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Swimming Pool Chemistry

Swimming Pool Chemistry involves a rich variety of chemical concepts and practical applications. Students with an understanding of equilibrium are equipped to learn about this chemistry by doing straightforward quantitative experiments and can get background on many issues by doing Internet research. Unlike many other topics, most Internet resources describing the care and maintenance of swimming pools are both technical and practical, and are written at an appropriate level for high school students.

In this paper I will describe how the various principles apply to chlorination in swimming pools, but these principles also apply to chlorination of drinking water, to wastewater treatment and even to small irrigation systems.

 I will divide this paper into three parts:

1. An outline of some important concepts taught in high school chemistry that are involved in chlorination of Swimming Pools, to give a brief background in the topic.

2. Descriptions of some student experiments that illustrate some of those concepts, suitable for microchemistry format.

3. A list of Internet links that are useful as resources for both teachers and students interested in more information about Pool chemistry, and links that deal with the social issues related to the chlorination of water supplies.

I think it is fair to say that Chlorine has had a lot of bad press lately. This is a high interest way to teach about the proper use of very common household chemicals.

With factual information, and by insisting on careful work using microchemistry techniques, students can be taught to have appropriate respect without fear for these chemicals that are in widespread consumer use.

Background Information

Introduction

Chlorination of water is used in many situations other than the backyard pool and each application has its own variations that must be taken into account. An important example is the formation of chloramines by the reaction of chlorine with nitrogen-containing organic matter. Chloramines are very toxic to fish, so conditions are sought to avoid their formation in the chlorination of sewage effluent. In swimming pools, they are nuisance chemicals, lowering the effectiveness of the chlorine load in the pool and leading to eye and skin irritation. In treatment of drinking water, however, they are advantageous, as low-level disinfectants that reside in the water long after hypochlorites have broken down. In fact, the City of Virginia Beach VA recently converted from Chlorine to Chloramines as the treatment of choice for drinking water.

In many North American municipalities, greater attention is being paid to the treatment of drinking water after some widely publicized failures of the treatment process. In Walkerton Ontario, Canada, over 2000 of the town's 7000 residents were hospitalized and seven deaths resulted from a malfunction of the municipal chlorination system and contamination of the water supply with a virulent strain of e-coli bacteria.

Since the Walkerton disaster, every tourist resort owner in the Province of Ontario who treats surface water for domestic use must attend a weeklong course in Water Treatment and pass a rigorous exam at the end. The exam deals with such topics as flow rates, chloramine formation, pH, alkalinity and buffer capacity to mention just a few. Without certification, they cannot use surface water for their customers. Without a background in chemistry, most candidates have a very difficult time understanding the required technical details and the policy has sent shock waves through the resort-owner community.

Throughout North America, utilities require increasing technical expertise in water treatment procedures as supplies of clean water become ever scarcer. Although alternative methods of disinfection exist, most still use chlorination as the treatment of choice. Most home pools and hot tubs use chlorine for water treatment and, chlorine has become more common as an ingredient in cleansers

Thus, the importance of understanding the principles and safe practices of water chlorination can be shown to go far beyond the classroom and lab.

Chlorination

There are a variety of ways to introduce chlorine into water… direct bubbling of gaseous chlorine, addition of OCl_2, electrolysis of NaCl in saltwater pools, etc. The most widely used method is addition of hypochlorites of sodium, calcium or lithium. Each of these salts has advantages and disadvantages in price and solubility. Slow dissolving calcium hypochlorite is easily compressed into pucks, but leaves a white insoluble residue that must be filtered out to maintain water clarity. Although more expensive, the lithium salt dissolves quickly and completely and is preferred in hot tubs where the rate of Chlorine loss is high. Sodium hypochlorite is stable in alkaline aqueous solution and is readily available as a 5% solution sold as a household bleach. [E.g. Chlorox™] or as 10% and 12% solutions sold in pool supply stores.

Once in the water, equilibrium is established between the strong oxidant HClO and the weaker ClO⁻ ion

$$H_2O + HOCl \Leftrightarrow H_3O^+ + OCl^- \qquad Ka = 3 \times 10^{-8}$$

The equilibrium is pH dependent and is very sensitive in the range of pH 7 to 8.


Effect of pH on [HCℓO] and [CℓO⁻]
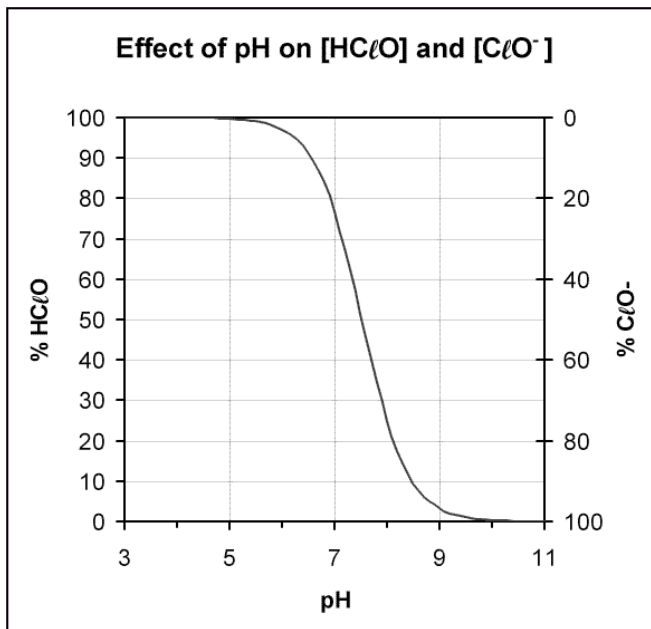
The negative charge on the hypochlorite ion hinders passage through bacterial membranes, so HOCl is the preferred species to oxidize the cell contents. (HOCl is about 80 times more effective than the OCl- anion.)

Conversion of almost all free chlorine to HOCl is easily accomplished by dropping the pH to 6 or so.

But at a pH of 2 or lower, chlorine gas is evolved and even mildly acidic water will corrode metals and grouting in tiled pools.

 The addition of calcium ions to the water to minimize leaching of tile grout is an interesting example of the common ion effect in solubility.

Most grouting preparations use Portland cement which contains calcium silicates and some $CaSO_4$ which, although only slightly soluble, does dissociate into free ions. In acidic water, the sulfate can combine with H^+ ions to form HSO_4^-.

$$CaSO_{4\,(s)} \Leftrightarrow Ca^{2+}_{(aq)} + SO_4^{2-}_{(aq)}$$

$$+$$

$$H^+_{(aq)}$$

$$\downarrow\uparrow$$
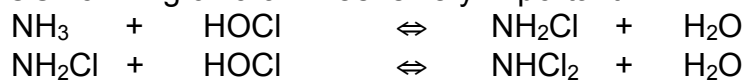
$$HSO_4^-_{(aq)}$$
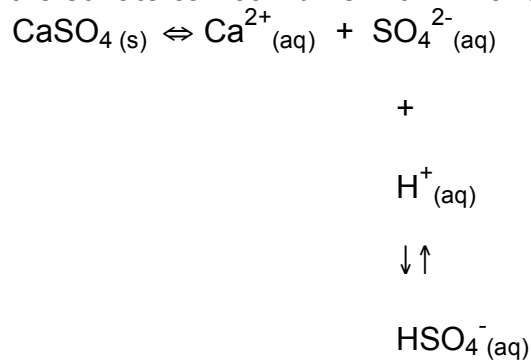
To prevent this, extra calcium can be added (as $CaCl_2$) which shifts the equilibrium in the direction of the solid $CaSO_4$.

Low calcium ion levels combined with low pH in pool water can lead to leaching of copper from pipes and that can lead to "green hair". If the water becomes acidic, copper elements in the pool heater, copper pipes and bronze pump impellers all leach copper ions into the water. The copper soaks into hair. Precipitation does not occur until the person shampoos with a high-pH shampoo. The green precipitate (a mixture of $CuSO_4$ -$Cu(OH)_2$) is most noticeable in blonde hair, especially bleached hair where the hair shaft often lacks natural oils that reduce water absorption.

The "Langelier Saturation Index" measures the relative concentrations of Ca^{2+} and CO_3^{2-} to indicate if $CaCO_3$ will precipitate out of solution and affect the clarity of the water or form scale that can be unsightly or cause harm to pumps and other pool equipment. Since CO_3^{2-} concentration is pH dependent and HCO_3^- is added to stabilize pH, the LSI is an interesting example of the "intersecting equilibria" that make pools so fascinating.

Chloramines

The tendency of ammonia and ammonia-like compounds (including proteins) to react with HOCl forming chloramines is very important:

$$NH_3 \quad + \quad HOCl \quad \Leftrightarrow \quad NH_2Cl \quad + \quad H_2O$$
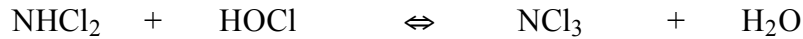$$NH_2Cl \quad + \quad HOCl \quad \Leftrightarrow \quad NHCl_2 \quad + \quad H_2O$$

Chloramines are mildly toxic to bacteria, but tend to be irritating to eyes and skin, so they are unwelcome additions to the pool.
Fortunately, Chloramines react with each other, as

$$NH_2Cl \quad + \quad NHCl_2 \quad \Leftrightarrow \quad N_{2\,(g)} \quad + \quad 3\,HCl$$
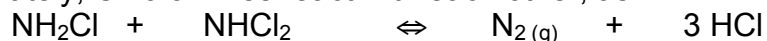
If too much HOCl is available, an undesirable competing reaction takes place.

$$NHCl_2 \quad + \quad HOCl \quad \Leftrightarrow \quad NCl_3 \quad + \quad H_2O$$

Nitrogen trichloride is very irritating to eyes and mucous membranes. It off-gases to the air creating a distinctive "swimming pool" smell that most people identify as the smell of chlorine. Ironically, if the pool has the correct levels of chlorine, there will be little if any odour.

This problem is especially troublesome in indoor pools where recent efforts at energy-conservation have reduced air-flows and the degradation products are not vented efficiently. This allows too much trichloramine to form which then off-gasses intact.

A recent paper in the European Respiratory Journal, (Vol. 19, Number 4) proposed that a cause-effect relationship has been established between the presence of chloramines in the air of indoor swimming pools and the increased occurrence of asthma in swimming instructors and lifeguards. It may also provide an explanation of why an abnormally large proportion of competitive swimmers suffers from asthma.

"Superchlorination" is used to rid pools of chloramines that build up through reaction with protein and other byproducts of humans swimming in the pool.

$$2\,NH_3 \quad + \quad 3\,HOCl \quad \Leftrightarrow \quad N_{2\,(g)} \quad + \quad 3\,HCl \quad + \quad 3\,H_2O$$

Superchlorination
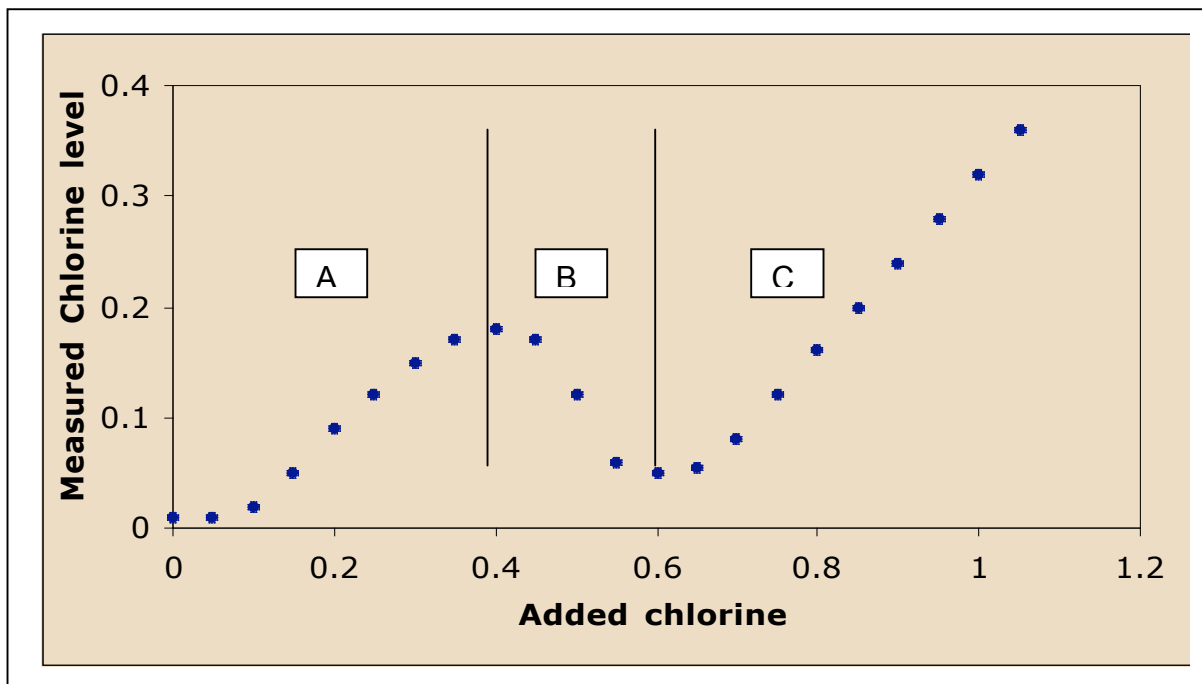
Region A shows a low slope as some of the added chlorine is used in reactions that produce chloramines.

Region B shows the destruction of chloramines as added HOCl is used up in the conversion of chloramines to $N_{2\,(g)}$ and HCl.

Region C shows the rise in free chlorine concentration, as added chlorine is no longer combined with organic compounds.

Superchlorination is used to break down the monochloroamine into off-gassed components.

[*Note the potential confusion between "hypo" the popular name for thiosulfate and the pool chemical "hypochlorite"*]

Indoor pools with low air circulation also suffer from "phantom chloramine". Chemicals like potassium monopersulfate destroy chloramines, but react with test kit chemicals in the same way that chloramines do. Current literature suggests that an unknown chemical in such pools also imitates chloramines in the test kits.

BUFFERING:
To maintain a stable pH level in the desired range, sodium bicarbonate can be added in amounts of about 100 mg/kg [about 6 kg for a medium sized 60,000 L pool].
In areas of high rainfall, the acidity of the rain can be a factor. Naturally "pure" rain has a pH of about 5.5 and "acid rain" has been measured with pH values as low as 2.

Fortunately, as the pH goes down, more HClO is formed from ClO^- ions and the germicidal activity of the residual free chlorine actually increases.
Since the use of NaOCl or $Ca(OCl)_2$ will slowly tend to raise the pH, acid salts like $NaHSO_4$ can be used to lower it. In some commercial pools, CO_2 is bubbled into the water to shift the bicarbonate equilibrium to a lower pH and Na_2CO_3 is used to raise it. (Some of these Pool products have entertaining technical names like pH Up, pH Down and "Quick Up" and "Quick Down".)

LOSSES IN SUNLIGHT:

Hypochlorite undergoes rapid photolysis in the presence of UV light
[λ = 290 to 350 nm] from sunlight.
About 90% of chlorine consumed by outdoor pools is the lost due to the photolysis reactions:

$$2\ OCl^- \ + \ \nu_{UV} \ \rightarrow \ 2\ Cl^- \ + O_{2\,(g)}$$
and
$$2\ HOCl^- \ + \ \nu_{UV} \ \rightarrow \ 2\ HCl + O_{2\,(g)}$$
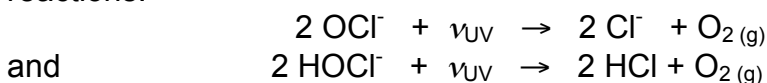
To stabilize chlorine levels, the herbicide **isocyanuric acid** [toxic to radishes and barley] is added to the water and reacts with OCl^- to give dichloro(iso)cyanuric acid. This is not broken down by sunlight, but the equilibrium reaction will shift to compensate for losses of OCl^-.

Cyanuric Acid - Chlorine Equilibrium

(iso)cyanuric acid + 2 O⁻-Cl ⇌ dichloro(iso)cyanuric acid + 2 HO⁻
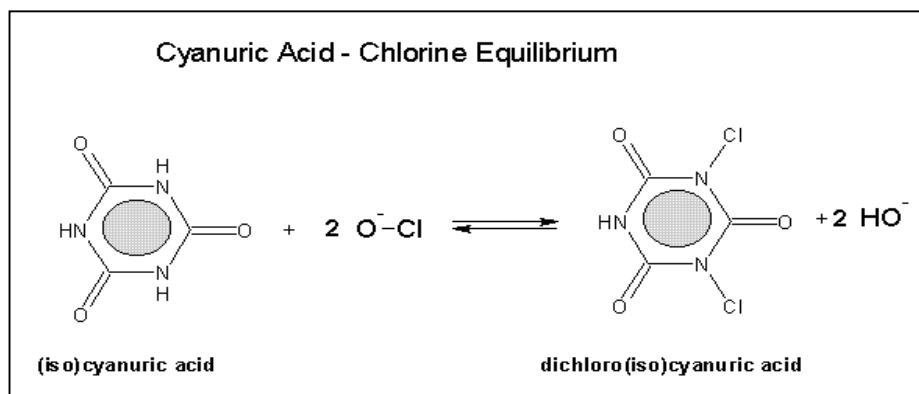
In this way cyanuric acid acts as a "chlorine buffer" for outdoor pools.

It is instructive to have students consider what the effect of adding an excess of cyanuric acid would be on the chlorine levels required for sanitation. It is an excellent example of how Le Chatelier's Principle shows that "More" is not always "Better".

Have students consider the effectiveness of using the commercially available dichlorocyanuric acid ["Stabilized Chlorine"] as the only source of chlorine for an outdoor pool. As the season progresses, more residual cyanuric acid would shift the equilibrium to require more and more of the "Dichlor" compound just to maintain a constant hypochlorite level in the water!
In fact, once the cyanuric acid level reaches about 50 ppm, the cheaper "unstabilized" hypochlorite salts are the best source of chlorine for an outdoor pool.
(Knowing some chemistry can save money!)

For an excellent reference article on Chloroisocyanurates for Disinfection of Water, see the article by Brian Rohrig and Gabriel Pinto in JChemEd (Vol 80, no. 1) Jan 2003.

For indoor pools, use of "stabilized chlorine" to avoid photolysis is unnecessary. However indoor pools usually are much smaller than outdoor ones, so the concentration of waste products left by each bather tends to be higher. To maintain a constant level of Free Chlorine in these smaller pools when many bathers arrive to swim, either the pool has to be run with much higher HOCl concentrations, or the "extra chlorine" can be stored by keeping a constant level of Cyanuric Acid (about 30 ppm) in the pool.

The higher levels of HOCl lead to formation of more irritating chloramines so the use of cyanuric acid is advantageous in these situations. But care is required.
Cyanuric acid has biological activity as a herbicide, and health regulations require that levels be kept below 200 ppm. A pool above that limit must be drained and refilled. Recent marketing of Trichlorocyanuric acid [trichloro-s-triazinetrione] in convenient tablet form shows the importance of understanding the underlying chemistry of the products. Use of this product not only continuously adds cyanuric acid, but also causes significant lowering of pool pH, especially in weakly buffered water.

[For specific quantitative information about these issues, check:
http://www.troublefreepool.com/viewtopic.php?t=628]

MEASUREMENT:

1. **pH** is measured using Phenol Red dye since this dye is resistant to the bleaching action of chlorine at levels of 1 or 2 ppm.

2. **Cyanuric Acid** levels are measured by adding melamine to form a salt that precipitates and creates turbidity proportional to the amount of cyanurate present.

Test For Cyanuric Acid

cyanuric acid   melamine   melamine cyanuric acid precipitate
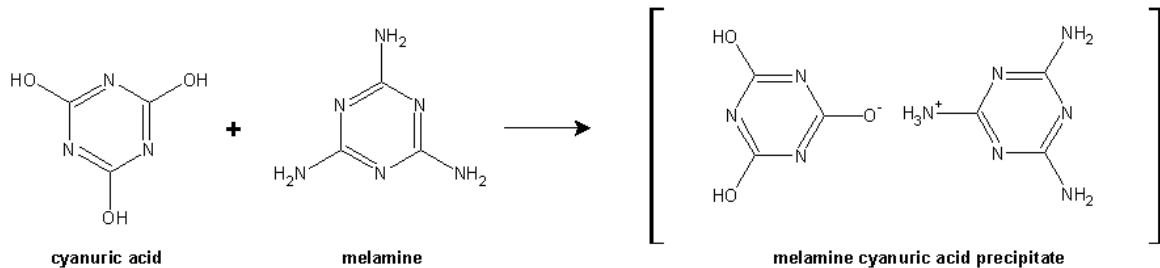
Pool stores do the test with a small test tube and a black spot on a calibrated stick. The marks on the stick follow Beer's Law where: **Conc. = K e$^{-a\ Depth}$**

Cyanuric Acid Test

$y = -33.753 Ln(x) + 160.15$

$R^2 = 0.9956$
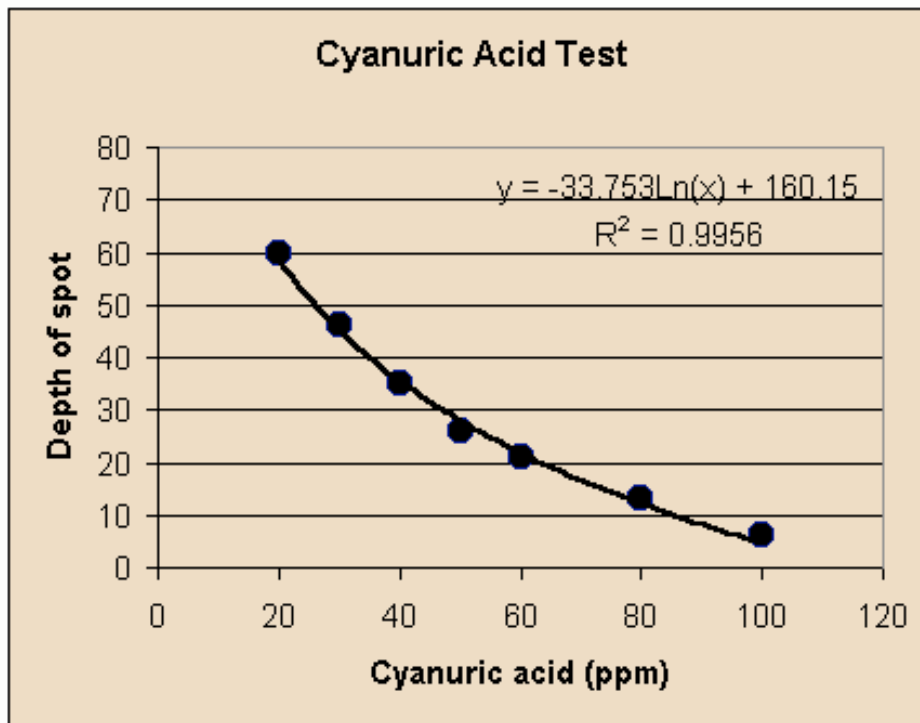
3. My next project is to explore this test and adapt it to the classroom setting. There are lots of related principles here… the test is exactly like taking Secchi disk readings to measure suspended solids in lake water.

4. % Available Chlorine Measurement Scale

This scale is a practical, if technically bizarre way, of rating various chlorine compounds. It accounts for different formulas and different purities of commercial preparations but is based on a chemical mistake.

When Cl_2 is bubbled into water, it forms <u>one</u> ClO^- molecule as
$$Cl_2 + H_2O \rightarrow HClO + HCl$$
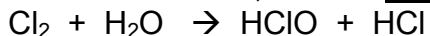
Thus the % available chlorine rating should be 50%.
However, by definition, chlorine gas is given a rating of 100.

Pure LiClO   would have a % available chlorine calculated as:
$$Cl/ LiClO = 35.5/58.5 = 0.61 \text{ or } 61\%$$
But we must <u>multiply by 2</u> to satisfy the definition   = 122%

However, commercial LiClO powders are about 30% pure
So Lithium hypochlorite Pool powder is 0.3 * 122 = 37% *available chlorine*.

Pure $Ca(ClO)_2$: $2*Cl / Ca(ClO)_2$ = 2 * 35.5 / 143 = 0.497
Multiply by 2   = 0.99 or 99%
But commercial preparations are 65 to 70% pure. So the % *available chlorine* rating for calcium hypochlorite Pool powder is 65-70

Sodium hypochlorite is not stable in the solid form, so is sold as solutions of various wt. % concentrations. Usually, the pool preparations for NaClO are 12 or 15% concentration.
Pure NaClO :   Cl / NaClO = 35.5 / 74.5 = 0.48
Multiply by 2 = 96%
A 10% solution would have an available chlorine rating of 9.6 or 10%
Household bleach (5.25% NaClO) has available chlorine rating of about 5

5. Chlorine levels in the range of 0 – 2 ppm are usually measured by simple color comparison kits.

(a) Ortho-tolidine [OTO] (which is a dimer of ortho-toluidine) has been widely used in the past, but concerns about its carcinogenic nature have caused it to fall out of favor. OTO reacts with hypochlorite easily, but also reacts more slowly with chloramines, so it is not completely reliable when measuring "free" chlorine – the chlorine in the form of OCl^- and HOCl, effective at sanitation. Reaction of the test solution with chloramines can lead to optimistic readings and thus to an underchlorinated pool.
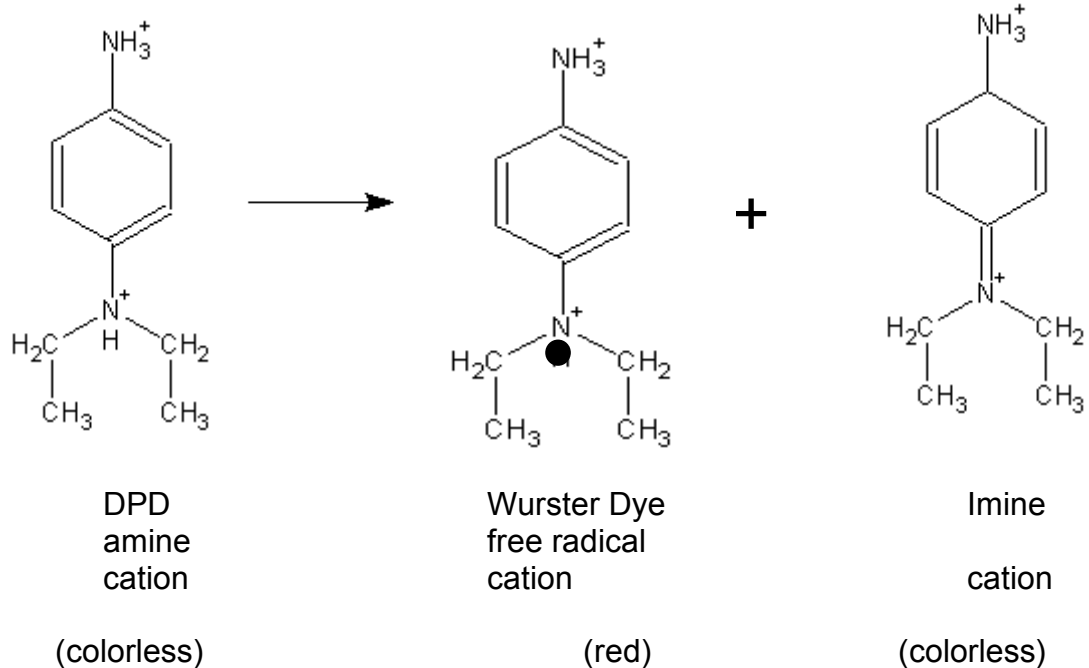

(b) Currently, commercial measurement kits usually use DPD

[N,N-diethyl-p-phenylenediamine]. A pre-measured amount in tablet form is added to a sample of pool water and the DPD quickly forms a red complex with free chlorine. Calibrated comparison tubes are matched to the color giving the chlorine content in ppm.
Chlorine concentrations above 10 ppm can result in bleaching of the DPD complex and the sample appears to have <u>no</u> chlorine. Usually, this condition is encountered only while shock treatment for the pool is being carried out and instructions warn users that they should "watch for a red flash" at the beginning of the test to indicate that the DPD is being bleached out.

If the test sample is allowed to react with DPD mixed with sodium iodide for 3 to 5 minutes, reaction occurs even with combined chlorine (in the form of chloramines etc.) and a reading of the "total chlorine" level results.

N,N-diethyl-p-phenylenediamine

| DPD | Wurster Dye | Imine |
amine	free radical	
cation	cation	cation
(colorless)	(red)	(colorless)

DPD is a 2+ cation, usually used as a sulfate salt. Rapid reaction with Chlorine produces "Wurster Dye", a red 2+ cation which is also a free radical. This dye further oxidizes to a colorless Imine product. With small amounts of chlorine near neutral pH, Wurster dye is the dominant product. At higher levels, the unstable, colorless Imine is produced and rapid fading of the colored solution occurs.

DPD can also be used to measure the amount of "combined chlorine" in the form of NH_2Cl and $NHCl_2$. The test sample is acidified and a small amount of KI is added. At pH 6.2 to 6.5, about 0.1 mg of KI is used in a 10 mL sample to determine the monochloramine as:

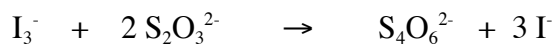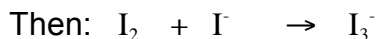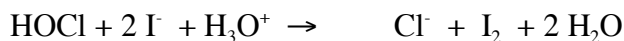$$NH_2Cl +3\ I^- + H_2O + H^+ \rightarrow\ NH_4OH + Cl^- + I_3^-$$
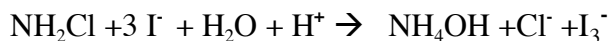
The tri-iodide then oxidizes DPD forming the red Wurster dye.
[Of course, the free chlorine in the sample also produces the red dye.]

By adding excess KI (>0.1 g per 10 mL sample) the dichloramine can also be measured as:

$$NHCl_2 +3\ I^- + H_2O +2\ H^+\ \rightarrow\ NH_4OH +2\ Cl^- + I_3^-$$
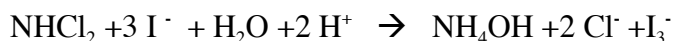
Since this last mixture will react DPD with all chlorine, it gives the total chlorine in the sample, so the dichloramine level can only be observed indirectly through sequential measurements

6. Laboratory measurement of Chlorine is usually done by the redox titration of HOCl using iodide and thiosulfate ions with a starch indicator to show the endpoint as I_3^- is completely consumed.

$$HOCl + 2\ I^- + H_3O^+\ \rightarrow\qquad Cl^- + I_2 + 2\ H_2O$$

$$\text{Then:}\quad I_2\ +\ I^-\quad \rightarrow\ I_3^-$$

$$I_3^-\ +\ 2\ S_2O_3^{2-}\qquad \rightarrow\qquad S_4O_6^{2-}\ +\ 3\ I^-$$

(*See oxychem experiments in sodium hypochlorite handbook at*
http://www.oxychem.com/products/handbooks/bleach.pdf. An excellent microtitration version of this experiment was published by Michael Jansen in Chem13News, [Jan. 1997, #254, Pg. 9].)

7. Student measurement of lower concentrations of Chlorine can be done by titrating the "pool water" directly into acidified methyl orange which reacts 1:1 with free chlorine.

Methyl Orange dye   Chlorinated dye
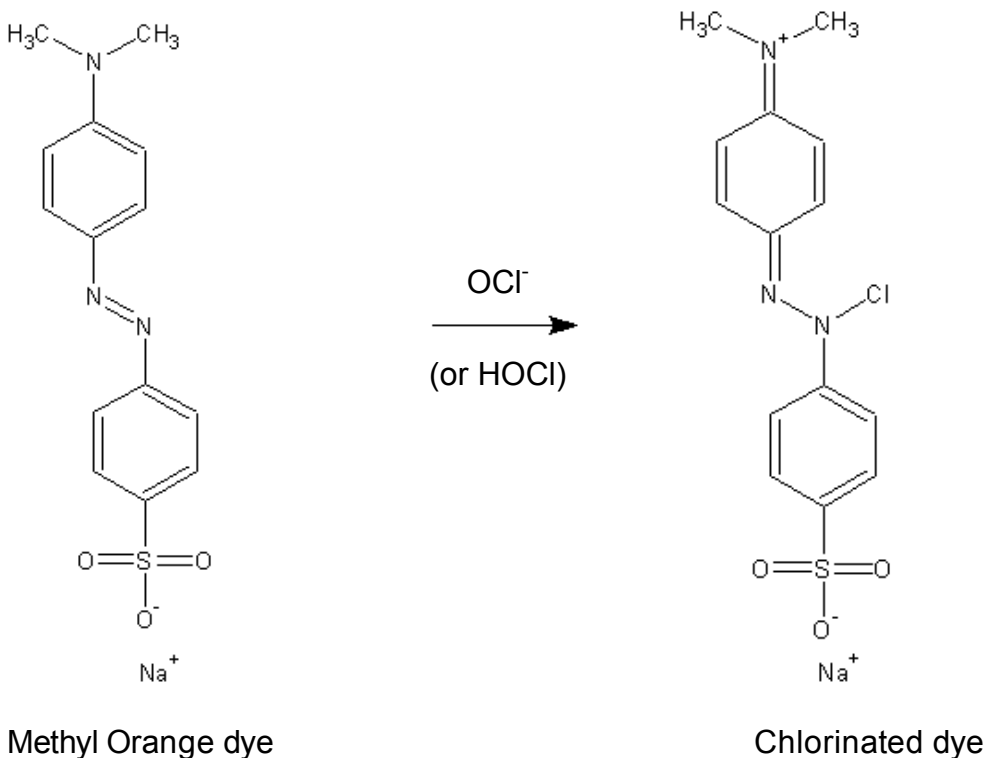
In the "Student Activities" link, I propose some student activities based on construction of "Pools" using ~100 PPM Chlorine. This higher concentration permits the use of tap water (which one hopes is already 0.5 to 1.0 PPM) and is more suitable to the precision of high school lab equipment. However, if you want to model the superchlorination graph, distilled water and 2-PPM pools must be used.

(I have tried superchlorinating 200 PPM pools, but any added urea seems to be converted completely to NCl_3, which collects as bubbles in the test tube.)

Safety Considerations

Chlorine compounds can be hazardous and must be treated with respect. Because of the widespread use of these compounds in household cleaning agents and as a disinfectant, it is important that students recognize the hazards of using Chlorine and learn to work with it in a safe manner.

The experiments have been designed to keep exposure of students far below what would be encountered by using an average household cleanser.

Nevertheless, Chlorine and chloramines do affect the respiratory system at low levels so CARE must be taken to minimize the chance that either will be generated in the classroom.

Chlorine gas is generated when HClO is placed in acidified solution.

Always add the Pool water to the acidified Methyl Orange so that the hypochlorite reacts with dye before Cl_2 gas is formed.

Using micro-techniques, there is a minimum amount of chlorinated water in the reaction vessel

[See "Student Activities" link for proposed experiments]