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# Comparison of Chlorine, Bromine, and Iodine as Disinfectants for Swimming Pool Water

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## ABSTRACT

KOSKI, T. A. (Pesticides Regulation Division, Agricultural Research Service, Beltsville, Md.), L. S. STUART, AND L. F. ORTENZIO. Comparison of chlorine, bromine, and iodine as disinfectants for swimming pool water. Appl. Microbiol. **14**:276–279. 1966—Studies on the germicidal activity of chlorine, bromine, and iodine were made by use of the Association of Official Agricultural Chemists official first action method for determining effectiveness of swimming pool water disinfectants. In this procedure, 0.3 ppm of available chlorine as chlorine gas has activity equivalent to 0.6 ppm of available chlorine in the buffered sodium hypochlorite control when *Escherichia coli* is used as the test organism. With *Streptococcus faecalis* as the test organism, 0.45 ppm of available chlorine as gaseous chlorine gives activity equivalent to the control. Liquid bromine at 1.0 ppm is as effective as the 0.6 ppm of available chlorine hypochlorite control with *E. coli* as the test organism, but 2.0 ppm of liquid bromine is necessary to provide activity equivalent to the 0.6 ppm of available chlorine control when *S. faecalis* is employed. With iodine as metallic iodine, 2.0 ppm is necessary to provide a result equivalent to the 0.6 ppm of available chlorine control with both *E. coli* and *S. faecalis*. In the various systems tested, gaseous chlorine was the most active form of available chlorine; liquid bromine provided the most active form of bromine, and metallic iodine provided the most active form of iodine.

A standard test for the efficacy of germicides and the acceptability of residual disinfecting activity in swimming pool waters was described by Ortenzio and Stuart in 1964 (7). This method has been accepted on a first action basis by the Association of Official Agricultural Chemists (AOAC). The procedure has also been evaluated and discussed by the Advisory Committee on Swimming Pool Water Treatment Chemicals and/or Processes of the National Sanitation Foundation. It was employed successfully by Stuart and Ortenzio in 1964 (9) to evaluate various chlorine stabilizers on the activity of available chlorine as a residual germicidal agent for swimming pool water.

The variety of recommendations in the literature describing the use of iodine and bromine as residual germicidal agents for swimming pool water indicated a necessity for a direct comparison of chlorine, bromine, and iodine by means of a common procedure designed to yield a valid comparison of their practical disinfecting activity in swimming pool waters.

The AOAC method referred to above is considered especially suitable for this comparison. This method is based upon the direct comparison of the unknown germicide at the concentration recommended with a buffered sodium hypochlorite control providing 0.6 ppm of residual available chlorine at a *p*H of 7.5 ± 0.1.

## EXPERIMENTAL

Direct comparisons were first made to establish the relative activities of gaseous chlorine in unbuffered water to the activity of the buffered sodium hypochlorite control. The results of these studies are presented in Tables 1 and 2.

Table 1 shows that 0.3 ppm of available chlorine as gaseous chlorine has activity against *Escherichia coli* equivalent to 0.6 ppm of available chlorine as the buffered sodium hypochlorite control. This difference in activity may be attributed to the difference in *p*H shown in the table. In the absence of buffer, gaseous chlorine reduced the *p*H of the test water to a significant degree.

Table 2 shows that 0.4 ppm of available

TABLE 1. *Activity of gaseous chlorine in unbuffered water compared with buffered sodium hypochlorite control on Escherichia coli*

| Sample | (Titratable Cl concn, ppm) | | *p*H | Bacterial count* per ml of test water after exposure for | | Complete kill time (sec)† |
|---|---|---|---|---|---|---|
| | Start | End | | 0 sec | 30 sec | |
| NaOCl control | 0.611 | 0.478 | 7.4 | $1.39 \times 10^6$ | $<10$ | 30 |
| Gaseous chlorine | 0.620 | 0.596 | 5.2 | $1.18 \times 10^6$ | $<10$ | 30 |
| Gaseous chlorine | 0.460 | 0.420 | 5.4 | $1.16 \times 10^6$ | $<10$ | 30 |
| Gaseous chlorine | 0.301 | 0.292 | 5.8 | $1.25 \times 10^6$ | $<10$ | 30 |

* Counts at 1, 2, 3, 4, 5, and 10 min also showed $<10$ organisms.

† Five replicate tube subculture check.

TABLE 2. *Activity of gaseous chlorine in unbuffered water compared with the buffered sodium hypochlorite control on Streptococcus faecalis*

| Sample | Titratable Cl Concn (ppm) | | *p*H | Bacterial count per ml of test water after exposure for | | | | | | | | Complete kill time (min)* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Start | End | | 0 sec | 30 sec | 1 min | 2 min | 3 min | 4 min | 5 min | 10 min | |
| NaOCl | 0.611 | 0.469 | 7.4 | $1.43 \times 10^6$ | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | 2 |
| Gaseous chlorine | 0.620 | 0.486 | 5.2 | $1.04 \times 10^6$ | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | 0.5 |
| Gaseous chlorine | 0.460 | 0.367 | 5.4 | $0.98 \times 10^6$ | 440 | 130 | $<10$ | $<10$ | $<10$ | $<10$ | $<10$ | 2 |
| Gaseous chlorine | 0.301 | 0.195 | 5.8 | $1.04 \times 10^6$ | 3,800 | 2,860 | 2,690 | 1,890 | 1,130 | 470 | $<10$ | $>10$ |

* Five replicate tube subculture check.

TABLE 3. *Activity of gaseous chlorine, liquid bromine, and metallic iodine dissolved in unbuffered water on Escherichia coli*

| Sample | Titratable concn (ppm) | | *p*H | Bacterial count* per ml of test water after exposure for | | Complete kill time (sec)† |
|---|---|---|---|---|---|---|
| | Start | End | | 0 sec | 30 sec | |
| Gaseous chlorine | 0.301 | 0.292 | 5.8 | $1.25 \times 10^6$ | $<10$ | 30 |
| Liquid bromine | 0.560 | 0.414 | 6.5 | $1.26 \times 10^6$ | $<10$ | 60 |
| Liquid bromine | 1.050 | 0.910 | 6.1 | $1.13 \times 10^6$ | $<10$ | 30 |
| Metallic iodine | 1.070 | 0.990 | 5.9 | $0.99 \times 10^6$ | $<10$ | 60 |
| Metallic iodine | 2.030 | 1.870 | 5.8 | $1.2 \times 10^6$ | $<10$ | 30 |

* Counts at 1, 2, 3, 4, 5, and 10 min also showed $<10$ organisms.

† Five replicate tube subculture check.

chlorine as gaseous chlorine without buffer has the activity of the sodium hypochlorite control at 0.6 ppm against *Streptococcus faecalis*, but that 0.3 ppm of available chlorine as gaseous chlorine failed to kill the test organism within 2 min. Thus, effectiveness depends upon the minimal concentration of available chlorine as gaseous chlorine in unbuffered water which will give activity equivalent to the buffered sodium hypochlorite control which is 0.4 ppm. This is considered by the American Public Health Association Committee on Swimming Pool Water Disinfection (1) to be the minimal concentration of available chlorine which must be maintained in swimming pool water at all times.

Table 3 shows results obtained against *E. coli* with elemental bromine and elemental iodine compared with gaseous chlorine at 0.3 ppm in unbuffered test water. The desired concentrations of bromine and iodine were obtained by use of saturated aqueous solutions of liquid bromine and metallic iodine with subsequent dilutions in the test water adjusted by titration.

With elemental bromine, a 30-sec kill with *E.*

TABLE 4. *Activity of gaseous chlorine, liquid bromine, and metallic iodine dissolved in unbuffered water on Streptococcus faecalis*

| Sample | Titratable Concn. (ppm) | | *p*H | Bacterial count* per ml of test water after exposure for | | | | Complete kill time (min)† |
|---|---|---|---|---|---|---|---|---|
| | Start | End | | 0 sec | 30 sec | 1 min | 2 min | |
| Gaseous chlorine... | 0.460 | 0.367 | 5.4 | $0.98 \times 10^6$ | 440 | 130 | <10 | 2 |
| Liquid bromine..... | 1.050 | 0.910 | 6.1 | $1.1 \times 10^6$ | 200 | 100 | <10 | 3 |
| Liquid bromine..... | 1.998 | 1.242 | 6.3 | $0.91 \times 10^6$ | 90 | <10 | <10 | 1 |
| Metallic iodine..... | 1.070 | 0.890 | 5.9 | $1.2 \times 10^6$ | TNTC‡ | 5,200 | 850 | 3 |
| Metallic iodine..... | 2.030 | 1.760 | 5.8 | $1.04 \times 10^6$ | 201,400 | 310 | <10 | 2 |

* Counts at 3, 4, 5, and 10 min also showed <10 organisms.

† Five replicate tube subculture check.

‡ Too numerous to count.

*coli* was obtained with 1.0 ppm but not with 0.56 ppm. The results also showed that 2.0 ppm of elemental iodine will kill within 30 sec. This is equivalent to the activity of 0.3 ppm of liquid chlorine or 0.6 ppm of the buffered sodium hypochlorite control. One ppm of elemental iodine killed the test organisms within 1 min but not within 30 sec. Thus, bromine at 1.0 ppm and iodine at 2.0 ppm are equivalent to the sodium hypochlorite standard for *E. coli.*

The results with *S. faecalis* are shown in Table 4. Gaseous chlorine at 0.46 ppm killed *S. faecalis* within 2 min. Elemental bromine did not kill *faecalis* at 1.0 ppm but did at 2.0 ppm in 1 min; 2.0 ppm of elemental iodine also killed this test organism within 2 min, but 3 min were required at 1.0 ppm.

The data shown in Tables 3 and 4 suggest that the minimal concentration of bromine and iodine which should be maintained in swimming pool water to provide activity equivalent to that obtained with the commonly accepted levels of available chlorine would be 2.0 ppm. The 2.0 ppm of bromine found effective in these studies corresponds with the 2.0 ppm of residual clearance given by the State of Illinois Department of Public Health (Circular No. 823, 1959) after actual use evaluation in 1959, and correlates well with the recent findings of McLean, Brown, and Nixon (5) that 2.0 ppm of bromine would provide effective biocidal control in swimming pool water.

## DISCUSSION

The 2.0 ppm iodine residual requirement found necessary in this study is considerably higher than indicated by other investigators. Campbell et al. (4) reported successful results with iodine residuals ranging from 0.2 to 0.8 ppm. The systems they studied used a potassium iodide bank, and chlorine feeding equipment to release free iodine. Thus, how much of the effectiveness could be attributed to available chlorine or iodine itself is not known. Putnam in 1961 (8) reported the successful use of iodine with a residual concentration of 0.35 ppm of iodine. The method of obtaining iodine was through the action of chlorine gas and a potassium iodide bank. Thus, the significance of the available chlorine and active iodine to the results cannot be estimated. Marshall, McLaughlin, and Carscallen in 1960 (6) also reported the successful use of 0.2 to 0.6 ppm of free iodine derived from a potassium iodide bank through the use of a gaseous chlorine feeder. As with the two earlier studies it is difficult, if not impossible, to differentiate between the results produced by the available chlorine or the free iodine. Black, Lackey, and Lackey (2) also conducted a series of in-use tests in which iodine residuals were maintained through the addition of available chlorine in various forms, and reported that residuals of 0.11 to 0.40 ppm provided effective disinfection. Studies by Byrd et al. (3) with 0.4 ppm of residual iodine in a Stanford University pool indicated an effective disinfection after the first week. Failures during the first week were attributed to improper stabilization of residual iodine. In this case also, iodine residual was maintained by use of a potassium iodide bank and an available chlorine-bearing organic compound. The Division of Environmental Engineering and Food Protection of the U. S. Public Health Service in 1962 suggested the maintenance of 0.3 ppm of residual iodine in swimming pool water to provide water of satisfactory bacteriological quality.

The observations reported here indicate clearly that chlorine is the most active of the three halogens for disinfecting swimming pool water. Bromine is the next most active, followed by iodine. This order of activity is in agreement with what could be expected from the existing knowledge on the activity of these halogens. It is also believed that the order of activity observed in the AOAC method employed can be expected to hold in the practical disinfection of swimming pool water.

It should be emphasized that the AOAC method required the addition of the test organism to the water containing the germicidal agent. When this procedure is followed with adequate chemical control, the results in any mixed system will be a measure of the activity of the end product of completed reactions. Thus, it is possible to eliminate the activity of chlorine from any bromine-chlorine or iodine-chlorine system. However, by introducing the chlorine after the inocula in test water containing potassium iodide or potassium bromide banks, it is possible to use this same procedure to determine activity on these systems exactly as they have been applied in field studies and to obtain direct comparisons between activity in the completely reacted system and the reacting system.

It is believed that results on pools in actual use, in which coliform indices and total plate counts were used as a guide to effective performance of various iodine-chlorine and bromine-chlorine systems, may have provided a background of misleading data insofar as the relative activity of the three halogens, Cl, Br, and I, is concerned. It is most difficult to make accurate estimations on the relative effectiveness of germicides in field studies where the number of bathers and other factors besides the concentration of the disinfectant are constantly changing. Reports attributing all measurable bactericidal activity to be the result of the action of iodine or bromine in iodine—available chlorine and bromine—available chlorine systems, respectively, have probably contributed to the confusion which seems to exist regarding the activity of these three elements.

Additional studies have been made on test waters in which the iodine was obtained through release from potassium iodide by available chlorine or from potassium iodide-metallic iodine mixtures, and on waters obtaining bromine from potassium bromide by liberation by use of available chlorine and potassium bromide-elemental bromine mixtures. With iodine-chlorine systems the method has been manipulated to determine differences between reacting and wholly reacted mixtures. Space does not permit a review here of the specific data obtained. However, the evidence to date indicates that ionization factors in these completely reacted, more complex dilute systems may retard the germicidal rate of both iodine and bromine. There is also evidence that germicidal activity in reacting chlorine-iodine systems is considerably greater than in fully reacted systems. These studies are being continued.

Accurate information is badly needed if we are to make practical evaluations on the great variety of systems now being recommended for the disinfection of swimming pool waters. The AOAC method used in these studies can be employed effectively in developing the required information.

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