BASIC
Water Chemistry & Testing

San Diego County Training

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presented by
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Topics and Logistics

- Sanitation & oxidation
- Water balance – pH, total alkalinity, calcium hardness, temperature and total dissolved solids
- Testing techniques
- Please hold questions to the end

Sanitation & Oxidation

- A sanitizer kills bacteria, viruses, and algae in water.
- When a sanitizer goes to zero in the water bacteria, viruses, and algae can grow!
- Oxidation destroys organic (carbon containing) contaminants.

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Sanitation & Oxidation

- Most common products used:

  chlorine & bromine

- Only 10% of the work of chlorine or bromine does is sanitation.
- The remaining 90% work is oxidation of contaminants.
- In no other type of operation do we try to change waste water to potable water other than pools and hot tubs.

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Available Chlorine Content – ACC (in a 1% solution)

Product	ACC	pH
Chlorine gas Cl2	100%	0
Sodium hypochlorite	10-12%	11-13
Calcium hypochlorite	45-78%	8.5-11.8
Lithium hypochlorite	35%	10.8
Dichlor	55-62%	6.7
Trichlor	90%	2.8-3.5

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Chlorine Residuals

- Free chlorine: both HOCl and OCl^- test as free chlorine, and both are capable of disinfection and oxidation.
- HOCl is about 80-100 times more effective than OCl^-.
- Free chlorine can be measured using DPD, FAS-DPD, syringaldazine, or tetramethylbenzidine methods, not OTO.

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Chlorine Residuals

- Combined chlorine (CC), also known as chloramines, forms when free chlorine reacts with ammonia or other nitrogen containing compounds. Sweat, urine, and dead skin are some sources.
- CC produce an irritating odor, along with skin and eye irritation for bathers if levels are too high.
- CC cannot be determined with an orthotolidine (OTO) sanitizer test.

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Chlorine Residuals

- Total chlorine (TC): a combination of *all* forms of chlorine in the water:

  FC + CC = TC or TC – FC = CC

- Total chlorine measurements are determined by an OTO, DPD, FAS-DPD, syringaldazine, or tetramethylbenzidine test.

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Cyanuric Acid (CYA) Maintains Chlorine Residuals

- Description: an odorless, white granular organic substance that helps chlorine last up to 3–5 times longer in UV light
- Sources: "pure" cyanuric acid or stabilized chlorine (chlorine-supplying chemicals which also have cyanurate ions as part of their molecular structure)

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Cyanuric Acid (CYA)

- CYA is an off-white granular solid, with a maximum solubility of 1,600 ppm in water.
- CYA is ***not destroyed*** by any current pool chemical. It can only be removed by draining and adding fresh water, splash-out, carry-out, or backwash.
- One pound per 5,000 gallons adds 25 ppm of CYA to the water.

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Cyanuric Acid (CYA) Update!

- CDC study presented in Austin in 9/06 at the "Second Annual World Aquatic Health Conference" showed that CYA levels > 50 ppm provided NO additional benefit to decrease chlorine degradation in UV light.

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Bromine Facts

- *Once a bromine pool…always a bromine pool*—as long as the bromide ion is present in water, addition of any oxidizer (chlorine, ozone, or monopersulfate) will regenerate hypobromous acid (HOBr).
  - BCDMH has a pH of 4.5–4.8
  - DBDMH has a pH of 6.6
  - BCDMH + DCDMH + DCEMH has a pH of 3.6
  - NaBr (pH of 6.5–8.0) + Na-based oxidizer
  - NaBr + dichlor has a pH of 4.5

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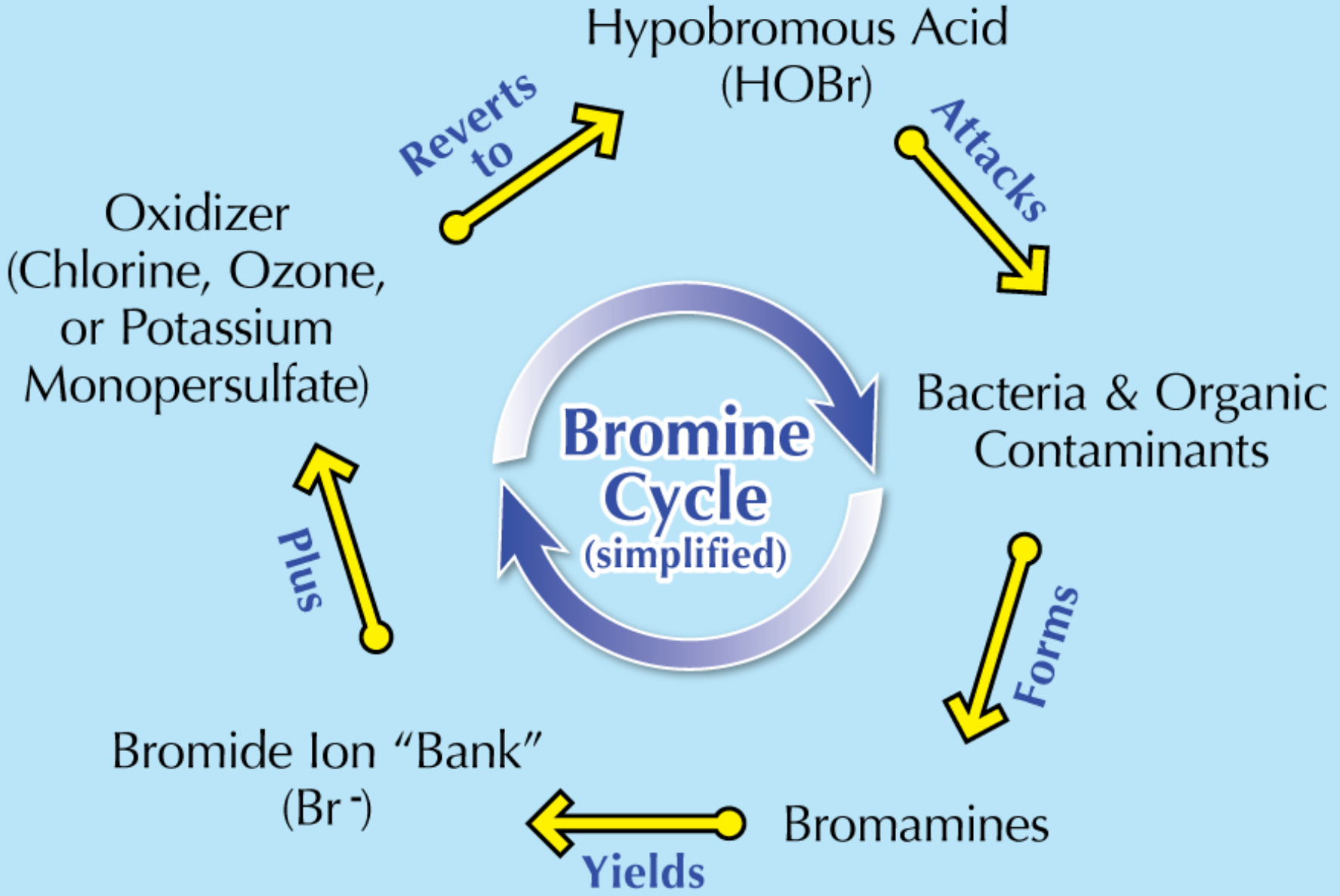
Hypobromous Acid
(HOBr)
Attacks
Bacteria & Organic
Contaminants
Forms
Bromamines
Yields
Bromide Ion "Bank"
(Br -)
Plus
Oxidizer
(Chlorine, Ozone,
or Potassium
Monopersulfate)
Reverts
to
Bromine
Cycle
(simplified)

Bromine Testing

- DPD, FAS-DPD, OT, syringaldizine, and tetramethylbenzidine all measure total bromine.
- No need to measure bromamines because they are nearly as effective a sanitizer as HOBr.

Shock Treatment

- Shocking
  - The periodic addition of chlorine (5–10 ppm) to help remove organic buildup
- Superchlorination
  - 10x the combined chlorine level to remove all combined chlorine—also called "breakpoint chlorination"
- Algae Shock
  - 30 ppm chlorine addition

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Breakpoint Alternative Calculation

Recent studies have suggested that the traditional breakpoint method of 10x the CC level addition of chlorine is "too much" and can lead to an increase in THMs and other undesirable DBPs. These studies suggest using:

BP = (10 x CC) – FC

- For example: FC = 3.0 ppm and CC = 0.5 ppm, then: BP = (10 x 0.5) – 3.0 or 5.0 – 3.0 = 2.0 ppm shock needed

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Secondary Disinfection Systems

- Salt Systems
- Ozone
- Ionizers
- Monopersulfate
- Biguanides

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Secondary Disinfection Systems

Chlorine generators (salt systems) pass an electric current through water treated with 2,500 to 8,000 ppm of sodium chloride (NaCl). This process forms HOCl.

- Increases pH levels
- Increases TDS
- Efficient system to produce HOCl
- Up-front costs are high but overall costs are lower than using regular chlorine

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Secondary Disinfection Systems

Ozonators use corona discharge or UV light to generate ozone (O_3). In each method, oxygen (O_2) is converted to ozone.

- Short life means that residuals cannot be maintained for normal disinfection, and a supplemental sanitizer must be used.
- Ozone/bromine combinations are very popular in spas and hot tubs.

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Secondary Disinfection Systems

Ionization generates copper and silver ions to provide algaecidal and biocidal properties. Effectiveness is solely related to solubility of metal ions.

- Not an oxidizer/sanitizer system; requires a supplemental level of chlorine.
- DO NOT use bromine with ionizers as silver bromide may form. Silver bromide is potentially hazardous if ingested and can damage acrylic/fiberglass shells.

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Secondary Disinfection Systems

Polymeric biguanide, a generic name for Baquacil®-like products, is used primarily for microbiological control.

- Lacks oxidation capabilities; hydrogen peroxide (H_2O_2) is used as an oxidizer and as a "shock" to eliminate organics
- Incompatible with all halogen-based products
- Requires specialized care for proper treatment
- Read all labels carefully!

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Non-chlorine Shock

Potassium monopersulfate ($KHSO_5$) is an oxygen-based oxidizer (*not* a sanitizer) used to remove organic buildup.

- Effective way to remove organics
- Does not damage vinyl liners
- Dissolves quickly
- Produces no odors or irritation
- Back in the water in 30–45 minutes

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Non-Chlorine Shock

- Dosing monopersulfate:
  - "oxidizing shock" dose is 2 lb./10,000 gallons
- Be aware:
  - has a low pH (2.3); overdosing may affect pH level
  - won't kill algae; only oxidizes
  - interferes with DPD test for CC and TC

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Water Balance

- A concern to operators and public health because pH is included.
- Definition: the *dynamic interaction* between certain chemical components in water and certain physical characteristics of water including pH, total alkalinity, calcium hardness, total dissolved solids, and temperature

pH

- Definition: the measure of the acidic or alkaline (basic) nature of water
- The measurement scale is logarithmic, ranging from 0 to 14, with 7 being neutral.
- Testing method: color-matching using phenol red or pH meter

pH

Measured logarithmically, an increase of 1 pH unit equals a 10-fold increase in strength of an acid or base.

- A pH of 5 is 10 times more acidic than a pH of 6, and 100 times more acidic than a pH of 7.
- A pH of 11 is 10 times more basic than a pH of 10, and 100 times more basic than a pH of 9.

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pH

Low pH	High pH
Corrosive water	Scaling Water
pits concrete	plugs filters
dissolves metals	reduces circulation
stains surfaces	cloudy water
	creates white crusty deposits
Non-balance problems	Non-balance problems
chlorine loss	chlorine inefficiency
skin/eye irritation	skin/eye irritation
vinyl wrinkles	

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Total Alkalinity (TA)

- Definition: the quantitative measure of water's ability to buffer itself from wide pH swings
- Buffer: a chemical system that resists change in pH when acids or bases are added
- Recreational water buffers: carbonate, bicarbonate, hydroxide, cyanurate, nitrate, sulfate, phosphate, etc.

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Total Alkalinity (TA)

- Testing frequency: weekly
- pH bounce: the rapid fluctuation of pH after adding acids or bases to low total alkalinity water
- When adjusting water balance, remember—alkalinity FIRST!

Total Alkalinity (TA)

- pH bounce: the rapid fluctuation of pH after adding acids or bases to low total alkalinity water
- When adjusting water balance, remember—alkalinity FIRST!
- Testing method: titration with an acid of known concentration to which a chemical indicator has been added - **green** to **gray** to **red** (pink) colors.

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Total Alkalinity (TA)

Low TA	High TA
Corrosive water	Scaling Water
pits concrete	plugs filters
dissolves metals	reduces circulation
stains surfaces	clouds water
	creates white crusty deposits
Non-balance problems	Non-balance problems
pH bounce	chlorine inefficiency
chlorine loss	skin/eye irritation

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Calcium Hardness (CH)

- Definition: the quantitative measure of the calcium ion concentration present in a water sample
- Hardness – the word came from to the degree of difficulty people experience when trying to lather soap

Calcium Hardness (CH)

- Sources of calcium: make-up or improperly balanced water plaster pools, the addition of calcium chloride to pool or spa water
- Testing method: titration using a reagent of known concentration until a distinct color change **red** to **purple** to **blue**
- Ignore "floaters"

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Calcium Hardness (CH)

Low CH	High CH
Corrosive water	Scaling Water
etches plaster	plugs filters
pits concrete	reduces circulation
dissolves grout	clouds water
pitting of pool decks	creates white crusty deposits
	heater inefficiency

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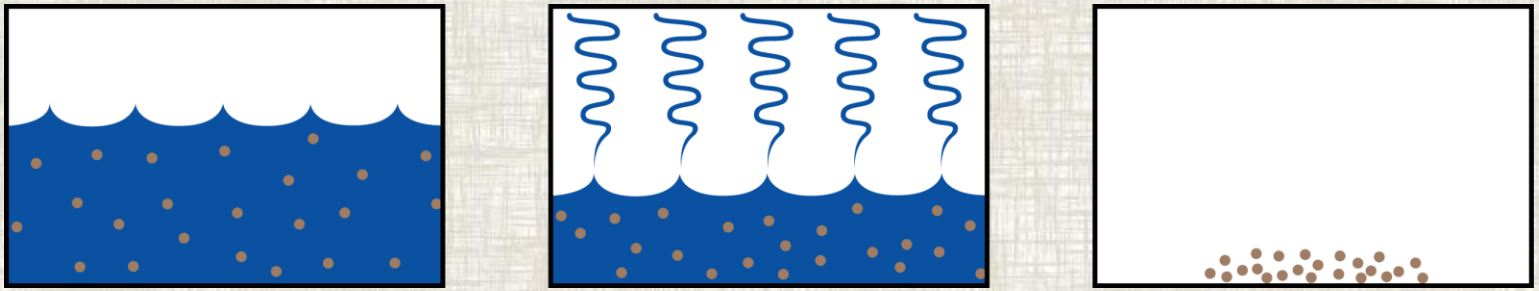
Temperature

- Definition: a measure of the heat content of the water
- Only non-chemical factor in water balance
- A small factor in the Langelier Saturation Index

Total Dissolved Solids (TDS)

- Definition: any chemical that remains after the water evaporates
- The remaining residue represents the "total" of all dissolved solids.



Total Dissolved Solids (TDS)

Recommended range:

- No more than 1,500 ppm over start-up TDS level
- For chlorine generators, add recommended salt concentration to start-up TDS to determine new start-up TDS.

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Total Dissolved Solids (TDS)

- Chemical measurement: TDS can be determined by an acid titration, then treated with a resin and titrated with a base to determine the total ionic strength of the water.
- Electronic measurement: a meter can be used to directly measure TDS expressed as ppm.

Water Balance – SI

SI = pH + logCH + logTA + TF – 12.3

SI	= saturation index
pH	= measured pH value
logCH	= log [calcium hardness]
logTA	= log [total alkalinity]
TF	= temperature factor
12.3	= constant

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Water Balance – SI

- Water is considered balanced if the result of the SI calculation is between +0.5 and -0.5 units.
- A positive value is generally more desirable than a negative value because it does not visibly "remove" grout and/or plaster.
- Potential for scaling above +0.5, and -0.5 units.

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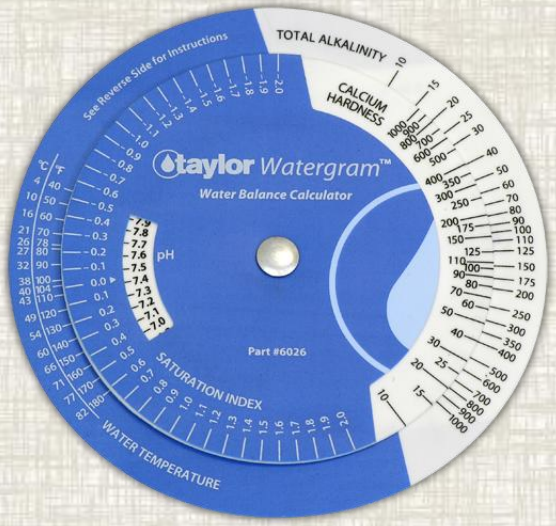
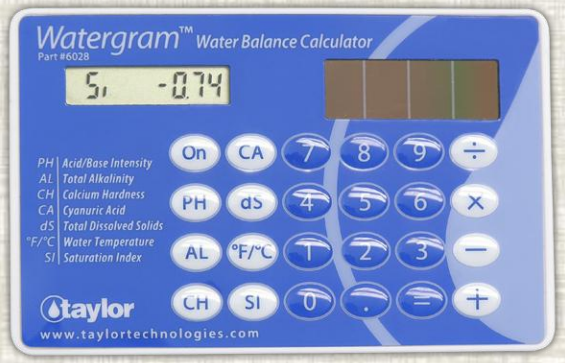
Water Balance Tables – SI

Calcium Hardness		Total Alkalinity		Temperature	
ppm	*logCH*	*ppm*	*logTA*	*°F*	*TF*
50	1.70	50	1.70	32	0.02
100	2.00	70	1.85	40	0.09
150	2.18	80	1.90	50	0.17
200	2.30	90	1.95	60	0.25
250	2.40	100	2.00	70	0.33
300	2.48	110	2.04	76	0.38
350	2.54	120	2.08	80	0.41
400	2.60	130	2.11	82	0.43
600	2.78	140	2.15	90	0.49
800	2.90	150	2.18	100	0.57
1000	3.00	200	2.30	104	0.61

Water Balance Alternative to Tables

Easy-to-use, handheld calculators do the math for you and act as a "what if…" to help you achieve proper water balance.





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Testing Techniques

- Read all instructions thoroughly.
- Rinse cells completely.
- Measure sample carefully. (What's a meniscus?)
- Cap cells to mix.
- Don't dispose of solutions in the pool or spa—follow local, state, or federal guidelines.

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Testing Techniques

- Use correct sample size to avoid variations in color development.
- Interpolate between known color standards for color matching.
- Monitor drop size for titration tests.

Testing Techniques

- Don’t interchange reagents between manufacturers’ test kits.
- Wait to match colors after sampling.
- Don’t use contaminated or old reagents.

Testing Interferences – Normal and Overcome

- Sanitizers
- pH
- Total Alkalinity
- Calcium Hardness

High Sanitizer Interference in a pH Test

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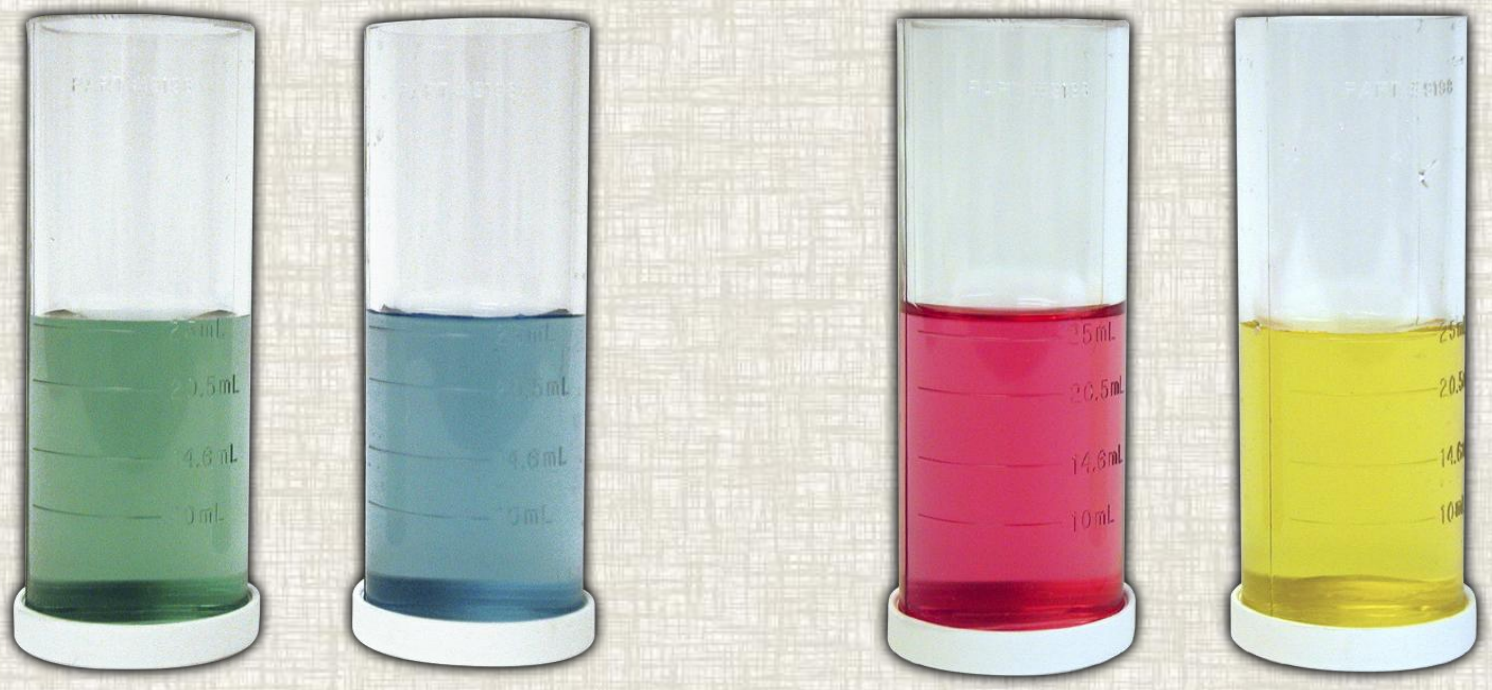
High Sanitizer Interference in a Total Alkalinity Test



High Sanitizer Interference in a Calcium Hardness Test

Final Questions

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