Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 1. Amperometric Titration

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■ The free available chlorine (FAC) amperometric titration measurement is subject to interference errors from chloramines. Current measurements from chloramines were as much as 17% of the total chlorine in the presence of a 2:1 molar excess of free amine at 0 V vs SCE. Interferences with this method increased as the positive applied voltage on the platinum electrode decreased. This trend was observed with both model compounds and chlorinated process waters. The interference from combined chlorine in one chlorinated and settled drinking water was up to 50% of the FAC response. Current increases after each addition of phenylarsine oxide (PAO) were observed with N-chlorosuccinimide, but not with the other chloramines tested.

Introduction

Chlorine is commonly used in the United States for the disinfection of drinking water, wastewater, and swimming pools. The presence of a free chlorine residual ([HOCl] + [OCl⁻]) is often regarded as a sign of adequate disinfection. U.S. Environmental Protection Agency regulations (1) allow for the replacement of microbiological assays with free available chlorine (FAC) residual measurements in some finished drinking waters. For this reason, accurate free chlorine residual measurements are imperative. Interference in the measurement of free chlorine by poorer disinfectants could result in a false assessment of the microbiological status of treated water.

Monochloramine and organic chloramines are formed by the reaction of chlorine and ammonia or chlorine and nitrogenous organics (2, 3). These compounds are poor disinfectants (4). Thus, it is important to investigate the ability of these substances to interfere with the analysis of free chlorine.

Two of the most commonly used methods for the analysis of free chlorine are the amperometric titration and N,N-diethyl-p-phenylenediamine (DPD) procedures. The amperometric titration method is discussed here and the DPD procedure is examined in the companion paper, which follows. Amperometric titration involves titration of active halogen with a reducing agent of known normality [usually 0.005 64 N phenylarsine oxide (PAO)] at constant applied voltage (5). The standard method (6) recommends

an applied voltage of +200 mV. Interferences in the amperometric titration FAC measurement have been observed with several organic chloramines, including the N-chloro derivatives of cyanuric acid (7) and piperidine (8) and the disinfectant halazone [4-(N,N-dichlorosulfamyl)benzoic acid] (9).

This study reports the response of the amperometric titration method to monochloramine and organic chloramines relative to the response to free chlorine. Relative response factors are examined as a function of applied voltage. Perturbation of the chlorine-free chlorine equilibrium by the titrant is investigated. Model compound results are compared to the analysis of chlorinated field samples.

Experimental Section

Nitrogenous organics and N,N-diethyl-p-phenylenediamine oxalate (Eastman Kodak Co., Rochester, NY) were used as received. Substrates were buffered at pH 7 with 0.005 M KH_2PO_4 neutralized with NaOH and chlorinated at a 2:1 molar substrate to chlorine ratio. The total chlorine concentration was 5.72×10^{-5} M. Ammonia (NH_4Cl) was chlorinated at a 3:1 molar ammonia to chlorine ratio. Chlorinated mixtures were stored in the dark at 25 °C for approximately 30 min prior to analysis.

Amperometric titrations were performed with a hook-type rotating platinum electrode (rotator S-76485, Pt electrode S-30421; Sargent-Welch Scientific Co., Skokie, IL), saturated calomel reference electrode (SCE), and MP-1000 series voltage source and signal conditioning components (McKee-Pedersen Instruments, Danville, CA). The applied voltage was +200 mV (vs SCE), unless otherwise stated. Current measurements for the current-voltage studies were made with a handheld digital multimeter (Micronta, Tandy Corp., Fort Worth, TX). The phenylarsine oxide titrant (Fisher Scientific Co., Pittsburgh, PA; nominally 0.005 64 N) was standardized against potassium biiodate. Otherwise the standard methods free available chlorine procedure was used (6).

All pH measurements were performed with an Orion Research Model 601A pH meter and a combination electrode (Model 13-639-252, Fisher Scientific Co., Pittsburgh, PA). Ammonia was measured by the indophenol method (10). Nitrate was measured as nitrite (11) after reduction on cadmium (12).

Unchlorinated secondary effluent samples from two secondary wastewater treatment plants (designated WW1
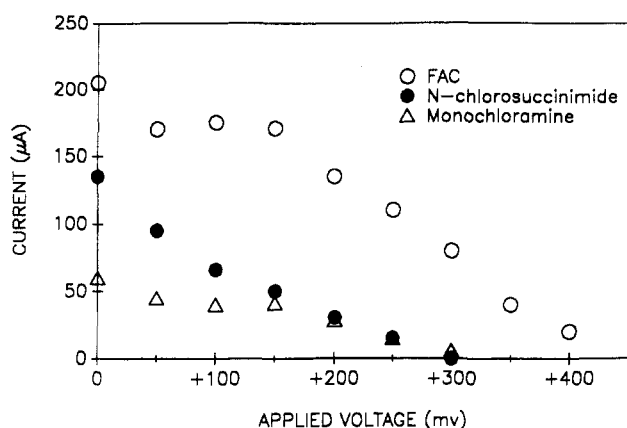
Figure 1. Current voltage curves for FAC, monochloramine, and N-chlorosuccinimide.

Figure 2. Amperometric titration, β values as a function of applied voltage.

and WW2) were obtained. Unchlorinated settled water from a drinking water filtration plant was also sampled. All samples were chlorinated in the laboratory to five points along their respective breakpoint curves. Samples were buffered to pH 6.74–6.82 and chlorinated for 2 h. Preliminary and final breakpoint curves were conducted 1 and 2 days, respectively, after sample collection. Breakpoint chlorinations were performed at room temperature (approximately 23 °C).

Experimental Approach

In order for interferences to occur, chloramines must produce a response at the platinum electrode *and* react with PAO. The primary focus of this work was to examine the response produced by the chloramines at the platinum electrode. Quantification of this response requires knowledge of the true free chlorine concentration in solution. This in turn relies on knowledge of the chloramine hydrolysis equilibrium constant. The theory of the determination of these hydrolysis equilibrium constants in the presence of interferents is discussed elsewhere (13). For the amperometric titration method, the current response to a mixture of chloramine (RR′NCl) and free chlorine is as follows:

current = (response factor for FAC)[FAC] +
                    (response factor for RR′NCl)[RR′NCl]

Dividing by the response factor for FAC

response (in [FAC] units) = [FAC] + β[RR′NCl]

where β is the relative response factor.

In the model compound experiments, previously determined (13) hydrolysis constants are combined with total chlorine measurements to calculate the true equilibrium FAC and chloramine concentrations. The relative response factor (β) can then be calculated. In the field samples, the organic nitrogen composition is complex and unknown. Therefore, the chloramine concentration in the equation above is replaced with the combined chlorine residual (total chlorine minus measured FAC). The β value is then estimated by the following β = [response (in [FAC] units) − measured [FAC]]/measured combined chlorine. The resulting estimated β values are response factors for combined chlorine relative to free chlorine.

The electrode response from chloramines discussed above will not result in an interference with the amperometric titration method for free chlorine unless the chloramine also consumes PAO. The reactions between chloramines and PAO were investigated in order to determine
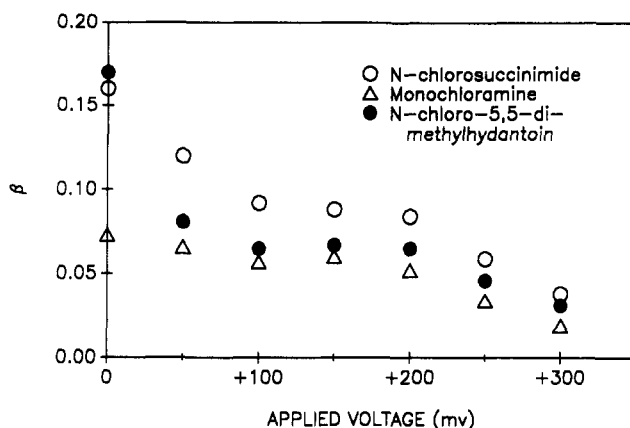
whether the chloramines would consume PAO within the time span of a typical amperometric titration.

Results and Discussion

Relative Responses vs Applied Voltage. Current-voltage curves for FAC and several chlorinated nitrogenous compounds are shown in Figure 1. The hydrolysis constants determined elsewhere (13) were used to calculate the distribution of active chlorine. The relative response factors, or β values, could be determined as a function of applied voltage. These platinum electrode β values are shown in Figure 2. Current responses for chlorinated alanine and glycine were close to the blank values at all applied voltages, and β values were very small (less than 0.02).

The β values for amperometric titration shown in Figure 2 demonstrate that interference is very much a function of the applied voltage. The sensitivity for FAC increases as the applied voltage is made less positive vs SCE (Figure 1). However, as the applied voltage is made less positive, the *relative* response from the chloramines increases. This proves that the selectivity for FAC decreases (and the sensitivity increases) as the applied voltage is made less positive. The amperometric titration β values (at +200 mV applied) for monochloramine, N-chlorosuccinimide, and N-chloro-5,5-dimethylhydantoin are similar to their β values for the amperometric membrane electrode operated at +200 mV (13).

Reactions between Chloramines and PAO. Chloramines must consume PAO to interfere with the measurement of free chlorine. Chloramines are known to react slowly with dechlorinating agents such as sulfite (14, 15). Chloramines were titrated according to the standard methods (6) amperometric titration for FAC procedure (i.e., at +200 mV applied) to see if the measured current decreased after the addition of PAO. Chloramines were synthesized so that the total chlorine was 6.04 × 10⁻⁵ M. An amount of PAO equivalent to 10% of the total chlorine was added. A decrease in signal was observed for the N-chloro derivatives of ammonia, glycine, alanine, cyanuric acid succinimide, and 5,5-dimethylhydantoin. The decrease in signal for inorganic monochloramine upon the addition of PAO was very small.

During the experiments described above, it was noticed that in some cases a recovery in the response occurred. In other words, the response decreased immediately after the addition of PAO, but increased past the initial value with time. No recovery in signal was observed for the N-chloro derivatives of 5,5-dimethylhydantoin, ammonia, glycine, or alanine. A small recovery was observed for N-chloro-
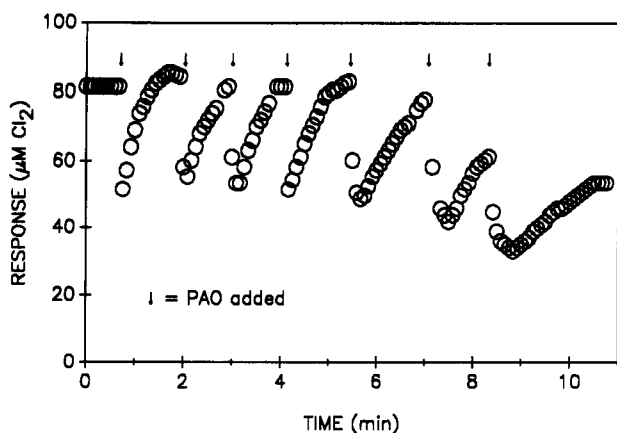
Figure 3. Response recovery for N-chlorosuccinimide after the addition of PAO.

Table I. Chemical Characteristics of the Wastewater and Drinking Water Samples

	wastewater		
	WW1	WW2	drinking water
nitrogen, mg/L as N			
nitrite	0.006	0.027	0.009
nitrate	16.8	7.68	0.155
ammonia	0.036	0.46	0.12
pH in laboratory	5.98	6.40	5.4

cyanurate. A 5.34 mg/L as Cl_2 solution of N-chloro-cyanurate gave a response equivalent to 1.11 mg/L as Cl_2. Upon the addition of PAO, the response decreased to 0.89 mg/L and slowly increased to 1.03 mg/L over 3 min. N-Chlorosuccinimide showed a very large degree of recovery. A typical titration is shown in Figure 3. The rate of recovery upon the addition of the first aliquot of PAO in Figure 3 corresponds to a first-order rate constant of 5.9×10^{-2} s^{-1} (standard deviation 1.7×10^{-3}).

All of the organic chloramines tested react with PAO. Inorganic monochloramine reacts only to a small extent with PAO. The response recovery study points out a potential problem with amperometric titration. The titration itself can alter the chloramine–FAC equilibrium. As the system reequilibrates, the response increases. This behavior was observed principally with N-chlorosuccinimide. The rate of recovery was rapid with respect to the typical titration time. About 50% of the recovery occurred in 11 s. This phenomenon could significantly increase the amount of titrant consumed and result in overestimation of the FAC residual.

Engineered Systems. The chemical characteristics of the field samples are listed in Table I. Breakpoint curves for samples WW1, WW2, and the settled drinking water sample are presented in Figure 4. Chlorine doses used in the amperometric titration and DPD (companion paper) experiments are labeled in the figure. The model compound data demonstrate that the platinum electrode responds to combined chlorine. The platinum electrode current responses across the breakpoint curve for the WW2 wastewater treatment plant are shown in Figure 5. Comparing the current responses in Figure 5 with the PAO titration breakpoint curve in Figure 4, one can see that at each applied voltage, the current responses show the characteristic morphology of the breakpoint curve. The FAC concentration is expected to be very small before the breakpoint at this pH and chlorine contact time. The electrode is responding to total chlorine, not FAC. One can calculate a β value for combined chlorine (relative to FAC) as a function of applied voltage. The combined
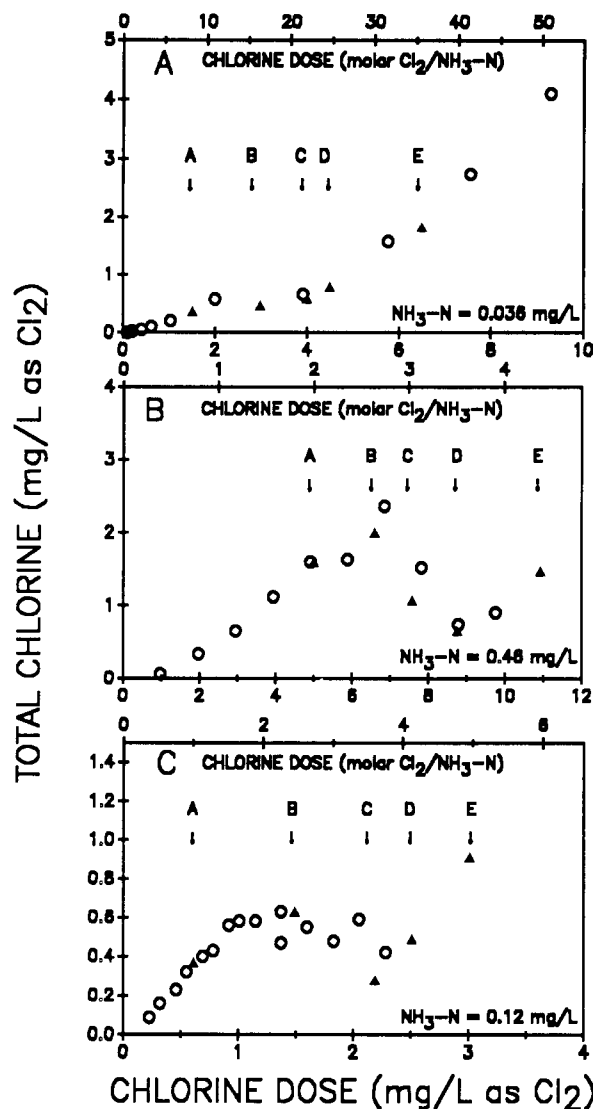

Figure 4. Breakpoint curve for wastewater and settled drinking water samples. A, WW1; B, WW2; C, settled drinking water (open circles, preliminary breakpoint data; filled triangles, final breakpoint data).
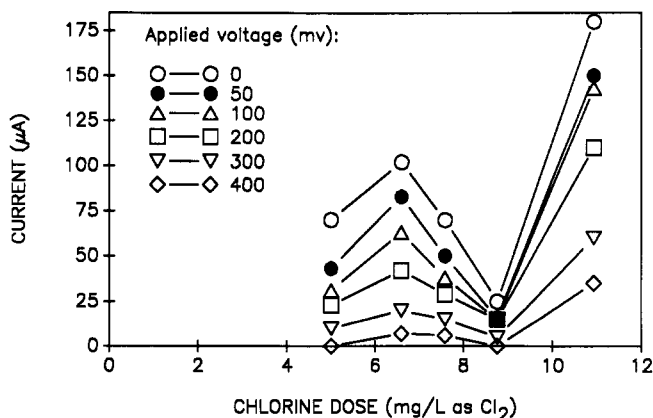

Figure 5. Current vs chlorine dose for wastewater sample WW2.

chlorine β values for the WW1 sample are shown in Figure 6. (The chlorine doses A–E are indicated in Figure 4A). The degree of interference in general decreases as the applied voltage increases. The same trend was observed with the WW2 sample, although the decrease in current was smaller and there was more scatter in the data after the breakpoint. Note that these β values are significantly larger than the model compound β values listed in Figure 2. The reasons for the large β values are unknown at

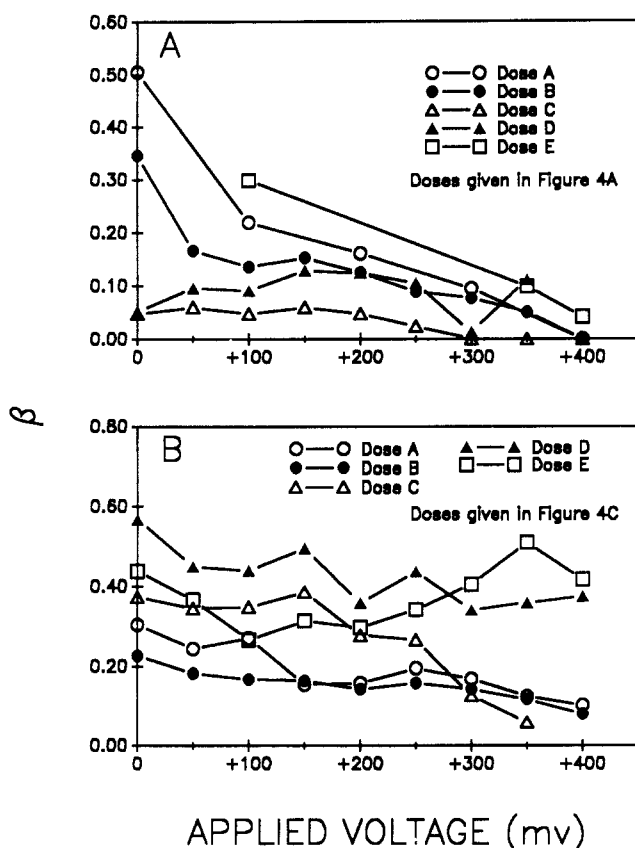**Figure 6.** β values for wastewater sample WW1 and the settled drinking water as a function of applied voltage. A, WW1; B, settled drinking water.

present. The degree of interference appears to be smallest near the breakpoint. This is not unexpected, because chloramine concentrations are minimized at the breakpoint.

In spite of the sensitivity of the platinum electrode for combined chlorine, the measured FAC values by amperometric titration for both wastewater plants before the breakpoint were less than 0.03 mg/L. This suggests that although the system responds to combined chlorine, the PAO is also selective in its reaction (16). The analytical measurement is given by the volume of PAO added to reach a constant, not necessarily zero current. The β values are still large, so higher amounts of combined chlorine might produce measurable interference.

The β values for the settled drinking water sample are also shown in Figure 6. (The chlorine doses A–E are indicated in Figure 4C). The trends observed with the wastewater samples are also seen here: β values generally decrease with increasingly positive applied voltage and β values are large compared to those of the model compounds. It is interesting to note that the β values for the chlorinated settled water are generally larger than the wastewater β values. The platinum electrode appears to be more sensitive to oxidants produced by the chlorination of this settled water. Again, although β values were large, the amperometric titration FAC response was zero before the breakpoint.

This work is in agreement with other field studies of amperometric titration performance in the field. In a previous study (17), we showed that the amperometric titration procedure was sensitive to interferents produced before the breakpoint in chlorinated cooling waters. Snead and co-workers (18) also observed interferences before the breakpoint with amperometric titration during the chlorination of ammonia.

Conclusions

Amperometric titration is subject to interference from organic chloramines and monochloramine. Interferences from monochloramine are large enough to obscure the assumed relationship between measured FAC residuals and disinfection. The degree of interference increases as the applied voltage is made less positive. The choice of an applied voltage depends on the chloramines present as well as the perceived relative importance of sensitivity and specificity. In any case, the data indicate that amperometric titration should be performed at greater than +100 mV applied (vs SCE). The standard method (6) recommends +200 mV applied. The present work raises concern about commerical instruments, many of which operate at zero mV applied.

In the case of N-chlorosuccinimide, it has been demonstrated here that the titration itself can lead to reequilibration of the system and an increase in the current response with time. Recovery occurs fast enough to result in the titration of total chlorine during the FAC titration of chlorinated succinimide. Response recovery was not observed with other chloramines.

The platinum electrode appears to be quite sensitive to oxidants produced during the chlorination of wastewater and drinking water. The β values decreased with increasing positive applied voltages. These studies confirm the conclusion from the model compound work that the titrator should be operated with greater than +100 mV applied voltage (vs SCE).

The platinum electrode response to combined chlorine was as high as 50% of the response to FAC (that is, $\beta = 0.5$). In spite of this, measured amperometric titration FAC readings were small for the drinking water and wastewater samples.

Registry No. Cl_2, 7782-50-5; water, 7732-18-5.

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Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 2. *N,N*-Diethyl-*p*-phenylenediamine

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■ Both inorganic monochloramine and organic chloramines interfere in the free available chlorine (FAC) measurement with *N,N*-diethyl-*p*-phenylenediamine (DPD). The reaction between chlorocyanuric acid and DPD, even with 100-fold excess of the free cyanuric acid and at 9 °C, was as fast as the free chlorine–DPD reaction. Thus, 100% of the chlorocyanuric acid appears as FAC. The rate of the reaction of the other chloramines decreased with increasing basicity of the nitrogen substrate. First-order interference rate constants were measured for 10 chloramines and ranged from 4.6×10^{-5} s^{-1} for *N*-chloro-alanine to 0.29 s^{-1} for *N*-chloro-5,5-dimethylhydantoin. Interference from monochloramine occurred by both direct and hydrolysis-based pathways. The interference appears to be catalyzed by trace iodide present in the phosphate buffers. The presence of Hg(II) in the buffer decreased the iodide effect, which appears most important with the strong base nitrogen chloramines such as monochloramine.

Introduction

As discussed in the companion paper, the assumed relationship between adequate disinfection and measured free available chlorine (FAC) residuals relies on the absence of interferences from poorer disinfectants. This paper examines interferences in the DPD method for FAC by the weak disinfectants monochloramine and organic chloramines. The *N,N*-diethyl-*p*-phenylenediamine (DPD) method is based on the oxidation of an indicator (DPD) by free chlorine to a colored species (1). Several investigators (1–10) have shown that monochloramine can also oxidize DPD, albeit slowly. Thus, monochloramine interferes slowly in the free chlorine measurement. Moore and colleagues have conducted a large study of the oxidation of DPD by monochloramine (8). Strupler (10) has questioned the applicability of their work to the field because Moore and co-workers did not include Hg(II) salts in their buffers as required in the standard method (11).

This study reports the kinetics of the oxidation of DPD by monochloramine and some organic chloramines under standard methods conditions (11). The effect of Hg(II) on the kinetics is examined. The contributions of chloramine hydrolysis and direct chloramine–DPD reaction to the rates of interference are evaluated. Interferences observed in chlorinated wastewater and drinking water samples are presented.
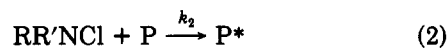
Experimental Section

Model compound chlorination conditions and sampling information for the two wastewater samples (denoted

WW1 and WW2) and the settled drinking water sample may be found in the companion paper. All DPD measurements were made with the reagents specified in ref 11. Spectrophotometric DPD measurements were made with a Cary 219 spectrophotometer (Varian Instruments, Sunnyvale, CA) at 515 nm. The temperature of the cuvette and its contents were held at 25.0 ± 0.5 °C with a recirculating water bath (Haake Buchler Instruments, Inc., Saddle Brooks, NJ). Mixing was achieved with two syringes connected by a three-way valve. The vertically mounted syringe contained 0.5 mL of DPD reagent and 0.5 mL of buffer and the horizontally mounted syringe contained 10 mL of sample. At $t = 0$, the contents of the first syringe were injected into the second syringe through the three-way valve. The mixture was then delivered to the cuvette. Usable data were typically obtained after approximately 5–10 s. This mixing technique was developed to duplicate the procedure used in the DPD colorimetric standard method (11). Unless otherwise stated, kinetic runs were conducted under conditions identical with the standard method (11) and can be referred to as standard method conditions. The spectrophotometer response was calibrated with free chlorine solutions that were standardized against amperometric titration (11). A few experiments were performed using a commerically available stopped-flow apparatus (Hi-Tech, Salisbury, England).

The instrument response vs time data were extracted by the manual measurement of recorder tracings. Typically, 30–40 data points were used. Kinetic parameters and the initial free chlorine concentration were estimated by the kinetic model described below.

Kinetic Model

Model Development. In order to quantify the rate of interference, one must be able to express the initial free chlorine concentration, initial chloramine concentration, and the rate of DPD oxidation as functions of experimental parameters. Consider a substance P which is oxidized to P* by both free chlorine and an organic chloramine, RR'NCl. For example, P may be iodide or DPD. The system is as follows:

$$RR'NCl + H_2O \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} RR'NH + HOCl \qquad (1)$$

$$RR'NCl + P \xrightarrow{k_2} P* \qquad (2)$$

$$HOCl + P \xrightarrow{k_3} P* \qquad (3)$$

We assume the following: (1) P is present in excess (thus, [P] = constant); and (2) the reaction between free chlorine

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