In swimming pool operation

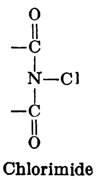
Comparison of Chlorinated Cyanurates With Other Chlorine Disinfectants

XAVIER KOWALSKI and THOMAS B. HILTON

THE CHLORINATED cyannurates have been used as disinfectants of swimming pool water for almost 6 years. These cyanurates include potassium dichlorocyanurate (potassium 1,3–dichloro–2,4,6–trioxohexahydro–*s*–triazine), sodium dichlorocyanurate (sodium 1,3–dichloro–2,4,6–trioxohexahydro–*s*–triazine), trichloroiso cyanuric acid (1,3,5–trichloro–2,4,6–trioxohexahydro–*s*–triazine), and dichloroiso cyanuric acid (1,3–dichloro–2,4,6–trioxohexadydro–*s*–triazine).

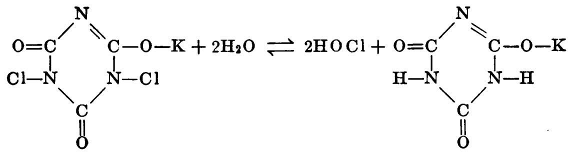
Early laboratory and in-use investigations indicated that the bactericidal properties of the chlorinated cyanurates are at least as effective as those of the hypochlorites (*1–5*). More recent laboratory findings (*6*, *7*) indicated that bacteria are killed at slower rates by the chlorinated cyanurates in the presence of at least 25 ppm cyanuric acid than by sodium hypochlorite, especially after only short exposure to the disinfectant solutions. Whether correlation exists between the laboratory methods and the swimming pool conditions was not shown.

The chlorinated cyanurates are imides characterized by two carbonyl groups flanking the nitrogen to which a chlorine atom is attached.



Chlorimide

In aqueous solutions the chlorinated cyanurates hydrolyze to form hypochlorous acid and a salt of cyanuric acid as indicated in the following equilibria expressions:



Potassium dichlorocyanurate — Potassium cyanurate

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

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

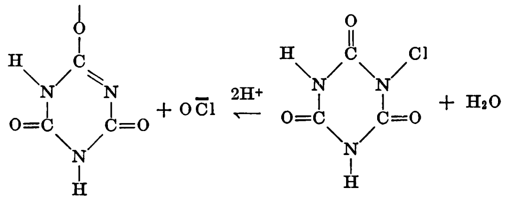
It is well known that chlorine in aqueous solution undergoes a series of complex reactions in the presence of ultraviolet light, resulting in the ultimate reduction to chloride ion and loss of available chlorine. Thus in sunlight, the chlorine in swimming pools is lost fairly rapidly when sodium hypochlorite, chlorine, or calcium hypochlorite are used as the chlorinating agents (*2*, *8*). Unless chemicals are added continuously or at frequent intervals, pools may experience critical periods when no disinfectant is present, especially when many bathers are in the pools.

However, chlorinated cyanurates or chlorine in the presence of 25 ppm or more cyanuric acid residual dissipate slowly in the presence of sunlight (*2*). This means that free chlorine residuals may be kept at a more constant level to provide the sanitizing protection required when it is most needed.

Mr. Kowalski is a senior research chemist in the inorganic chemicals division, research department, Monsanto Company, St. Louis, Mo. Mr. Hilton, now with Emery Industries, Inc., Cincinnati, Ohio, was a group leader for Monsanto. Mr. Allan Dickinson, Monsanto scientist, made the statistical analyses of the 1960 and 1963 swimming pool records.

Cyanuric acid residuals for stabilizing free chlorine may be obtained in swimming pool water in two ways. The preferred method is simply to add either cyanuric acid or one of its sodium salts in the desired amount at the beginning of the pool season. An alternate procedure is to allow a concentration of cyanuric acid to build up in the pool water as a natural consequence of the repeated use of chlorinated cyanurates, which hydrolyze to form cyanuric acid as a chemically stable and nonvolatile residue.

The exact mechanism for stabilizing chlorine by cyanuric acid is unknown. In strong solutions of available chlorine containing a high molar ratio of cyanuric acid to chlorine, little (probably less than 0.1 to 1 percent) free hypochlorite exists in the equilibrium mixture, as indicated by the heavier arrow below.



Presumably, chlorine in this form is not as labile to sunlight. Kinetically, this means that the rate of decomposition of available chlorine is a function of the concentration of the actual hypochlorite ion species as well as the ultraviolet energy received (*8*, *9*). Furthermore, regardless of the concentration of cynaurate ion, the biocidal effectiveness of chlorine must not be affected, as evidenced by the in-use pool data that we collected.

A practical and controlled test program was conducted in St. Louis County during the summer of 1960 to compare the disinfecting ability of the chlorinated cyanurates and the other commonly used sources of chlorine used in swimming pools. In addition, data representing normal routine operations for the 1963 season in St. Louis County were obtained from 138 semipublic and public pools to further document the the bactericidal effectiveness of the various sanitizing agents used.

Since the number of controlled variables was different in each period, it was necessary to evaluate separately the results for the 1960 and 1963 test periods.

In-Use Data 1960 Tests

Table 1 lists the 15 pools tested in 1960. Private pools A, B, C, and D and semipublic pool F were treated with potassium dichlorocyanurate. Two public pools, outdoor E and indoor

Table 1. Swimming pools in 1960 tests, St. Louis County, Mo.

Code and type	Capacity (thousand gallons)	Type of chlorination	Type of filtration	Water temperature (° F.)[1]	Bather load [2]
A. Private, outdoor	55	Potassium dichlorocyanurate.	Pressure, diatomite	80	0.2
B. Private, outdoor	19	do	do	82	.2
C. Private, outdoor	35	do	do	80	.1
D. Private, outdoor	29	do	do	80	.2
E. Public, outdoor	134	Chlorine gas with cyanuric acid.	do	82	2.1
F. Semipublic, outdoor	40	Potassium dichlorocyanurate.	do	81	.7
G. Public, indoor	82	Chlorine gas with cyanuric acid.	Pressure, sand	81	2.2
E*1*. Public, outdoor	162	Chlorine gas	do	81	1.0
E*2*. Public, outdoor	210	do	Pressure, diatomite	81	1.0
E*3*. Public, outdoor	450	do	do	79	.6
F*1*. Semipublic, outdoor	50	Sodium hypochlorite	Pressure, sand	82	1.1
F*2*. Semipublic, outdoor	35	Calcium hypochlorite.	do	82	1.2
F*3*. Semipublic, outdoor	75	Chlorine gas	do	82	.6
F*4*. Semipublic, outdoor	228	do	Pressure, diatomite	81	1.4
G*1*. Public, indoor	125	do	Pressure, sand	81	2.2

[1] Average high for season.
[2] Average daily number of bathers per 1,000 gallons.

Table 2. Disinfection records of test swimming pools, 1960, St. Louis County, Mo.

Month and day	Chlorine residual (ppm)	Cyanuric acid (ppm)	pH	Bather load [1]	*Escherichia coli*	Plate count	Quality ratings [2]
Private test pool B:							
July 19	0.4	19	7.3	0.42	0	4	0
July 26	.2	27	7.2	.10	0	1	0
July 30	.6	32	7.4	.05	1	29	2
August 5	.3	38	7.4	.14	0	7	0
August 17	.5	51	7.2	.11	0	9	0
August 26	.5	59	7.4	.18	0	1	0
August 30	.3	62	7.5	.27	0	0	0
September 2	.3	64	7.5	.16	0	82	0
September 7	.5	77	7.4	.11	0	82	0
Public outdoor test pool E:							
July 1	.7	29	7.5	1.33	0	0	0
July 5	.5	20	7.6	1.87	0	1	0
July 7	.8	16	7.3	2.99	0	22	0
July 8	.7	17	7.6	2.07	0	2	0
July 11	.4	17	7.3	1.50	0	4	0
July 14	.9	17	7.3	1.04	0	7	0
July 20	.8	42	7.3	3.87	0	260	0
July 26	.8	30	7.2	2.98	0	6	0
July 27	.8	29	7.1	3.26	0	1	0
July 30	.8	29	7.3	2.07	0	30	0
August 1	1.0	23	7.2	1.20	0	120	0
August 4	.6	22	7.2	2.40	0	10	0
August 11	.9	19	7.2	.96	0	340	0
August 18	.6	7	7.5	.37	0	200	0
August 25	.7	0	7.0	2.54	0	50	0
Semipublic outdoor test pool F:							
July 1	.3	0	7.5	.35	0	0	0
July 5	.6	10	7.5	.35	0	70	0
July 7	.3	12	7.3	.68	0	6	0
July 11	.4	16	7.1	.78	0	0	0
July 14	.4	18	7.3	.50	0	0	0

[1] Average daily number of bathers per 1,000 gallons.
[2] 0=satisfactory; 1=unsatisfactory, plate count > 200; 2=unsatisfactory, *E. coli* > 0; and 3=unsatisfactory, plate count > 200 and *E. coli* > 0.

G, were treated with chlorine gas plus cyanuric acid. Among the pools treated with other chlorine sources, six were treated with chlorine gas, one with sodium hypochlorite, and one with calcium hypochlorite.

St. Louis County Health Department inspectors checked the pools every week during the season to insure their operation according to accepted procedures (*10*). Standard commercial test kits (model H, W. A. Taylor Co., Baltimore, Md.) with orthotolidine and phenol red indicators were used to determine the available chlorine and pH. The term "available chlorine" is defined for purposes of this paper as "free available chlorine" corresponding to the colorimetric equivalent of the test kit standard when read immediately after adding the orthotolidine hydrochloride solution to the tested water at ambient temperature. The terms "chlorine residual" and "available chlorine" are used interchangeably in this paper.

During inspections, the sampling time in each pool was varied, and water samples were taken alternately from the deep end, shallow end, and sides of the pools. Each pool operator kept records of the chemicals used and performed tests for pH and available chlorine twice a day to maintain conditions recommended by the St. Louis County Health Department. The recommended levels for public and semipublic pools were 0.3 to 0.6 ppm available chlorine and pH 7.2 to 7.6 and for private pools, 0.4 to 0.8 ppm available chlorine and pH 7.2 to 7.8. Cyanuric acid, where required, was introduced into test pools as sodium cynaurate, the levels of which were determined periodically by Monsanto personnel by wet chemical analysis, ultraviolet spectroscopy, or both.

The bacteriological tests were performed in the St. Louis County Health Department laboratory by using the standard plate count procedures outlined in the 11th edition of "Stand-

Table 2. **Disinfection records of test swimming pools, 1960, St. Louis County, Mo.—Continued**

Month and day	Chlorine residual (ppm)	Cyanuric acid (ppm)	pH	Bather load [1]	*Escherichia coli*	Plate count	Quality ratings [2]
July 18	.3	22	7.3	.78	0	60	0
July 20	.3	25	7.3	.60	0	26	0
July 27	.3	28	7.2	.85	0	2	0
July 30	.5	30	7.2	1.33	0	3	0
August 5	.4	34	7.3	.78	0	2	0
August 8	.4	36	7.2	.43	0	87	0
August 17	.4	42	7.2	.60	0	18	0
August 22	.3	45	7.1	.80	0	1	0
August 29	.5	49	7.0	.45	0	10,000	1
August 30	.4	51	7.1	.70	0	2	0
September 1	.5	52	7.3	1.05	0	13	0
September 8	.5	57	7.2	.30	0	6	0
Public indoor test pool G:							
June 7	.30	0	7.2	.81	0	3	0
June 13	.25	0	6.8	3.26	0	0	0
June 16	.55	56	6.8	1.75	0	0	0
June 20	.5	48	6.8	3.45	0	0	0
June 22	.45	45	7.2	4.12	0	0	0
June 24	.5	41	7.4	3.40	0	22	0
June 28	1.0	35	6.8	1.50	0	0	0
July 5	1.0	32	7.1	1.97	0	3	0
July 7	.5	32	7.5	1.95	0	44	0
July 11	.2	33	7.2	2.48	0	8,500	1
July 14	.6	33	7.4	1.80	0	1	0
July 18	.4	33	7.2	2.39	0	15	0
July 20	.6	33	7.5	2.99	0	27	0
July 27	.6	33	7.5	3.07	0	8	0
July 30	.5	34	7.5	1.11	0	6	0
August 5	.6	35	7.4	2.86	0	270	1
August 8	1.1	33	7.3	2.23	0	340	1
August 17	.6	30	7.3	2.42	0	108	0
August 22	.7	35	7.3	2.34	0	10	0
August 24	.6	37	7.3	2.69	0	1,400	1
August 30	.7	38	7.2	.30	0	0	0
September 1	.9	36	7.1	.42	0	18	0

ard Methods for the Examination of Water and Water Waste" (*11*). Examinations for the presence of coliform organisms were carried out by the multiple-tube fermentation technique. Five 10-ml. portions of each sample were used to confirm the tests. The department's acceptable pool sanitation criteria require "that not more than 15 percent of the samples covering any considerable period of time shall either (*a*) contain more than 200 bacteria per milliliter as determined by the standard (35° C.) agar plate count or (*b*) show a positive (confirmed) test for coliform organisms in any of the five 10-ml. portions of a sample" (*10*).

The St. Louis County Health Department routinely inspects all public or semipublic pools in the county and regularly performs bacteriological tests on water samples from these pools to insure that all operators follow established operating practices. These services were also extended to the private pools tested in 1960.

The testing period lasted approximately 2 months. The large quantity of data collected precluded an exhaustive listing of all the information. Data from one set of records on each of the four types of pools are given in table 2. Table 3 is a summary of the statistical analyses of the records from all pools tested.

Statistical analyses. Data obtained in the 1960 tests were evaluated statistically to determine whether significant differences could be found between the chlorinated cynaurates and other common sources of chlorine as measured by the incidence of disinfection failures.

The linear regression analysis used for the statistical evaluation of results is represented by the following general equation:

$$\bar{y}=b_o+b_1x_1+b_2x_2+\ . \ . \ . \ +b_kx_k$$

where the controlled variables were

x_1=available chlorine, ppm

x_2=pH

x_3=bather load (daily number of bathers per 1,000 gallons)
x_4=cyanuric acid, ppm
$\bar{y}$=mean representing either *Escherichia coli* or total plate count

There were wide variations in the important variables investigated, as indicated by deviations from the average (± signs, table 3).

We are aware of the shortcomings of conclusions from a statistical analysis based on a small number of pools, especially when conditions in the pools varied considerably. Nevertheless, our conclusions not only point out the presence or absence of differences between the disinfectants but also indicate the complexity of making such comparisons.

There were no statistically significant differences (table 3) in the incidence of disinfection failures between the pools treated with chlorine plus cyanuric acid or potassium dichlorocyanurate plus cyanuric acid and pools treated with other chlorine sources in either large outdoor public pool E or small outdoor semipublic pool F. A statistically significant difference existed between pool G, using chlorine gas plus cyanuric acid, and pool G*1*, using chlorine gas alone. The pool with chlorine gas plus cyanuric acid had 24 percent failures due to total plate count greater than 200 and no failures due to *E. coli* greater than zero. The pool with chlorine gas alone had 66 percent failures due to total plate count greater than 200 and 22 percent failures due to *E. coli* greater than zero.

The private and semipublic residential pools as a group had good disinfection records: only 11 percent failures due to total plate count greater than 200 and 4 percent due to *E. coli* greater than zero.

The 1960 data were obtained on pools over which greater control was exercised than for pools with routine operations. It was of great interest to know what degree of disinfection was achieved under routine operating conditions with the most commonly used disinfectants.

In-Use Data 1963 Tests

Data for the 1963 season were obtained from the St. Louis County Health Department inspection records on semipublic and public pools in St. Louis County. Private residential pools, where chlorinated cyanurates are widely used, were not included, as the health department does not inspect them routinely.

Statistical analyses. Bacteriological data

Table 3. Summary of results, 1960 swimming pool tests, St. Louis County, Mo.

Pool code	Source of chlorine	Number of pools	Number of tests	Average conditions in pools [1]				Percent disinfection failures	
				Chlorine (ppm)	pH	Bather load [2]	Cyanuric acid (ppm)	Plate count > 200	*Escherichia coli* > 0
E	Chlorine gas with cyanuric acid.	1	15	0.7±0.3	7.3±0.4	2.0±2.0	25±31	13	0
E*1*–E*3*	Chlorine gas	3	37	0.6±0.5	7.7±0.8	0.9±1.0	0	5	2
F	Potassium dichlorocyanurate with cyanuric acid.	1	17	0.4±0.2	7.2±0.3	0.7±0.5	31±33	6	0
F*1*–F*4*	Chlorine gas, sodium hypochlorite, calcium hypochlorite.	4	54	0.6±0.5	7.6±0.4	1.1±1.0	0	15	2
G	Chlorine gas with cyanuric acid.	1	22	0.6±0.5	7.2±0.5	2.2±2.0	33±25	24	0
G*1*	Chlorine gas	1	9	0.9±0.3	7.1±0.3	2.2±0.8	0	66	22
A–D	Potassium dichlorocyanurate with cyanuric acid.	4	28	0.4±0.3	7.4±0.3	0.2±0.3	40±29	11	4

[1] 95 percent confidence limits.
[2] Daily average number of bathers per 1,000 gallons.

from 138 pools were evaluated statistically by means of a computer. There were 7 pools among the 138 evaluated that used chlorinated cyanurates for the 1963 season. Two were large outdoor public pools, and five were small outdoor semipublic pools (table 4). Information on the cyanuric acid levels in the pools with chlorinated cyanurates was not available. Pools with less than five inspections for the season were excluded from the evaluations.

A linear regression analysis, as used for the 1960 test results, was also used for the statistical evaluation of the 1963 test results.

The known independent variables were

x_1=available chlorine, ppm

x_2=pH

x_3=number of bathers observed in a pool during each inspection

x_4=potassium dichlorocyanurate (1 when present, 0 when absent)

x_5=sample from deep end

x_6=sample from shallow end

x_7=sample from side of pool

x_8=pool cleanliness index, comprised of the following: dirt in gutters, dirt on the pool bottom, dirt on walks, dirt on sidewalls, algae, and general cleanliness. All were stated on the inspection data form. The highest index number possible was 6, indicating poor cleanliness or poor housekeeping practices; the lowest was 0.

A preliminary computer evaluation of the results showed that the location of sampling the swimming pool water was not statistically significant; therefore, variables x_5, x_6, and x_7 were eliminated from further evaluations.

Table 4. Swimming pools with chlorinated cyanurates, 1963, St. Louis County, Mo.

Type and code	Capacity (thousand gallons)	Type of filtration	Bather load [1]
Public			
A	110	Pressure, sand	1.2 or more
B	110	do	1.2 or more
Semipublic			
C	50	do	Up to 0.5
D	125	Pressure, diatomite.	0.5 to 1.2
E	35	do	Up to 0.5
F	125	do	0.5 to 1.2
G	35	do	Up to 0.5

[1] Daily average number of bathers per 1,000 gallons

Table 5. Summary of results, 1963 swimming pool tests, St. Louis County, Mo.

Type of pool and source of chlorine	Number of pools	Number of tests	Average conditions in pools [1]				Percent disinfection failures [1]	
			Chlorine (ppm)	pH	Number of bathers [2]	Cleanliness index	Plate count >200	*Escherichia coli* >0
Large outdoor public pools: [3]								
Potassium dichlorocyanurate	2	15	0.6±0.5	7.5±0.3	17±14	0	0	0
Other [4]	58	463	0.4±0.8	7.6±0.9	26±87	0.1±0.8	6±19	8±19
Small outdoor semipublic pools: [5]								
Potassium dichlorocyanurate	5	42	0.7±1.1	7.4±0.9	5±15	0.1±0.4	3±11	6±5
Other [4]	19	204	0.5±1.5	7.7±0.8	4±9	0.3±1.3	14±39	11±38
Small outdoor public pools [4 5]	43	332	0.5±1.2	7.7±0.9	8±25	0.2±1.1	15±34	16±37
Indoor pools [4]	6	47	0.6±0.7	7.6±0.5	15±49	0.1±0.8	2	6
Municipal pools [4]	5	36	0.5±0.7	7.3±0.9	92±146	0.0±0.3	3	0

[1] 95 percent confidence limits.
[2] Daily average number of bathers observed in a pool during inspection.
[3] 100,000-gallon or larger capacity.
[4] Source of chlorine: Chlorine gas, sodium hypochlorite, and calcium hypochlorite. No breakdown available on number of pools treated with each disinfectant.
[5] Less than 100,000-gallon capacity.

There were relatively wide variations in the swimming pool conditions as represented by the available chlorine, pH, number of bathers, and cleanliness index (table 5). The large number of tests in 1963, however, allows us to conclude that—

• The most important variable in the disinfection of swimming pool water was the available chlorine residual, irrespective of its source. The higher the chlorine residual, the lower the incidence of disinfection failures.

• The pools treated with chlorinated cyanurates had a significantly (92 percent confidence level) lower incidence of disinfection failures due to *E. coli* than pools using other chlorine sources.

• The chlorinated cyanurates had no significant effect on the incidence of disinfection failures resulting from a total plate count exceeding 200.

• A low cleanliness index, indicating good housekeeping, significantly decreased the incidence of disinfection failures due to total plate count but had no significant effect on the failures due to *E. coli*.

Summary

Data collected from the practical operation of swimming pools in St. Louis County, Mo., in 1960 and 1963 were evaluated statistically to compare the disinfecting ability of the chlorinated cyanurates with other sources of chlorine. The results from each period had to be evaluated separately since the number of controlled variables was different in 1960 and 1963. Both sets of data showed that pools treated with chlorinated cyanurates had a better disinfection record than pools treated with other common chlorine sources. The good disinfection record of pools treated with the chlorinated cyanurates apparently was related to the uniform level of the chlorine residual provided by the stabilizing action of cyanuric acid. Bad housekeeping practices increased the disinfection failures. Good disinfection was obtained with any chlorine source investigated provided adequate available chlorine residual was maintained continuously in the pool.

It appears that an organized effort is advisable on the part of health department officials and industrial organizations to educate pool owners in the necessity of maintaining safe and healthful pool water by following strict housekeeping practices. Choosing the right chlorine disinfectant from among those investigated in this work may allow the operator to maintain a uniform supply of the disinfectant and thus minimize the periods of poor disinfection. The chlorinated cyanurates with cyanuric acid as a stabilizer meet the disinfectant requirements.

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