

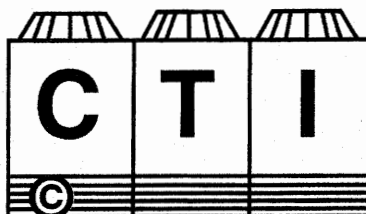
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HYPHALOUS ACID AND HALOAMINE FLASHOFF IN INDUSTRIAL EVAPORATIVE COOLING SYSTEMS

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The studies and conclusions reported in this paper are the results of the author's own work. The paper has been presented before, and reviewed by the Cooling Tower Institute, and approved as a valuable contribution to cooling tower literature.

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Hypohalous Acid and Haloamine Flashoff in Industrial Evaporative Cooling Systems

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ABSTRACT

The application of hypohalous acids and haloamines as industrial antimicrobials for evaporative cooling systems is an essential technology. One process that can effect the fate of oxidizing halogen in recirculating cooling water is flashoff (forced-air stripping). However, flashoff of bromine has never been studied. This subject is important because of the increasing use of bromine chemistry for industrial water treatment. Quantitative volatility comparisons of hypohalous acids and certain haloamines were obtained by determining the Henry's law constant (air-water partition coefficient) in air-stripping towers. Henry's law constant for hypobromous acid was determined to be 0.0295 ± 0.0051 atm at 20 °C. The order of decreasing volatility is ozone > chlorine dioxide > chloramine > hypochlorous acid > hypobromous acid, where ozone is about 167,000 times more volatile than hypobromous acid at 20 °C.

INTRODUCTION

One process that can effect the environmental fate of oxidizing halogen in evaporative water-cooling systems is "flashoff" (the escape of dissolved substances into the atmosphere due to forced-air stripping). The first relevant study to deal with this issue was published by Holzwarth, *et al.* in 1984 (6,7); they calculated flashoff factors based on Henry's law constant. The major conclusions from this work were:

- the dissociated acid (hypochlorite ion) is virtually non-volatile; therefore, flashoff of chlorine in cooling towers is pH sensitive and is about 10 times faster at pH 6 than at pH 8.5
- only about 5-10% of the hypochlorous acid was stripped from a cooling tower at pH 8.5 in the field trial; however, about 30% would be expected to flashoff at pH <7
- chloramine flashoff was much faster than hypochlorous acid flashoff; so fast, in fact, that chloramines probably did not contribute to biocidal efficacy in the cooling system
- most (>80 %) of the chlorine delivered to the cooling tower was consumed by halogen demand in the water

The tendency of bromine and its derivatives to flashoff into the atmosphere has not been determined previously. The effect of flashoff on bromine and its derivatives is important because of the increasing use of bromine chemistry for industrial water treatment (1,3,15). These data are essential in order to adequately describe the environmental fate of oxidizing antimicrobials in the water treatment industry. An important hypothesis never before tested states that flashoff of HOBr will be much slower compared to flashoff of HOCl because of the molecular weight difference. Therefore, it may be reasonable to postulate that converting the oxidant to bromine will reduce the flashoff loss of halogen to the atmosphere because bromine is inherently less volatile. The practical implication of testing this hypothesis and then constructing a more general theory of oxidation disinfection is that a clear description of oxidizing biocide volatility may allow better management strategies for water treatment applications.

Materials And Methods

Henry's Law Constants (air-water partition coefficient). The solubility of a gas is increased as its partial pressure above the solution is increased. Quantitatively, this is expressed as Henry's Law, H , which states that at constant temperature and at equilibrium, the ratio of the partial pressure of solute gas, P , divided by the mole fraction of the gas in solution, X , is constant.

$$H = P / X$$

This constant is a useful predictor in the design of gas-absorption systems (14). Henry's constant does hold very well for many gases when the partial pressure of the solute is less than about 100 kPa (1 atm). However, H is seldom independent of the solute partial pressure when that partial pressure is greater than about 100 kPa. Nevertheless, the constant may still be useful over a narrowly defined range even if the partial pressure is high (11,14). For this study, very low concentrations of dissolved substances (about 1-5 ppm w/v) were used in relatively cool water (20 °C) at atmospheric pressure. Henry's Law is expected to hold for the substances of interest over this narrow range of conditions and can be adequately called an air-water partition coefficient (11).

Henry's law constants can be calculated if the solubility and vapor pressures are known for a given temperature and pressure. The vapor pressures of certain oxidizing antimicrobials are so low, however, that it becomes analytically impossible to calculate H using this technique. In that case, H is determined empirically by air-stripping the solute from a column of water under defined conditions at equilibrium (9,10,11). Accordingly, Henry's law constants were determined for very low concentrations of dissolved substances in water using a glass sparging column with a fine glass frit sealed into the lower end (Figure 1).

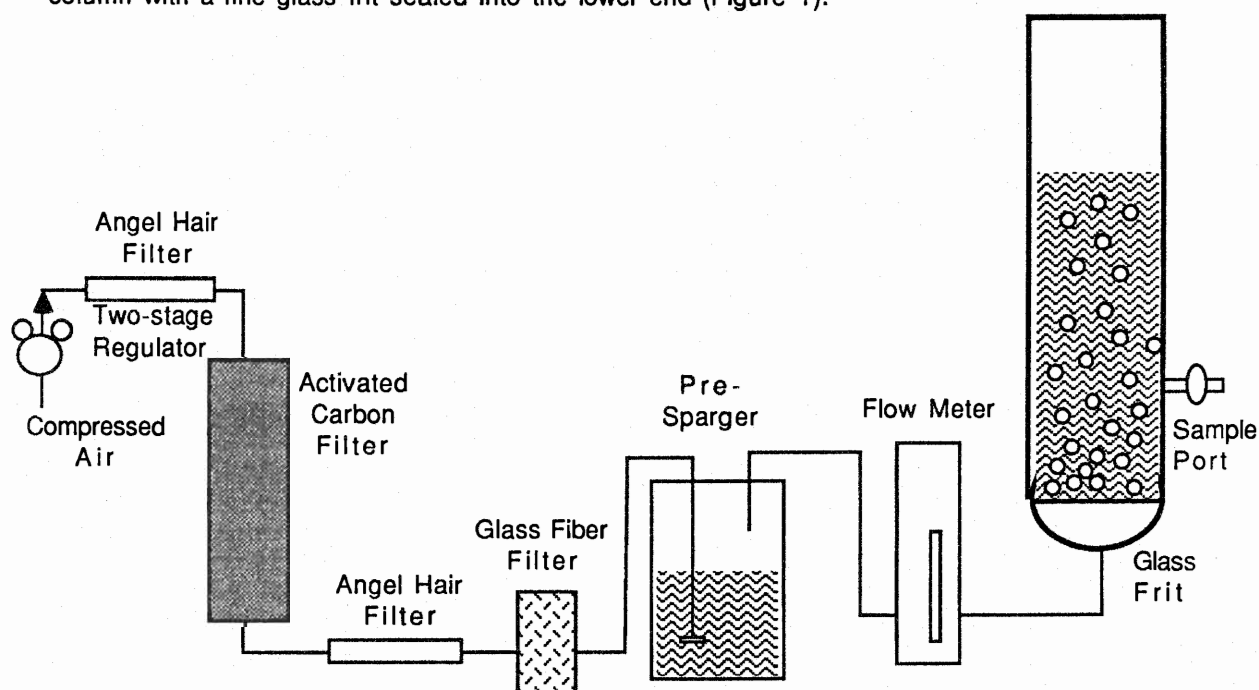


Figure 1. Schematic diagram of the air-stripping experimental apparatus.

The air stream was sequentially passed through a train of pretreatment columns for conditioning. An angel hair filter and an activated carbon column were used to exclude compressor oil from the stripping gas stream. The carbon column was manufactured by filling

a 90 cm long, 9 cm diameter borosilicate glass tube with granular activated carbon. The carbon was contained within the tube by packing both ends of the tube with glass wool plugs. A second angel hair filter and a glass fiber filter were used to remove dust that escaped the carbon column. A 500 ml gas washing bottle filled with deionized water was used as a pre-sparger to fully saturate the compressed air. The stripping gas flowrate was measured with tapered tube flowmeters, i.e., rotameters (Dwyer models VFB 65 and VFB 66). Each rotameter was calibrated against a wet test meter (Precision Scientific, Chicago) to improve accuracy of the measurement. Gas flow rates of 3.5-4 liters/min (1.0 atm) were maintained throughout the experiment. Demand-free air was passed through the frit and the liquid phase concentration of oxidant was monitored by removing 50 ml aliquots from the sampling port (40 cm above the frit) and then immediately analyzing residual halogen using the standard N,N-diethyl-p-phenylene diamine (DPD) titration with ferrous ammonium sulfate (FAS) (13, 16). The liquid volume in the air-stripping column was 5.0 liters at $t=0$.

It was essential that the air-stripping process should be the only loss of halogen in the system. Several modifications of the system were made to eliminate reactive losses of halogen. The filters shown in Figure 1 were used to produce "halogen demand-free" air. All tubing was demand-free and there was no rubber in the system. The pre-sparger was used to saturate the compressed air with demand-free water before delivery to the air-stripping column. The entire apparatus was set-up in a dark room to avoid UV degradation of oxidizing halogen.

The kinetics of this process can be used to measure depletion due to the air-stripping of a volatile solute, C, when the liquid and gas are in equilibrium. The material balance yields,

$$dC/dt = -k C$$

where C equals the concentration of solute in the liquid with k equal to the depletion rate [1/t] due to air-stripping. In practice, the concentration (w/v, in ppm) of solute was measured in 50 ml samples removed from the column. A correction for volume change was made since relatively large volumes were required and because of evaporation. Henry's law constant can be derived from these kinetic data according to the methods of Mackay, *et al.* (11) and the derivations of Lincoff and Gossett (10) because,

$$\ln(C_t/C_0) = -(H G)/(R T) \sum_{j=1}^i \Delta t_j/V_j$$

where C is concentration (w/v, ppm), G is the flow rate of air through the column [m^3/hr], R is the gas constant [$atm \cdot m^3/mole$], T is the temperature in degrees Kelvin, Δt_j is the duration of the j^{th} interval [hr], V_j is volume of water during the j^{th} interval [L], i is the number of samples removed from the column, and therefore, H is in $atm \cdot m^3/mole$. By convention, H is often expressed simply in atmospheres when the solvent is water (5.56×10^4 moles H_2O/m^3 , at standard temperature and pressure). The last term, $\sum \Delta t_j/V_j$, accounts for the removal of discrete sample volumes from the stripping column during the course of the experiment (10).

This method has been used to measure H of low concentrations of HOCl and various chloramines (6). We have applied essentially the same method to measure Henry's constant for HOBr. As a control, we have also measured Henry's constant for NH_3 , and HOCl in order to standardize the method against previously determined constants.

The first experiments using the air-stripping column were with ammonia. Henry's law constant in dilute aqueous solutions is well-known for ammonia, having been determined by a number of workers previously (6). The value of H for ammonia in our system was well within experimental error of the literature value (data not shown). These calibration experiments also confirmed that the system was at equilibrium.

Hypochlorous acid experiments were done following the method of Holzwarth, *et al.* The source of chlorine was Purex[®] bleach (5.25% available chlorine). Experiments were done over a range of pH from 5 to 10 using a phosphate-buffering system (16). The initial concentration of chlorine was in the 4-5 mg/l as chlorine for all experiments. An important fact that was confirmed by these experiments is that the hypochlorite ion is not volatile (the same is true for hypobromite). There was no loss of free residual chlorine at pH 10 even after hundreds of hours in the air-stripping column. This work essentially confirmed the published literature and also served to calibrate the system.

Hypobromous acid experiments were performed next. A stoichiometric excess of sodium bromide was oxidized by sodium hypochlorite (Purex® bleach, 5.25% avail. chlorine). The solution was then analyzed for free bromine and free chlorine (13) and shown to be entirely the former. Appropriate dilutions were made, titrated to assay free bromine and then, dosed to the air-stripping column. The experiments were run at pH 5.4-5.8 so that >99% of the bromine was as hypobromous acid.

Haloamines were produced by combining a molar excess of ammonium chloride with hypochlorous acid or with hypobromous acid. In the chlorine experiments, all of the residual was combined, and although no differential chloramine analyses were performed, it is known from the literature that both mono- and dichloramine were present in the pH range from 5 to 8 (17). In the bromine experiments with ammonium chloride, dibromamine predominates in the pH range 5 to 8 (8) but it decomposes so fast (half-life = about 20 minutes) that it is impossible to measure H in an air-stripping experiment. In order to generate a stable monobromamine residual, 20-50 molar excess ammonium chloride was combined with HOBr at pH 9-10. Of course, at this elevated pH, flashoff is very slow which makes the measurement of H very difficult.

Antimicrobial Efficacy Testing. Antimicrobial efficacy of bromamines and chloramines were determined as follows. A stock borate buffer was prepared by dissolving 95.3 g Na₂B₄O₇·10H₂O (sodium borate), 43.5 g K₂HPO₄, and 34.9 g NaC₂H₃O₂·3H₂O (sodium acetate) in 1.0 liter deionized water, autoclaving, and cooling. Working buffer solutions were prepared by making a 1% v/v dilution of the stock buffer in ultrapure deionized water (18 megaohm/cm by reverse osmosis) and adjusting to pH 7.0 or pH 9.0 with 0.1 N NaOH and 1:20 H₂SO₄ as required. Aliquots of 200 ml each were measured into three sets of 500 ml Erlenmeyer flasks.

Ammonium chloride, glycine or distilled water were added to flasks so that each set contained at least one flask of each treatment. Stock solutions of amines were added as 1% w/v solutions in 18 megaohm/cm water. Additions to individual flasks delivered twenty-five times the stoichiometric amount of amine necessary to combine in a 1:1 molar ratio with 0.5 mg/l oxidizing halogen expressed as chlorine. Each set was then dosed with either bromine, chlorine, or distilled water. Halogens were dosed at 0.5 mg/l oxidizing halogen as chlorine by adding either bromine water (1 ml redistilled liquid bromine in 100 ml distilled water) or household chlorine bleach (Purex Bleach, 5.25% NaOCl). The actual amount of oxidizing chlorine present was measured by titrating duplicate 10.0 ml aliquots with 1.41x10⁻³ M ferrous ammonium sulfate to DPD and DPD/KI endpoints. Oxidizing bromine concentration was determined by treating two of four 10.0 ml aliquots with 0.5 ml 10% sodium nitrite and titrating all four aliquots to DPD endpoints (13). Only those amine+halogen treatments for which 100% of the oxidizing halogen existed as combined residual were included in the final analysis. Amine+halogen treatments were performed in triplicate at each pH. Amine treatments, halogen treatments, and untreated viability controls were performed in duplicate at each pH.

An inoculum was prepared by transferring growth from an overnight, 37 °C nutrient agar streak of *Pseudomonas aeruginosa* into sterile phosphate buffer dilution water (Official Methods of Analysis of the Association of Official Analytical Chemists, 13th Ed., 1980, W. Horwitz (ed.), p. 62). This initial suspension was washed three times by centrifugation (1500 g, 10 min) and resuspension of the pellet in fresh sterile phosphate buffer. The final suspension was adjusted to 10⁸-10⁹ colony forming units per milliliter (CFU/ml) with the phosphate buffer.

All flasks were inoculated to a concentration of about 10⁶ CFU/ml. The microorganism populations in the flasks were quantified at 0.5, 10, 30, 60, and 180 minutes after inoculation by making appropriate dilutions in phosphate buffer dilution water containing 0.05% sodium thiosulfate and pour-plating (16) on tryptone glucose extract agar (Oxoid). Colonies were counted after 24 hr incubation at 37 °C.

RESULTS AND DISCUSSION

Figure 2 shows the results of air-stripping experiments with hypochlorous acid and with hypobromous acid. Each experiment was analyzed individually to determine if the linear

least-squares regression was significant (data not shown). All but one of the HOBr experiments were significant at the 95% confidence level; the linear regression that was not significant (open squares in figure 2) was omitted from further analysis.

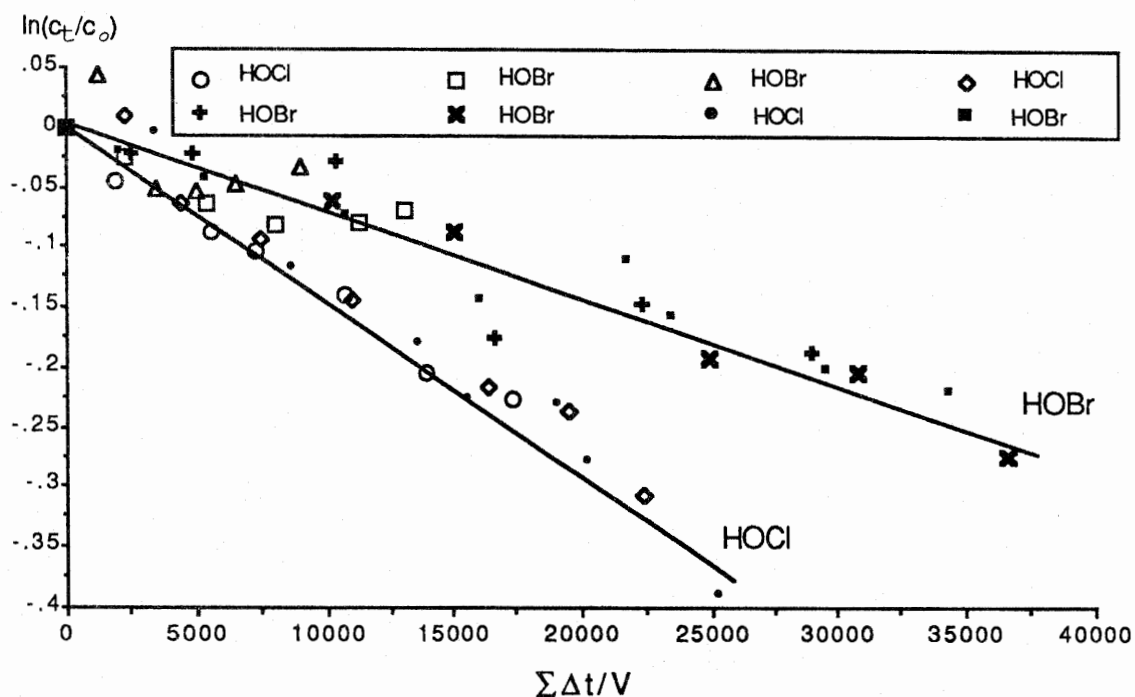


Figure 2. Hypochlorous and hypobromous acids in air-stripping experiments. To insure that all of the halogen was as hypohalous acid, the pH was held constant at about 5. Each symbol type represents results from an independent experiment. The use of $\Sigma\Delta t/V$ in the x axis is to indicate that a correction was made for the volume of sample removed for analysis (see Materials and Methods); the units of the x axis are proportional to time.

Table 1 shows the calculated values of H using the data from Figure 2. The value of H for hypochlorous acid is somewhat lower than that reported by Holzwarth (0.076 atm). The value that we report is corrected for the wet test meter calibration of the rotameters and to atmospheric pressure. No mention of these corrections were made in the Holzwarth paper. The uncorrected value of H in our experiments was 0.0803 ± 0.0035 atm, which is within experimental error of the published value.

Table 1 shows the only published Henry's law constant for hypobromous acid. The value of H_{HOBr} was about two times less than the value of H_{HOCl} at 20 °C. This means that hypochlorous acid is inherently twice as volatile as hypobromous acid.

Table 1. Replicate estimates for hypochlorous acid and hypobromous acid in air-stripping experiments

Compound	Observed H (atm) @ 20 °C
Hypochlorous acid	0.0589
	0.0590
	<u>0.0635</u>
	Average \pm s.d. = 0.0605 \pm 0.0026
Hypobromous acid	0.0370
	0.0283
	0.0256
	<u>0.0271</u>
Average \pm s.d. = 0.0295 \pm 0.0051	

The pH effect on flashoff must be considered in order to make the volatility comparison of hypohalous acids relevant for industrial water treatment. As was stated earlier, flashoff of HOCl is markedly influenced by the effect of pH because OCl^- is virtually non-volatile due to its high energy of solvation in water. In alkaline cooling water, there will be much more undissociated hypobromous acid than undissociated hypochlorous acid in equimolar solutions (the pK_a of HOBr is about 8.8 and the pK_a of HOCl is about 7.4). Comparison of chlorine and bromine flashoff will depend on the quantitative difference in volatility and the pH. The experimentally derived quantitative volatility data for bromine is, of course, essential.

Comparisons of hypohalous acid flashoff can be made using the data in Table 1. Figure 3 shows an analysis of the relative flashoff rates of chlorine and bromine in water from pH 5 to 10. The data were calculated by normalizing to flashoff of HOCl at pH 5 and then factoring in the acid dissociation due to pH:

$$\text{relative flashoff rate, } (F_{\text{HOX}}/F_{\text{HOCl at pH5}}) = (\text{OX}^-/\text{HOX})_{\text{pH}} \times (\text{H}_{\text{HOX}} / \text{H}_{\text{HOCl}})$$

where X is bromine or chlorine, F is flashoff rate, and H is Henry's law constant. When the pH is above about 8, HOBr and HOCl flashoff slowly. The field work of Holzwarth shows that less than 10% of the HOCl applied at pH 8.5 was lost due to flashoff and that this loss was not significant. For the case of equal mass comparisons, flashoff of HOCl and HOBr are essentially negligible when the pH is greater than about 8. The flashoff of HOBr is greater than for HOCl at $\text{pH} > 8$ in equimolar concentrations because there is far more undissociated hypobromous acid in solution. Of course, hypohalous acids are more often compared on an equal mass (pound for pound) basis in the real world of industrial water treatment. Figure 3 shows that the flashoff of HOCl in evaporative cooling water systems is much greater than HOBr when the pH is less than about 8. Field trial data suggest that flashoff of HOCl can be a significant loss at $\text{pH} < 7$. Therefore, the lower volatility of HOBr is an important practical consideration for certain evaporative cooling water applications.

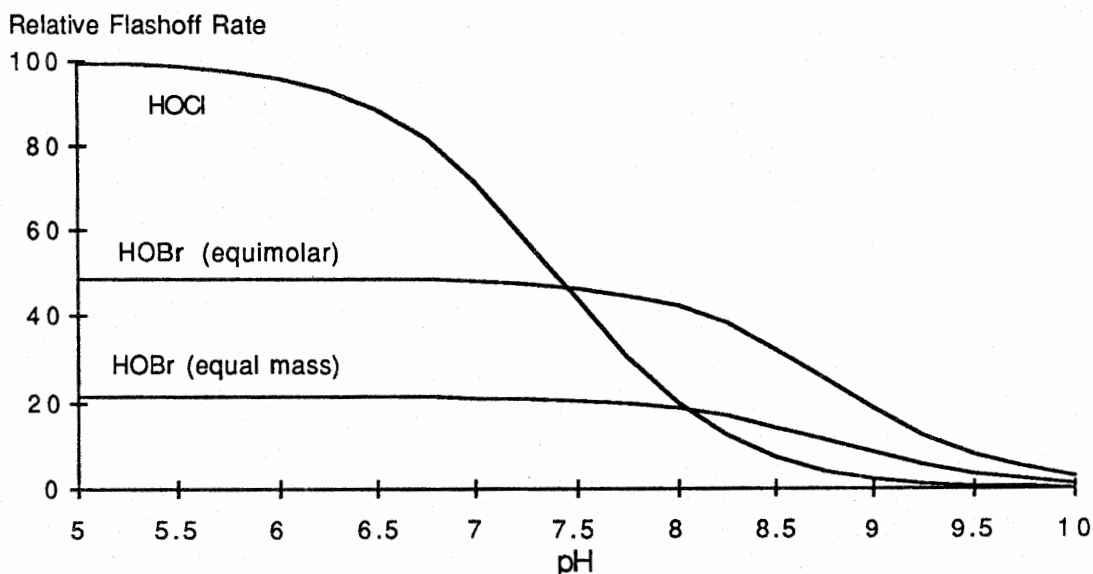


Figure 3. Relative flashoff rates for hypohalous acids from hypothetical identical cooling towers employing equimolar or equal mass HOBr and HOCl concentrations. Flashoff (air-stripping) rates are given as a fraction of the HOCl flashoff rate at $\text{pH} < 5$.

An important consideration in water treatment applications of chlorine and bromine is the effect of combined residual on performance. As is well-known, hypohalous acids will react with the reduced forms of nitrogen in water to form haloamines. The volatility of chloramines is much greater than hypochlorous acid, as is shown in Figure 4. At the pH and molar ratios

used in this experiment, mono- and dichloramine were present (17) and this simulates the case for most water treatment applications. The value of H for the chloramines ($\text{HOCl} + \text{NH}_4\text{Cl}$) was calculated from the data in Figure 4 and was equal to about 0.84 atm. Previously published values for H of monochloramine and for dichloramine were 0.45 atm and 1.52 atm, respectively. Therefore, the value we report for the combination is reasonable.

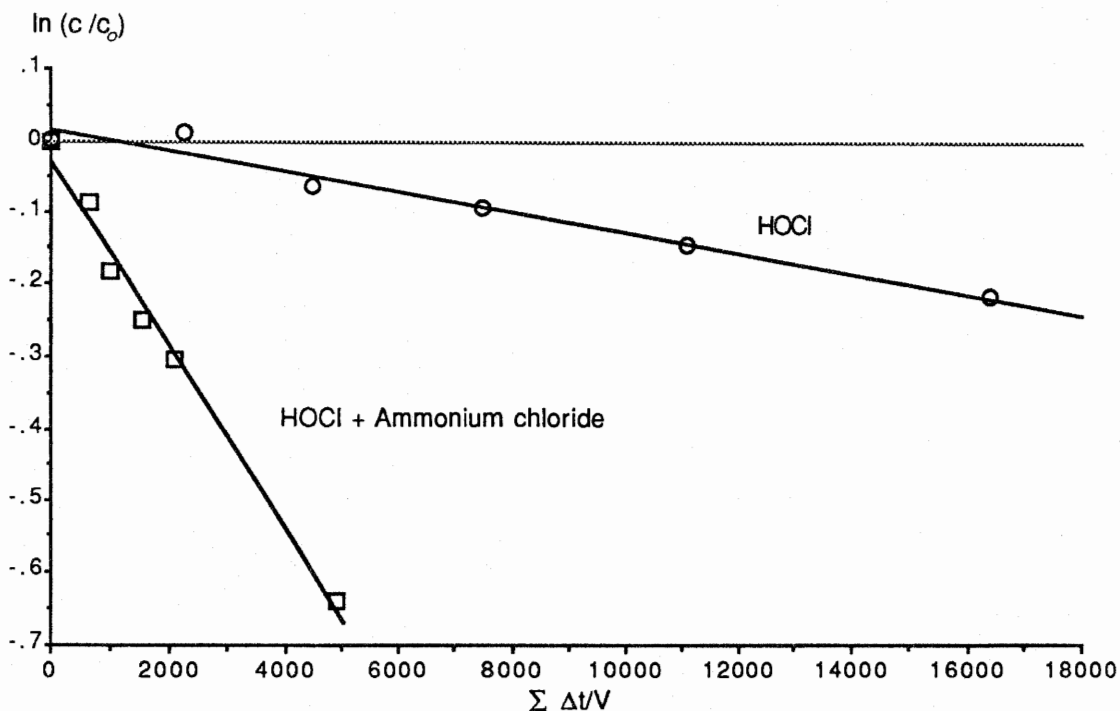


Figure 4. Hypochlorous acid and HOCL + NH_4Cl in air-stripping experiments.

Chloramines do act as antimicrobial agents and are used extensively in drinking water disinfection today. However, chloramines require longer contact times with microorganisms compared to hypochlorous acid. As is shown in Figure 5, chlorine plus ammonium chloride at pH 9 (closed triangles) required considerably longer contact time compared to bromine, chlorine, or bromine+ammonium chloride at pH 9. Organic chloramines like, for example, the combined residual generated from the addition of chlorine and glycine (an amino acid) at pH 9 are even less effective as antimicrobials. This longer contact time requirement makes volatility of chloramines a relevant issue in recirculating evaporative cooling water systems. The familiar odor of "chlorine" around heavily chlorinated water is actually the odor of the volatilized chloramines. All of this evidence suggests that flashoff in evaporative cooling systems may render chloramines essentially unavailable as antimicrobials unless much higher residuals are maintained for longer times compared to free chlorine.

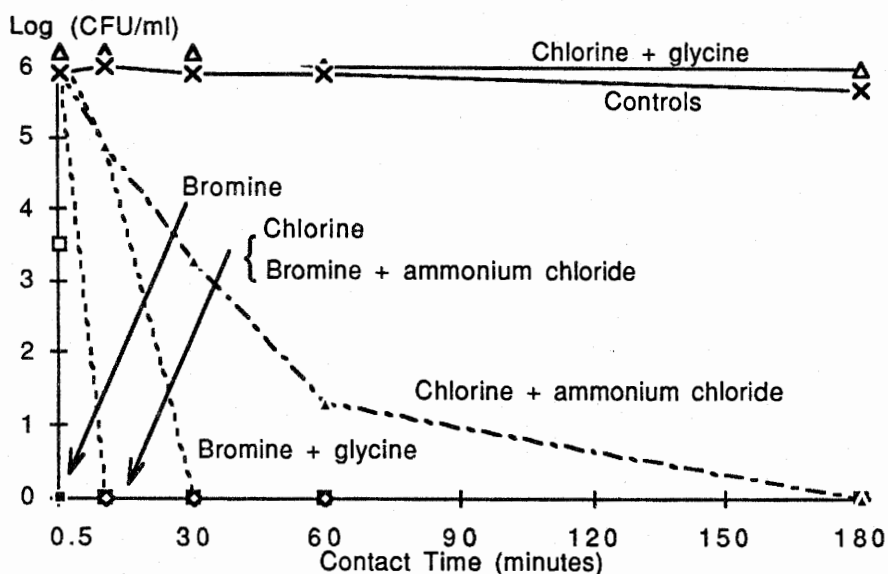


Figure 5. Effect on antimicrobial efficacy of 0.5 ppm (total residual as Cl_2) bromine and chlorine combined with ammonium chloride or glycine (25X molar concentration of oxidizing halogen) at pH 9. The logarithm of viable cell concentrations, colony forming units (CFU) per milliliter, of the bacterium *Pseudomonas aeruginosa* are given at various contact times after addition of the halogen.

Figure 5 shows that the contact time required for antimicrobial performance of bromamines is quite similar to the hypohalous acids. This suggests that volatility of bromamines is much less critical compared to chloramine volatility. Nevertheless, a quantitative measure of the air-water partition coefficients for bromamine would be useful. Hypobromous acid combined with ammonium chloride at $\text{pH} < 9$ generates predominantly dichloramine which decomposes to nitrogen and bromide ion (half-life about 20 min). Determination of H is therefore, not possible with our system since the decomposition rate is faster than the air-stripping depletion rate. Thus, flashoff is probably not a relevant issue for dibromamine. In order to measure the value of H of a stable combined residual of bromine (monobromamine), high pH (> 9) and high nitrogen (20-50 molar excess) are required. These experiments are currently in progress.

Table 2 compares the volatility data developed in this report to values that were present in the literature (references are indicated). The tendency to flashoff antimicrobial in recirculating evaporative cooling water systems can be directly related to Henry's law constant which, in this case, is an air-water partition coefficient. Of course, hypochlorous acid will flashoff much more slowly than Cl_2 ; this is because of the reaction of Cl_2 and water to form the hypohalous acid, a less volatile species. Chloramines will flashoff much faster than HOCl as is indicated by the constants in Table 1. Flashoff of the chloramines is extremely important in systems where reduced nitrogen compounds are present. Interestingly, the familiar odor that nearly everyone has experienced around chlorinated swimming pools is due to volatilized chloramine. Chlorine dioxide is far more volatile than hypochlorous acid or the chloramines and therefore, compensation due to flashoff losses must be made in open recirculating cooling systems. The same is true for ozone, which will also flashoff rapidly in open systems. There are no values reported for hypohalite ions because their volatilities are so low that air-stripping experiments did not cause any depletion even after hundreds of hours in the column (see Materials and Methods).

Table 2. Henry's law constants (air-water partition coefficients) of oxidizing antimicrobials

Antimicrobial	Formula	H (atm) @ 20 °C	References
Ozone	O ₃	5000	12
Chlorine	Cl ₂	585	12
Bromine	Br ₂	59.3	5
Chlorine dioxide	ClO ₂	54.0	12
Monochloramine	NH ₂ Cl	0.45	6
Hypochlorous acid	HOCl	0.076	6
		0.061	This paper
Hypobromous acid	HOBr	0.030	This paper

An interesting observation has been recently reported in the area of vapor phase corrosion of hydrostatic cookers (4). Corrosion rates on mild steel exposed to vapors from hot water disinfected with chlorine dioxide were far greater than in the same system disinfected with hypochlorous acid. Vapor phase corrosion was reduced to virtually nil when the disinfectant was predominantly hypobromous acid. These observations are in accord with the known volatility data given in Table 2.

CONCLUSIONS

Hypobromous acid is some 167,000 times less volatile than ozone, 1800 times less volatile than chlorine dioxide, 15 times less volatile than monochloramine, and about 2 times less volatile than hypochlorous acid. Hypobromous acid is often the preferred oxidizing antimicrobial for industrial cooling water at pH > 8 because of its favorable dissociation constant compared to chlorine. The volatility data presented in this paper suggest that HOBr may also be preferable to chlorine in cooling tower water with pH < 8. Chloramines are only effective after relatively long contact time with microorganisms. Flashoff of chloramines in cooling water is, therefore, an important issue. In contrast, antimicrobial properties of the bromamines are essentially like hypohalous acids since very short contact times are required for efficacy. Flashoff of bromamines from evaporative cooling systems is not likely to result in significant loss of antimicrobial activity.

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