

Cyanuric Acid Technology

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Cyanuric acid was identified as a chemical substance over two centuries ago. However, it was not until the late 1950's that it attained industrial significance with the introduction of chlorinated isocyanurates by Monsanto and FMC. Although the majority of cyanuric acid production is used in the manufacture of chlorinated isocyanurates, some of it is also used as a swimming pool available chlorine stabilizer. Cyanuric acid is also used in the manufacture of specialty intermediates used in the production of plastics and coatings. The properties, chemistry, uses, etc. of cyanuric acid and chloroisocyanurates have been comprehensively reviewed (Wojtowicz 1993a and 1993b). In addition to its function as a stabilizer for available chlorine, cyanuric acid also contributes to buffering of swimming pool water. This paper discusses the structure, properties, analysis, chemistry, manufacture, and uses of cyanuric acid as well as the mechanism of stabilization, the effect on disinfection, and the effect of chloramine formation.

Typical Analysis

Typical analysis of commercial cyanuric acid (CA) is shown in Table 1. The product also typically contains small amounts of ammonium sulfate or ammonium nitrate (<0.2%).

Structure

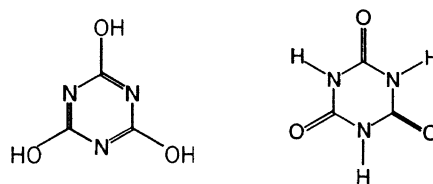
Cyanuric acid can exist in either of two structures as shown in Figure 1. The keto form

Cyanuric Acid	>99%
Ammelide and Ammeline	≤0.5%
Water	~0.1%*
pH of saturated solution at 25°C	4.5-5.0

*Water content will vary with manufacturer; some products can contain up to 4% water.

Table 1 – Typical Analysis of Commercial Cyanuric Acid

predominates in the solid whereas the enol form predominates in solution. The keto form is technically referred to as isocyanuric acid whereas the enol form is simply cyanuric acid. Both forms are collectively referred to as cyanuric acid.



enol

keto

Cyanuric Acid Isocyanuric Acid

Figure 1 – Cyanuric Acid Structures

Properties

Physical

Cyanuric acid is a white crystalline solid. Some

Journal of the Swimming Pool and Spa Industry

Volume 4, Number 2, pages 9-16

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The Journal of the Swimming Pool and Spa Industry

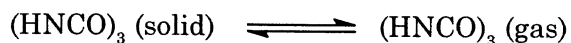
of its physical properties are summarized in Table 2.

Solid Forms	Granular, powder
Aqueous Solubility at 25°C	1500 mg/L
“ “ “ 50°C	7000 mg/L
Density (anhydrous)	1.75 g/mL
“ (dihydrate)	1.66 g/mL
Melting Point	Does not melt up to 350°C

Table 2 – Some Physical Properties of Cyanuric Acid

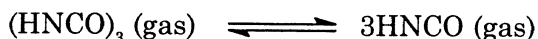
Sublimation

Solid cyanuric acid does not melt, instead it undergoes sublimation, i.e., it volatilizes directly from the solid to the gaseous state. Significant sublimation commences at about 350°C as shown by the reaction below, where (HNCO)₃ is a linear representation of the tricyclic formula of CA.



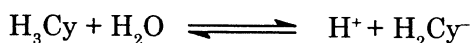
Dissociation in the Gaseous State

Heating gaseous cyanuric acid above 400°C causes dissociation into isocyanic acid as shown below.



Ionization in Aqueous Solution

Cyanuric acid (H₃Cy, where Cy represents the triisocyanurate anion) is a weak acid, even weaker than carbonic acid. The pH of a saturated solution is only 4.8. Ionization forms hydrogen and cyanurate ions as shown below:



Effect on Swimming Pool Water Alkalinity

Addition of cyanuric acid will lower the pH of

pool water. When the pH is restored to the normal range, total alkalinity will be increased, due to formation of cyanurate ions. Cyanuric acid is 73–91% neutralized at pool pH. Total alkalinity is corrected for cyanurate alkalinity by the following equation to yield carbonate alkalinity (Wojtowicz 1995):

$$\text{Alk}_{\text{CORR}} = \text{Alk}_{\text{TOTAL}} - 0.33 \cdot \text{CA}$$

Buffering Effect

Aqueous cyanuric acid and cyanurate ion form a buffer system similar to carbonic acid and bicarbonate ion and therefore will contribute to the buffering of swimming pool water (Wojtowicz 1999).

Toxicity

Cyanuric acid is essentially non-toxic to humans, animals, wild-life, and aquatic life. The toxicology of cyanuric acid and chlorinated isocyanurates have been reviewed (Hammond *et al* 1986). The acute toxicity (oral LD₅₀) is >10 g/Kg for rabbits.

Biodegradability

Cyanuric acid undergoes biodegradation by some soil bacteria (Bagnall *et al* 1984).

Analysis of Cyanuric Acid

Solid Cyanuric Acid

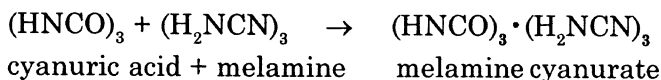
Solid cyanuric acid dissolved in water can be titrated with sodium hydroxide solution using a recording pH meter; the equivalence point is at about pH 8.8–9.0. Ammelide and ammeline are also titrated (Wojtowicz 1974). Ammelide and ammeline do not interfere if the titration is performed in a dimethyl sulfoxide (DMSO)–benzene mixed solvent using tetrabutyl ammonium hydroxide instead of sodium hydroxide (Morales 1968). Ammelide and ammeline can be determined by gas chromatography after dissolving cyanuric acid in trimethylsilylacetamide (Wojtowicz 1974).

In Swimming Pool Water

By Test Kit – The swimming pool test kit

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analysis is based on the turbidity caused by precipitation of cyanuric acid as melamine cyanurate. Since melamine cyanurate has a small solubility (5–10 ppm), the method is not suitable for very low cyanuric acid concentrations (<10 ppm). The accuracy of the test kit method is ±10%. The reaction is shown below.

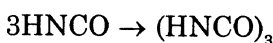
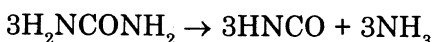


Other Methods – Dilute aqueous solutions of cyanuric acid can also be analyzed by liquid chromatography (Downes *et al* 1984), ion chromatography (Wojtowicz 1985), uv spectrophotometry (Downes *et al* 1984), and differential pulse polarography (Struys and Wolfs 1987). These methods are more accurate than swimming pool test kits.

Manufacture of Cyanuric Acid

Pyrolysis Of Urea

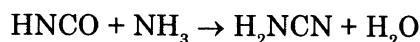
Cyanuric acid is manufactured by pyrolyzing (i.e., heating) urea (see Figure 2). A molten or a concentrated aqueous solution of urea is sprayed onto a moving bed of crude cyanuric acid granules in a directly heated rotary kiln. The crude cyanuric acid is maintained at about 250°C for about one hour. About 90% of the crude cyanuric acid exiting the kiln is recycled to the front of the kiln. Urea dissociates into isocyanic acid and ammonia in the kiln. The isocyanic acid trimerizes to cyanuric acid.



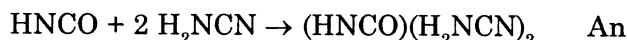
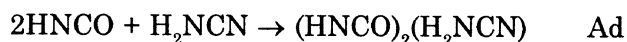
The ammonia offgas from the kiln is scrubbed in the urea feed solution to remove small amounts of volatilized urea and cyanuric acid and can either be flared (i.e., burned) or recovered as ammonium nitrate by reaction with nitric acid for use as fertilizer.

Byproduct Formation

Pyrolysis of urea also produces undesirable aminotriazine byproducts which can form by reaction of ammonia with isocyanic acid to yield cyanamide.



Cyanamide can react with isocyanic acid or with itself to produce ammelide (Ad), ammeline (An), or melamine (Mm). The formulas for Ad, An, and Mm shown below are linear representations for the structural formulas shown in Figure 3. Crude cyanuric acid usually contains 80% cyanuric acid, 18% ammelide, 2% ammeline, and <0.1% melamine.



Hydrolysis of Aminotriazines

The crude cyanuric from the kiln is pulverized

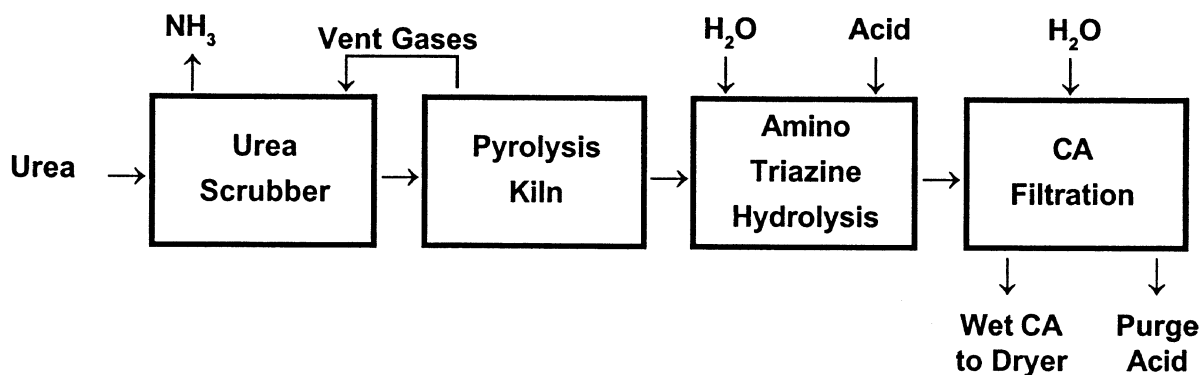
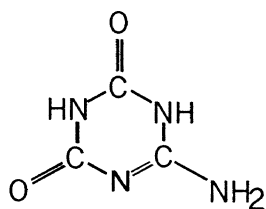
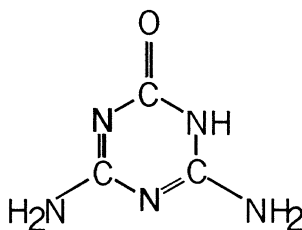


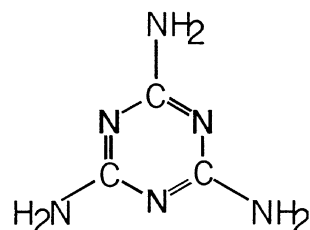
Figure 2 – Process Flow Diagram for Manufacture of Cyanuric Acid



Ammelide



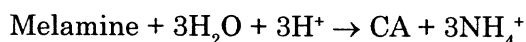
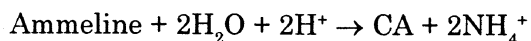
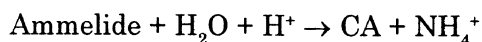
Ammeline



Melamine

Figure 3 – Structures of Aminotriazines

to a powder, slurried in dilute sulfuric (or nitric) acid, and heated at the boiling point for about one hour. This hydrolyzes the aminotriazines to cyanuric acid as shown below.



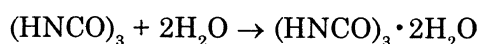
Recovery of Purified Cyanuric Acid

The purified cyanuric acid crystals from the hydrolysis step are filtered, washed with water to remove the digestion acid, and flash dried. The dry powder is compacted and granulated.

Reactions of Cyanuric Acid

Hydrate Formation

Cyanuric acid forms a dihydrate on reaction with water.

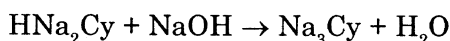
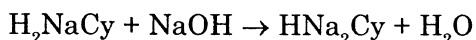
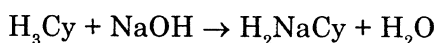


The dihydrate effloresces, i.e., it loses water on exposure to air of low to moderate humidity. When heated to 57°C, the dihydrate undergoes a transition to anhydrous cyanuric acid and water.

Neutralization (Salt Formation)

On reaction with sodium hydroxide, cyanuric

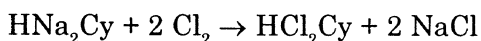
acid forms a series of sodium salts, i.e., mono-, di-, and trisodium cyanurate as shown by the reactions below, where Cy represents the triisocyanurate anion, i.e., $(\text{CNO})_3^{3-}$.



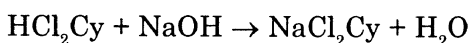
The solubilities of these salts are greater than that of CA, e.g., the solubilities of mono-, di-, and trisodium cyanurates are: 0.9, 5.7, and 14.1 g/100 mL of solution at 25°C.

Chlorination

Preparation of Dichlor – Chlorination of an aqueous slurry of disodium cyanurate produces dichloroisocyanuric acid.



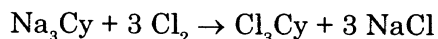
The dichloroisocyanuric acid is recovered by filtration and is washed with water to remove the byproduct sodium chloride. It is reslurried in water and reacted with sodium hydroxide to produce sodium dichloroisocyanurate (Dichlor).



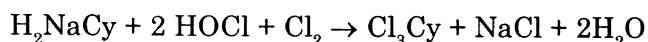
The sodium dichloroisocyanurate crystals are isolated by filtration. The crystals are flash dried with hot air to so-called anhydrous sodium dichloro-

isocyanurate (~2% water, ~63% available chlorine). The resultant powder is then compacted and granulated. Treatment with water converts anhydrous sodium dichloroisocyanurate to the dihydrate (12.5–13.0% water, 55–56% available chlorine). Dichlor is used primarily for spa sanitation. Another important use for Dichlor is in commercial dishwasher formulations.

Preparation of Trichlor – Reaction of an aqueous solution of trisodium cyanurate with gaseous chlorine yields trichloroisocyanuric acid (Trichlor).



Trichloroisocyanuric acid is also manufactured by reaction of an aqueous slurry of monosodium cyanurate with chlorine and hypochlorous acid.



The trichloroisocyanuric acid crystals are recovered by filtration and water washing to remove the byproduct sodium chloride. Flash drying with hot air gives a dry powder which is compacted and granulated and then pressed into 1" and 3" tablets as well as sticks for use in swimming pool sanitation.

Uses of Cyanuric Acid

Manufacture of Chloroisocyanurates

Most of the cyanuric acid produced commercially is converted to chloroisocyanurates. See above for a discussion of the chemistry.

Stabilizer for Available Chlorine

Cyanuric acid is used in swimming pools as a stabilizer for available chlorine. See below for a discussion of the mechanism of stabilization.

Other Uses for Cyanuric Acid

Cyanuric acid has a number of important non-pool uses which include preparation of high performance magnet-wire enamels and in electrical varnishes, plastics with enhanced properties, flame retardant resins and solid lubricants, cross-linking and curing agent in the manufacture plastics and coatings. CA is also used to reduce nitrogen oxides (NOx) in stationary diesel engine exhaust gases.

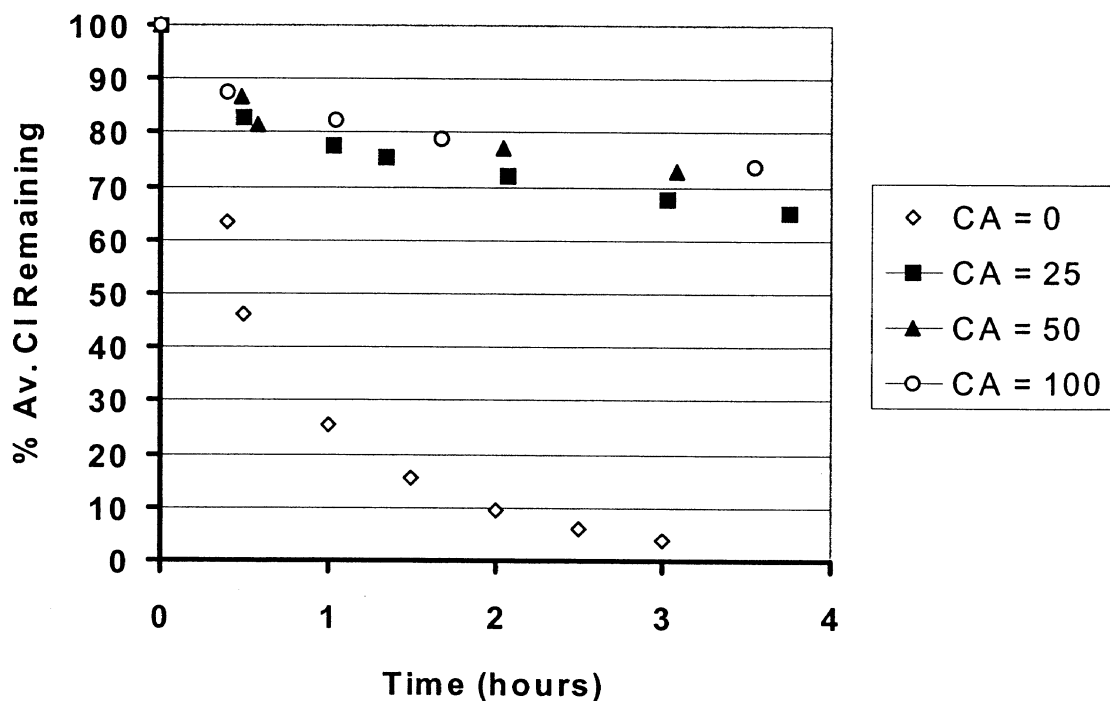
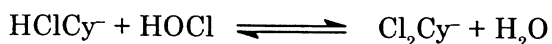
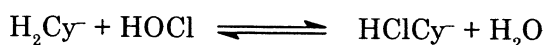
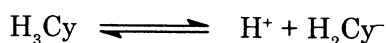
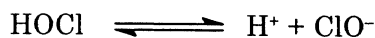


Figure 4 – Effect of Cyanuric Acid on Photochemical Decomposition of Available Chlorine

Stabilization of Available Chlorine by Cyanuric Acid

Cyanuric acid is used in outdoor swimming pools to stabilize free available chlorine against photochemical decomposition by sunlight (Fuchs and Lichtman 1961). Near optimal stabilization occurs at 25–50 ppm cyanuric acid as shown in Figure 4. (Nelson 1974). The main equilibria in swimming pool water are (Wojtowicz 1996):



All of the above chlorine compounds absorb ultraviolet light. The wavelengths (λ) of maximum absorption are tabulated in Table 3.

Ultraviolet light from the sun is partially absorbed by the ozone layer in the upper atmosphere (the stratosphere), i.e., all wavelengths below 290

Compound	λ_{max} nm
Hypochlorous acid, HOCl	235
Hypochlorite ion, ClO^-	290
Monochlorisocyanurate ion, HClCy^-	215
Dichlorisocyanurate ion Cl_2Cy^-	220

Table 3 – Absorption Maxima for Main Chlorine Species

nm are absorbed. Since HOCl and the chloroisocyanurates absorb primarily below 290 nm, they are relatively stable to decomposition. By contrast, hypochlorite ion whose absorption maximum occurs at 290 nm, absorbs uv light out to about 350 nm and therefore will be decomposed by sunlight. Since available chlorine exists predominately in the form of chloroisocyanurates, photodecomposition is greatly reduced, i.e., the available chlorine is considered to be stabilized. Addition of bromide to the pool will result in a drastic reduction in the stabilizing effect of cyanuric acid (see Wojtowicz 2001).

Swimming Pool Disinfection

Bacterial Kill Time

The following equation was obtained on analysis of literature data on the effect of cyanuric acid on

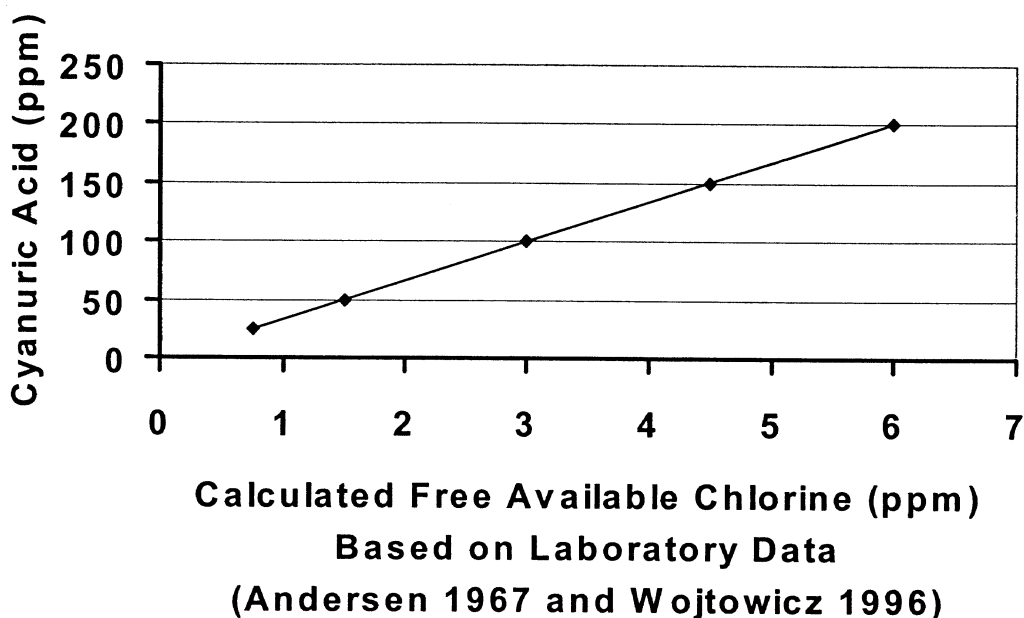


Figure 5 – Minimum Available Chlorine for 30-second 99% Kill Time of *S. Faecalis* at pH 7.5 and 85°F

the kill time of *S. faecalis* in distilled water (Wojtowicz 1996):

$$t_{0.99} (\text{pH } 7.5 @ 85^{\circ}\text{F}) = 0.03 + 0.014[\text{C}_{\text{yT}}/\text{Cl}_{\text{T}}]$$

where $t_{0.99}$ is the 99% kill time, C_{yT} is the total cyanurate concentration in ppm and Cl_{T} is the free available chlorine concentration in ppm. This equation was used to calculate the minimum available chlorine for a 30-second 99% kill time at 85°F for various cyanuric acid concentrations which are plotted in Figure 5. The plot predicts that higher free av. Cl concentrations are required to achieve a 99% kill for *S. Faecalis* in 30 seconds at pH 7.5 at 85°F with increasing CA concentration. The NSPI recognizes that cyanuric acid affects the rate of disinfection by chlorine and recommends higher av. Cl levels for stabilized pools compared to that in unstabilized pools, i.e., 1–3 ppm vs. 0.4 ppm (ANSI/NSPI–5 1995). In fact the NSPI has a draft proposal to raise the ideal recommended av. Cl range to 2–4 ppm (ANSI/NSPI–4 199X).

Interferences in Swimming Pool Disinfection

Combined Chlorine Formation

Impurities introduced by bathers (i.e., sweat and urine) add nitrogen compounds to the water. Some of these compounds (e.g., ammonia, creatinine, amino acids, etc.) react with free available chlorine to form combined chlorine. Combined chlorine compounds are poor disinfectants because they bind chlorine very strongly, and consequently do not hydrolyze significantly to hypochlorous acid. An increase in combined chlorine reduces the concentration of free available chlorine and therefore increases the kill time of bacteria for a given total av. Cl. Indeed, experimental data (Fitzgerald and DerVartanian 1967) show that ammonia greatly increases the kill time of chlorine whether CA is present or not. At low to moderate levels of added ammonia, the CA system as expected showed longer kill times than the CA-free system.

Studies in swimming pools report that kill times are comparatively long whether CA is present or not. Gardner (1972) states that “the reason for this is presumably the effect of ammonia and amines on the free HOCl concentration...”. He also states that “The aim of breakpoint chlorination, however,

is that the total chlorine concentration should always be kept in excess of the ammonia and amine concentration, and the effect of cyanuric acid on the HOCl concentration is then expected to be similar to the effect in the absence of ammoniacal nitrogen, i.e., as in the distilled water experiments”.

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About the Author

Now retired, **Mr. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U. S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 3266 N 151st Drive, Goodyear AZ 85338, phone number 623-535-8851. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide-UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.