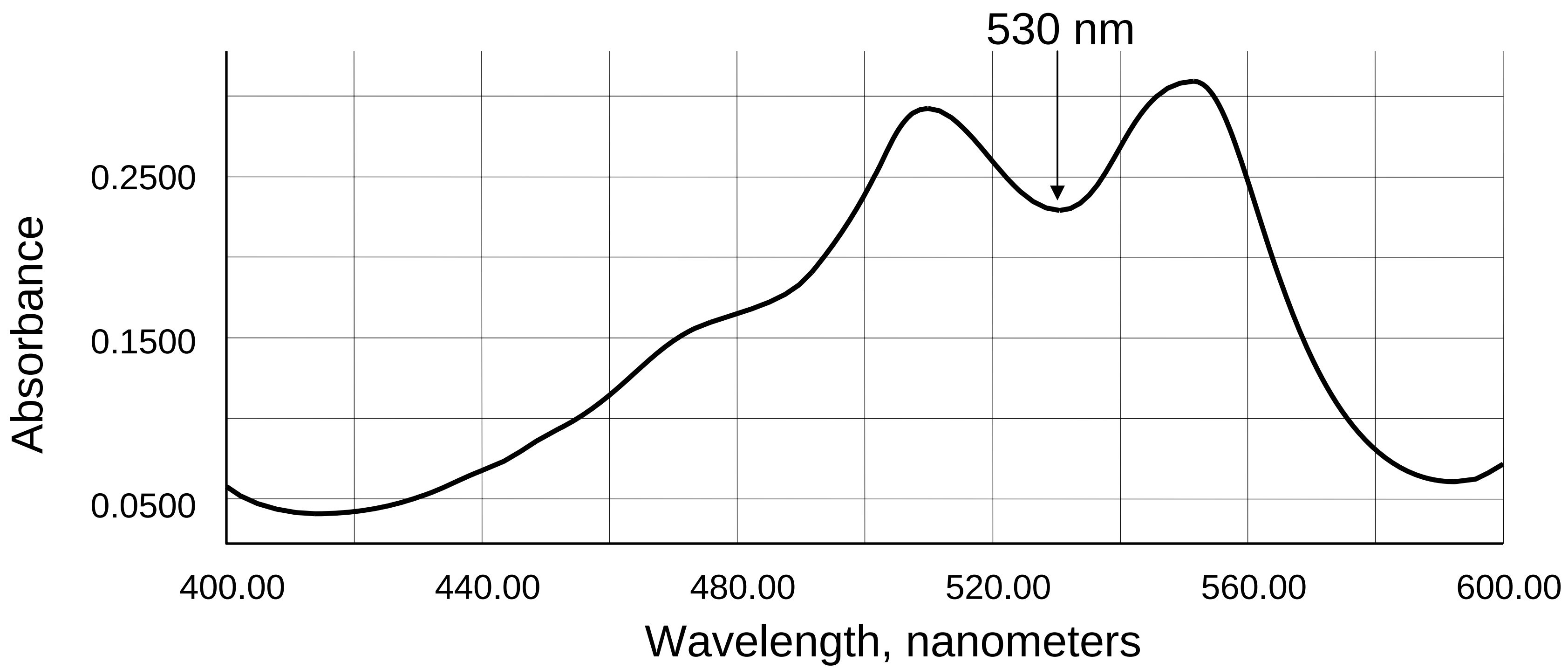
DPD Würster Dye Absorbance

- DPD Würster dye may be measured photometrically at wavelengths from 490 to 555 nm.
- Absorption spectrum indicates a doublet peak with maxima at 512 and 553 nm
- Maximum sensitivity for measurements is between 510 and 515 nm

DPD Würster Dye Absorbance Spectrum



- Hach Cl-17 on-line analyzer: 510 nm
- Hach Ultralow Range DPD (ULRDPD) method: 515 nm



- Most Hach tests use wavelength of 530 nm to
  - minimize variation in wavelength accuracy
  - extend working range on some instruments

CL17 Chlorine Analyzer

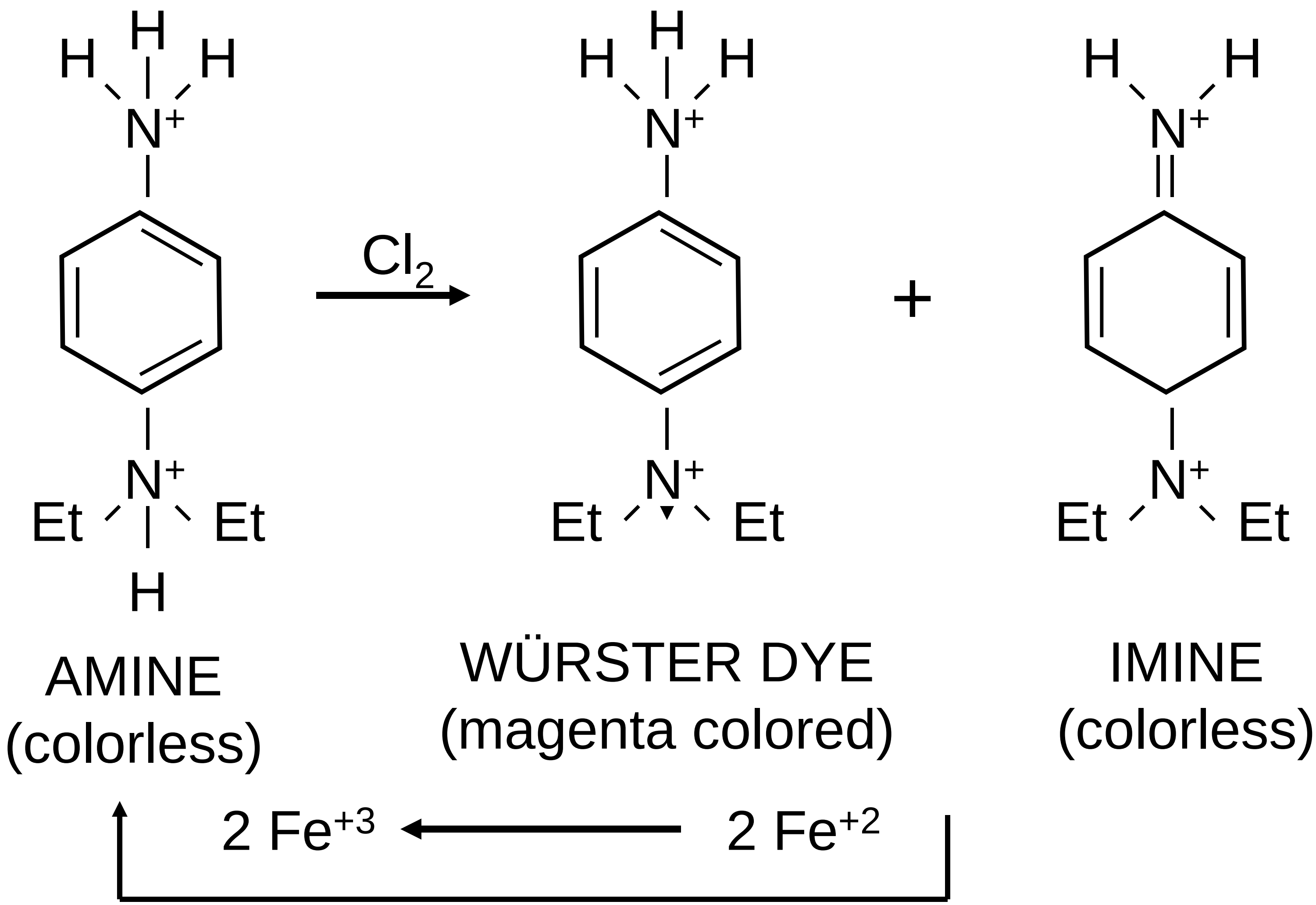
Pocket Colorimeter

Color comparators should be avoided when practical

DPD-FAS Titration Method

- DPD-FAS (ferrous ammonium sulfate) titration method is based on the same chemistry as the colorimetric method
- Magenta Würster dye is titrated with the ferrous reducing agent to a colorless end point
- Hach uses ferrous ethyleneammonium sulfate (FEAS) to improve stability of the titrant solution

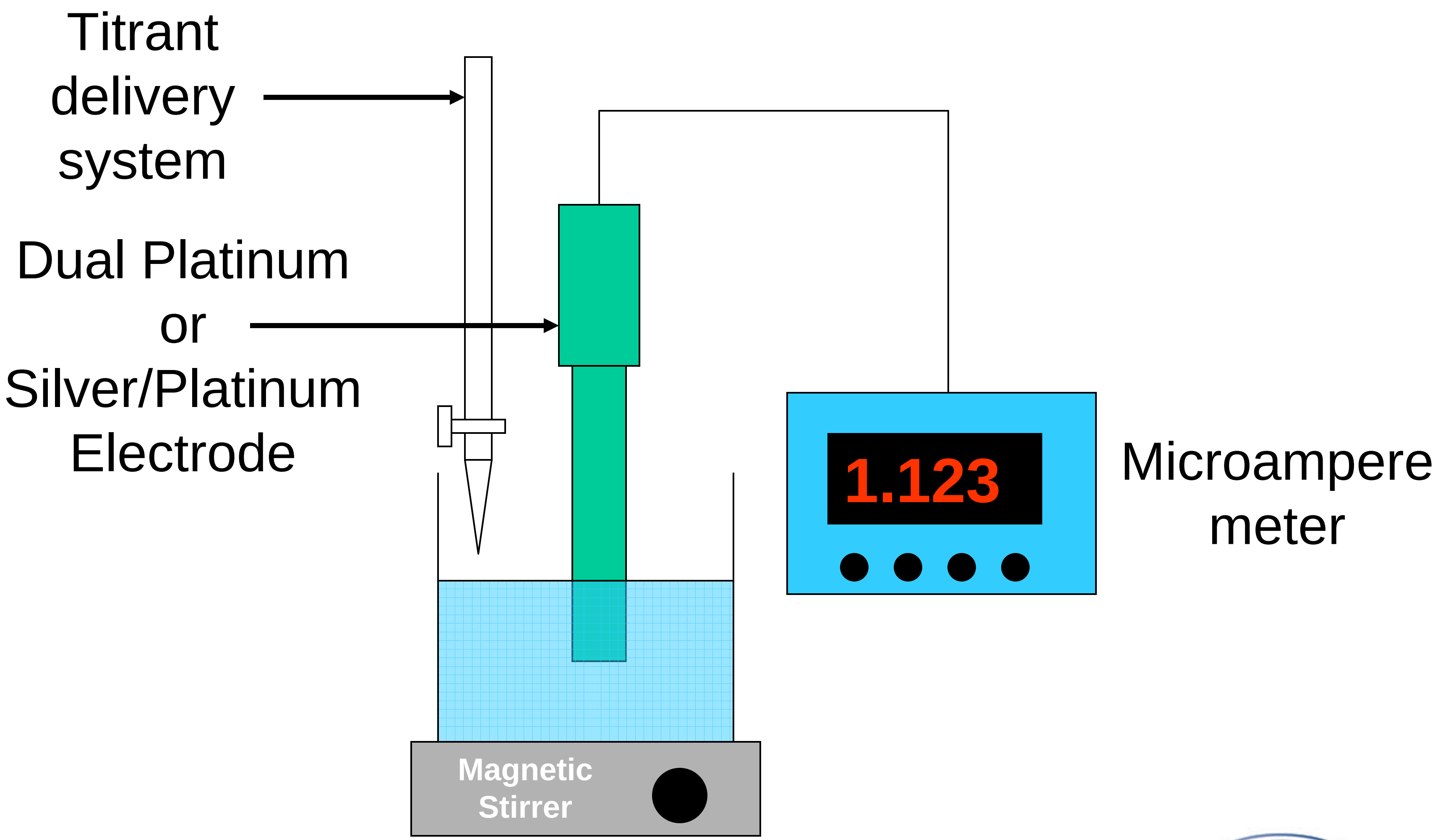
DPD-FAS Titration Reaction



Amperometric Titration Methods

- Electrochemical technique applies small voltage across two electrodes
- Measures change in current resulting from chemical reactions
- Measures change in current vs. amount of titrant added
- Uses two platinum (bi-amperometric), or dissimilar electrodes (typically silver/platinum).
  - GLI AccuChlor2 uses gold/copper electrodes.

Typical Amperometric Titration System



Amperometric Reaction

- Titrant is either PAO* or thiosulfate
- Titration at pH 7 for free chlorine
- Titration at pH ≤ 4 for total chlorine
- Chlorine is reduced at the cathode
- Titrant oxidized at the anode

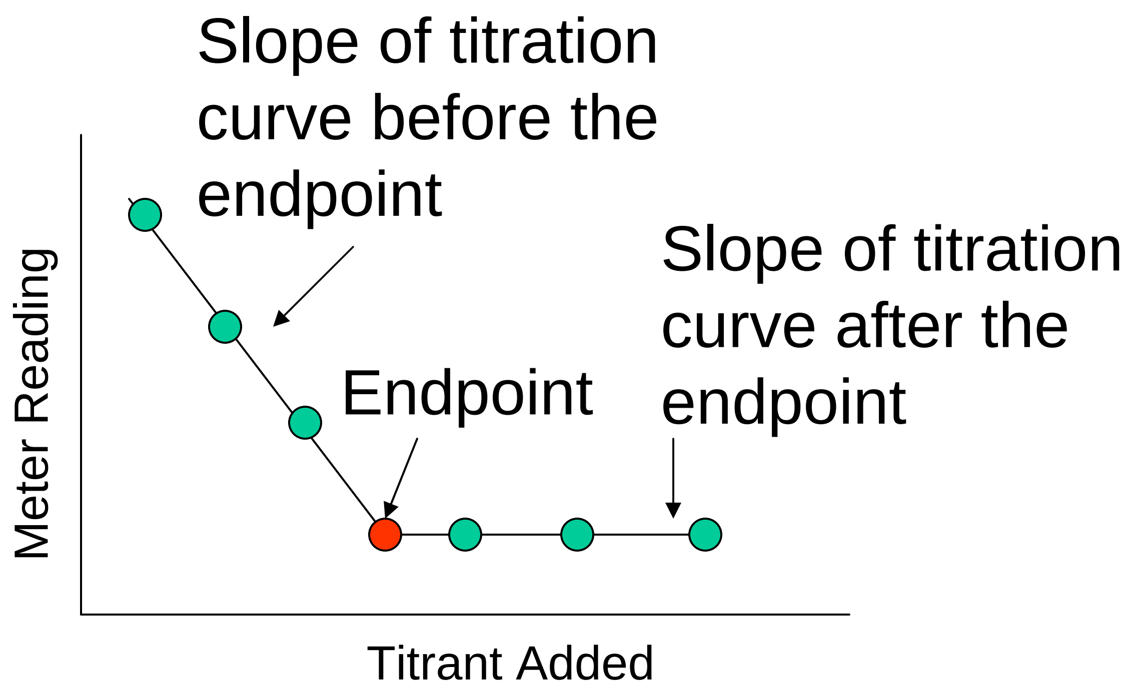
$$PhAsO\ (PAO) + Cl_2 + 2H_2O \longrightarrow PhAsO(OH)_2 + 2Cl^- + 2H^+$$

*Phenylarsine oxide Ph=phenyl

Amperometric Reaction (continued)

- Current flow continues as long as oxidation/reduction is occurring
- After all free chlorine is reacted, the current stops thus marking the end of the titration
- Chlorine concentration is proportional to the titrant used

Typical Forward Titration



Amperometric Chloramine Measurement

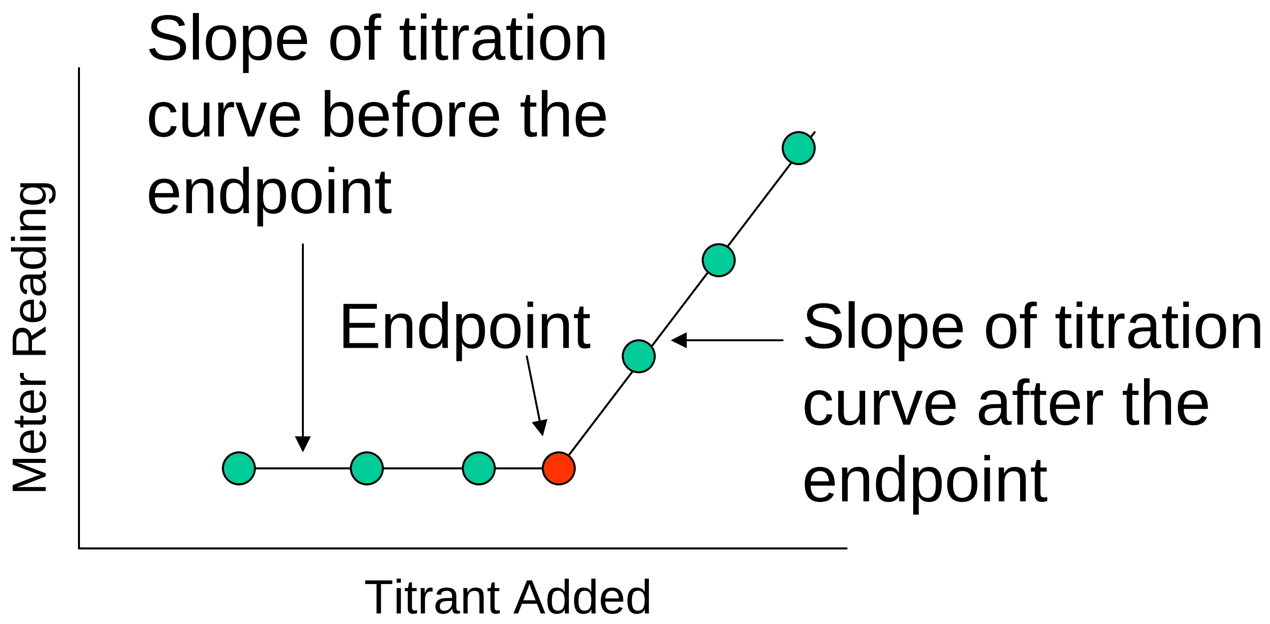
- Potassium Iodide is added
- Reacts with chloramine to release triiodide ion, I_3^-
- Triiodide is tritrated at pH 4

$$PhAsO\ (PAO) + I_3^- + 2H_2O \longrightarrow PhAsO(OH)_2 + 3I^- + 2H^+$$

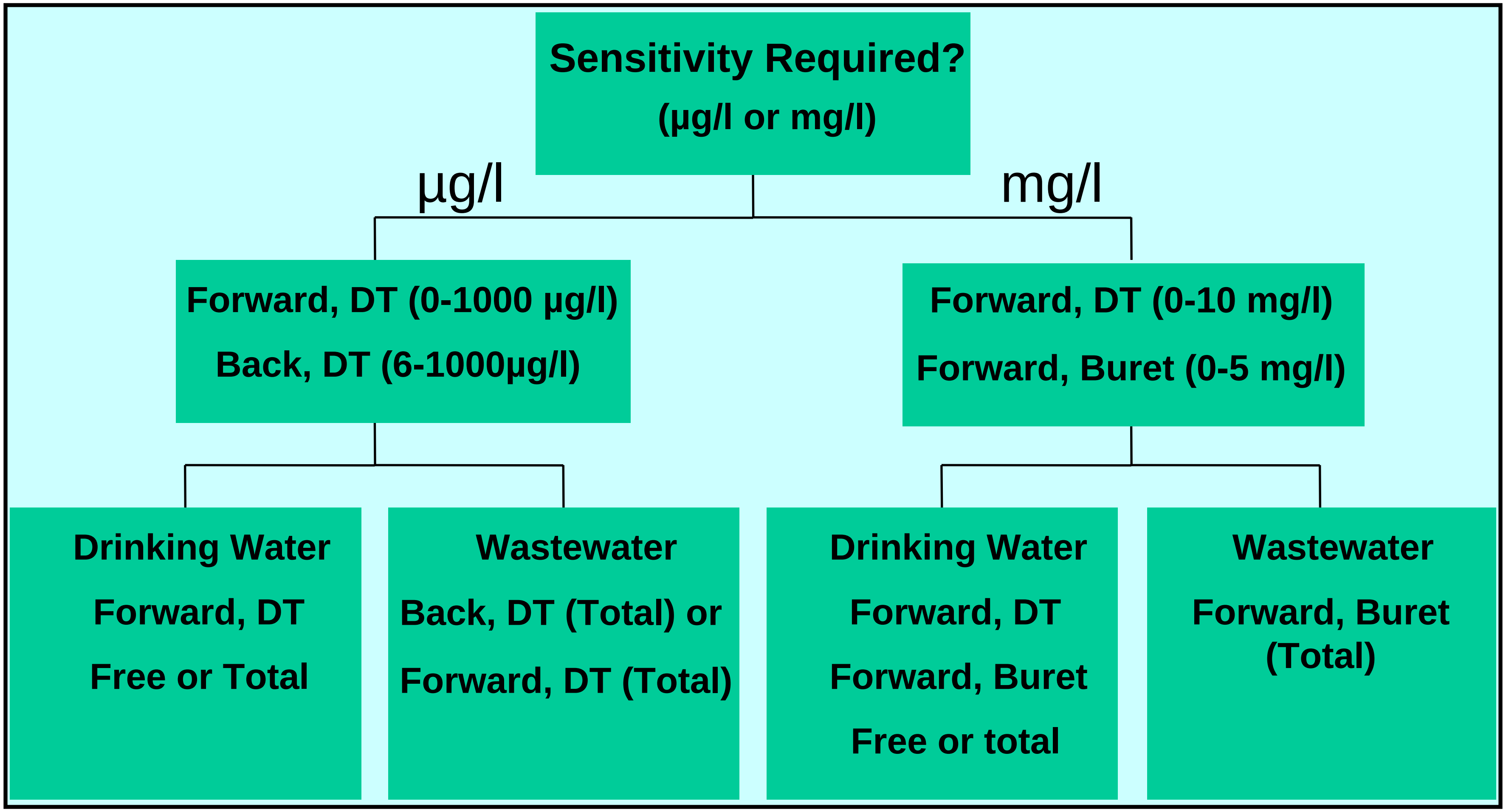
Back Amperometric Titration

- Used to ‘fix’ the chlorine by addition of excess reductant
- Sample then is titrated with iodine or iodate
- Endpoint of the titration is the <u>beginning</u> of current flow

Typical Back Titration



Selection of Amperometric Procedure



DT = Digital Titrator

Sampling Considerations

- Obtain a representative sample
- Allow water to flow at least 5 minutes prior to sampling
- Use chlorine demand-free sample containers
- Measure immediately on site except ULR-DPD and Amperometric
- Use different containers for free and total chlorine measurements
- Avoid exposure to sunlight or excess agitation

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Common Interferences

- Other oxidants: ClO_2, O_3, Br_2, H_2O_2, I_2, $KMnO_4$
- Disinfection by-products, I.e. chlorite and chlorate
- Particulate contamination - turbidity
- Buffer capacity
- Sample color
- Mn^{+3} to Mn^{+7}
- Cr^{+7}
- Organic N-Cl (organic chloramines in wastewater)

Compensating for Manganese Interference

- Split sample. Analyze first portion as usual
- Second Portion:
  - Adjust pH w/1N sulfuric acid
  - Add drops of 30 g/l potassium iodide; wait one minute
  - Add drops of 5 g/l sodium arsenite
  - Add DPD and complete test
- Subtract result of second portion from first portion

Sample Size	5 ml	10 ml	25 ml
H_2SO_4, 1N	Adjust to pH 6-7	Adjust to pH 6-7	Adjust to pH 6-7
Potassium Iodide, 30 g/l	2 drops	2 drops	3 drops
Sodium Arsenite, 5 g/l	2 drops	2 drops	3 drops

THANKS FOR YOUR TIME

QUESTIONS????????