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Aqueous Chemistry of Chlorine: Chemistry, Analysis, and Environmental Fate of Reactive Oxidant Species

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AQUEOUS CHEMISTRY OF CHLORINE: CHEMISTRY, ANALYSIS, AND ENVIRONMENTAL FATE OF REACTIVE OXIDANT SPECIES

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ABSTRACT

Chlorine is used extensively as a biocide for treatment of drinking water, wastewater, and cooling water. The chlorinated wastewaters and process waters discharged to aquatic ecosystems can contain reactive chlorine species and chlorine-produced oxidant species. The environmental fate and possible hazards associated with these chemical compounds are of much public concern. This report reviews (1) the chemistry of chlorine relative to its reactions in fresh, estuarine, and marine waters and the formation of reactive oxidant species; (2) the current status of chemical analysis of reactive chlorine species and chlorine-produced oxidant species relative to analysis of low concentrations (microgram-per-liter range) and determination of accuracy and precision of methods; and (3) the environmental fate of chlorine and chlorine-produced oxidant species.

The nature and concentrations of reactive chlorine species and chlorine-produced oxidant species formed in chlorinated waters are a function of the chlorine dosage and chemical composition of the water [e.g., pH, temperature, ammonia concentration, salinity, organic constituents (such as organic-nitrogen compounds), inorganic constituents (such as bromide or manganese), and presence of sunlight]. The effects of these variables on chlorine and oxidant speciation are discussed.

A large number of analytical methods are available for determining chlorine or oxidant species in water. The methods are grouped and discussed in the following categories: (1) direct property measurement (potentiometry, amperometry, and spectrophotometry); (2) colorimetry; (3) chemiluminescence; and (4) titrimetry. A principal objective of this review of analytical methods was to provide comparative data to permit assessing the significance of chlorine species analyses reported in toxicity data.

The ultimate decomposition products of free chlorine in natural water are chloride, oxidized organics, chloroorganics, oxygen, nitrogen, and possibly chlorate and nitrate. Depending on the bromide content of the chlorinated waters, other possible products are bromate and bromo-organics. The environmental fate of chlorine in natural waters involves sets of complex reactions that are integrated into a conceptual model.

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1. INTRODUCTION

Chlorine is commonly used as a wastewater disinfectant and an antifouling agent for cooling water systems. The biocidal and antifoulant capabilities of chlorine are a function of the reactive chlorine and oxidant species produced in chlorinated water. Much evidence indicates that effluents containing reactive chlorine species, chlorine-produced oxidant species, and reaction products may be toxic to a variety of biological species in the receiving waters. Consequently, an understanding of the formation and environmental fate of toxic species and reaction products, in addition to their toxicity, is necessary to establish limits regarding chlorination of wastewater and cooling water effluents.

This report reviews the chemistry of chlorine relative to the formation and degradation of reactive chlorine species, chlorine-produced oxidant species, and reaction products in fresh, estuarine, and marine waters. The analytical methods for chlorine and oxidant species are presented in detail with two principal objectives, namely: (1) determination of the accuracy and precision of the methods to assist in evaluation of toxicity data, and (2) determination of the sensitivity and reliability of the methods relative to analysis of low concentrations of chlorine and oxidant species. The environmental fate of the chlorine and oxidant species is discussed with respect to time and concentration.

2. AQUEOUS CHEMISTRY OF CHLORINE

The aqueous chemistry of chlorine with respect to chlorination of water and wastewater has been reviewed by several investigators (Hall et al., 1981; Jolley, 1973, 1978; Jolley et al., 1978b, 1980; McKee et al., 1960; Morris, 1975, 1978a, 1978b; Opresko, 1980; Safe Drinking Water Committee, 1980; and White, 1972). The following review summarizes the chemistry of chlorine relevant to the discharge of chlorinated waters and wastewaters to the environment.

When pure water is chlorinated, the principal chlorine-containing species excluding chloride ion are chlorine (Cl_2), hypochlorous acid (HOCl), and hypochlorite ion (OCl^-). If ammonia is present in the water undergoing chlorination, chloramines are also formed. Monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and nitrogen trichloride (NCl_3) may be present. The types and quantities of molecular species present are determined by the reactant concentrations, reaction rates and equilibria, pH, and temperature. Bromide and iodide, if present even at low concentrations, are oxidized by chlorine forming oxidation products such as hypobromous acid (HOBr) and iodine (I_2). Hypobromous acid may, in turn, react with ammonia, if present, to form bromamines analogous to chloramines. Bromine and iodine-containing oxidants become increasingly significant with increasing bromide and iodide concentrations (e.g., in estuarine and marine waters). Sugam and Helz (1980) have schematically summarized these chemical reactions of chlorine in freshwater and seawater, as shown in Fig. 1. This diagram indicates in a simplified fashion the complex interrelationship of the reaction pathways.

Chlorine present in aqueous solution as hypochlorous acid and hypochlorite ion is called "free chlorine" (free residual chlorine). Although generally of little consequence in waters at near-neutral pH values, molecular chlorine and nitrogen trichloride are also usually analyzed as free chlorine. Chlorine present as monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and organic N-chloro-compounds in which the chlorine-containing compound has a lower oxidation potential than free chlorine is called "combined chlorine" (combined residual chlorine). Nitrogen trichloride

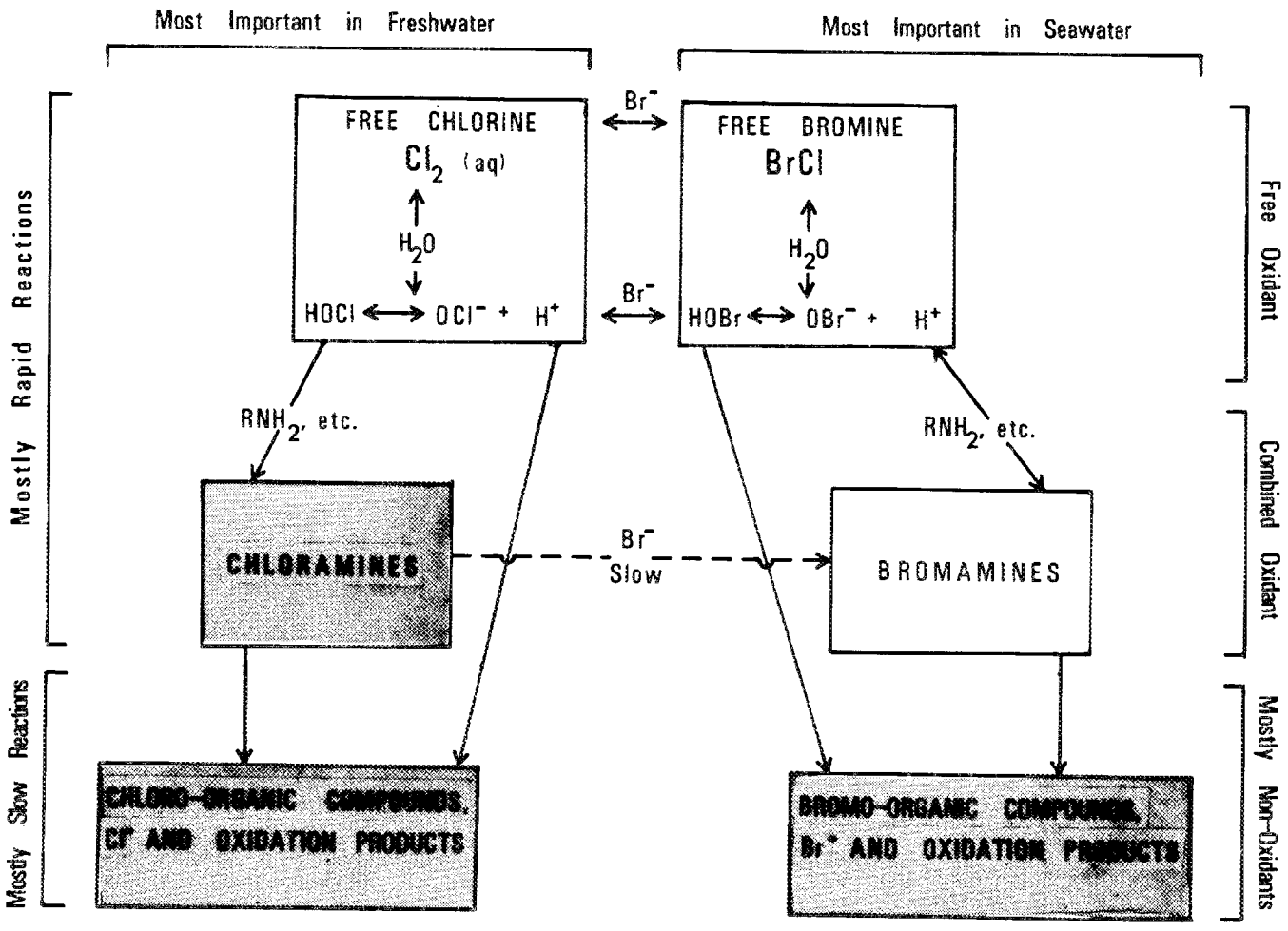

Fig. 1. Schematic outline of chemical reactions in freshwater, estuarine, and marine waters (Sugam and Helz, 1980).

(NCl_3), although analytically usually appearing as free chlorine, is defined as combined chlorine. "Total chlorine" (total residual chlorine) is the sum of the free and combined chlorine.

Hypobromous acid and hypoiodous acid are detected by the usual analytical methods as free chlorine. HOBr will also react with ammonia to produce bromamines that are also detected as free chlorine. Thus the terms "free oxidant" and "combined oxidant" are more appropriate than free chlorine and combined chlorine when solutions containing bromide or iodide (e.g., seawater) are the subject of analysis. However, present analytical methods may not differentiate between free and combined bromine species.

Analytical results are customarily reported as nominal chlorine mass units (e.g., as mg/L chlorine). Hall et al. (1981) believe a convenient and more general unit is microequivalent per liter or micronormality (μN) particularly when chemical reactions are considered.

The possible chemical reactions of chlorine in aqueous solution are quite varied and complex. The major types of reactions are given in Table 1. Compilations of thermodynamic, equilibrium, and kinetic data for many reactions of concern have been made by Lietzke (1978), Haag and Lietzke (1980), and Hall et al. (1981). These scientists and others (e.g., Sugam and Helz, 1980) are making significant efforts to integrate water quality data with known kinetic and equilibrium data for the possible chemical reactions in order to predict the products of the chlorination of natural waters. Such computer programs and models should facilitate a more thorough understanding of both chlorination products and their ultimate fate and distribution.

The major objective of this report is to review the chemistry of chlorine in wastewaters and natural waters (fresh and marine) as it pertains to the formation, degradation, and reaction products of free and combined oxidants. Thus it deals principally with the inorganic chemistry of chlorine and oxidant products that are environmentally correlated with acute toxicity. A major aspect of the chemistry of chlorine or chlorine-produced oxidants is that dealing with the many possible organic reactions

Table 1. Free oxidant reactions: principal reactions of environmental concern for chlorine in aqueous solutions[a]

Reaction type	Example
Water	$Cl_2 + H_2O = HOCl + HCl$
Ammonia	
Substitution	$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$
Oxidation	$2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3H^+ + 3Cl^-$
Inorganic oxidation	$Mn^{2+} + HOCl + 2H_2O \rightarrow MnO(OH)_2 + 3H^+ + Cl^-$
Disproportionation	$3OCl^- \rightarrow 2Cl^- + ClO_3^-$
Decomposition	$2HOCl \rightarrow 2H^+ + 2Cl^- + O_2$
Organic reactions	
Oxidation	$RCHO + HOCl \rightarrow RCOOH + H^+ + Cl^-$
Addition	$RC{=}CR' + HOCl \rightarrow RC(OH)C(Cl)R'$
Substitution	
N-Cl bond	$RNH_2 + HOCl \rightarrow RNHCl + H_2O$
C-Cl	$RCOCH_3 + 3HOCl \rightarrow RCOOH + HCCl_3 + 2H_2O$

[a]Analogous reactions may occur for bromine and iodine by-products of water chlorination.

and reaction products; however, it is mentioned only very briefly because it was not within the specified scope of this review. Although the ultimate environmental "sink" or fate of chlorine as "Cl^+" is Cl^-, haloorganics and oxidized organics play a role of considerable importance in the reactions and degradation of chlorine. Indeed, haloorganics and/or oxidized organic products may be associated with possible long-term chronic toxic effects of chlorine reactions in natural waters and, consequently, of some environmental significance.

2.1 Free Oxidant Chemistry

2.1.1 Chlorine chemistry

Chlorine gas hydrolyzes very rapidly in water according to the following reaction:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \quad . \qquad (1)$$

The hydrolysis constants for this reaction range from 1.5×10^{-4} at 0°C to 4.0×10^{-4} at 25°C (Connick and Chia, 1959; Morris, 1978a). The forward rate constant is 13.7 s^{-1} at 25°C, indicating a reaction half-life for Cl_2 of 0.05 s (Hall et al., 1981). Morris (1966, 1978b) concluded that for normal conditions of chlorination of fresh water and wastewater, the hydrolysis is essentially complete at pH values >6. While Morris made calculations for "seawater," he neglected the ionic strength effects and the reaction of chlorine with bromide so that the values have relatively little applicability to actual seawater (Carpenter, 1978).

Hypochlorous acid is a weak acid. It dissociates or ionizes with a dissociation constant ranging from 1.6×10^{-8} at 0°C to 3.2×10^{-8} at 25°C (Morris, 1966). At pH 7.5 and 25°C, HOCl and OCl^- are equimolar in concentration.

$$HOCl = H^+ + OCl^- \quad . \qquad (2)$$

At higher pH, OCl^- becomes the major form of chlorine and at lower pH, HOCl becomes dominant. Morris (1978a) calculated the distribution of principal oxidizing species for aqueous solutions at 15°C as a function of pH and chloride concentration (Table 2). These equilibria are important because the toxicity and/or reactivity depend on the particular chemical

Table 2. Distribution of principal oxidizing species for aqueous chlorine solution at 15°C (Morris, 1978a)

pH	pCl	Fraction of oxidizing chlorine		
		Cl_2	HOCl	OCl^-
5	2[a]	3.6×10^{-4}	0.997	0.003
6	2[a]	3.6×10^{-5}	0.975	0.025
7	2[a]	2.9×10^{-6}	0.797	0.203
8	2[a]	1.0×10^{-7}	0.280	0.720
9	2[a]	1.0×10^{-9}	0.038	0.962

[a]Freshwater, chloride at 350 mg/L.

species present. The fraction of molecular Cl_2 is a very small fraction of the total oxidizing chlorine, but this does not necessarily preclude its involvement in reactions or disinfection. Vapor transport of molecular Cl_2 is insignificant at low concentrations of chlorine and neutral pH values. However, at acidic pH values and high concentrations of chlorine (e.g., pH 2 and 3500 mg/L chlorine), an appreciable amount of molecular Cl_2 is present, and vapor transport of molecular Cl_2 may become significant (White, 1972). Other possible transient oxidizing species are principally of academic interest. For example, H_2OCl^+ would be present only at extremely low concentration at pH 5 to 9 (Safe Drinking Water Committee, 1980). It is probably the species responsible for acid catalysis of many reactions of HOCl (Morris, 1978a).

Hypochlorite solutions. If sodium or calcium hypochlorite are used as the source of active aqueous chlorine, they provide hypochlorite ions as follows:

$$NaOCl \rightarrow Na^+ + OCl^-, \quad (3)$$

$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^- . \quad (4)$$

The hypochlorite ion very rapidly establishes equilibrium with hypochlorous acid [see reaction (2)]. Thus at the same pH and temperature, the composition of the aqueous solution is the same whether starting with chlorine gas or a hypochlorite (Morris, 1978b).

Although hydrolysis of chlorine gas (reaction 1) produces hydrogen ions thus tending to lower the pH, and dissolution of hypochlorite consumes hydrogen ions in reaching equilibrium [reactions (2), (3), and (4)], thus tending to raise the pH, the pH effect is generally very small at the lower milligram-per-liter concentrations of chlorine used in water and wastewater treatment (Morris, 1978b). However, in the immediate vicinity of the injection of strong solutions of chlorine or hypochlorite, the pH change may be very significant.

2.1.2 Bromine chemistry

If bromide is present as in some freshwaters, brackish waters, and seawater, the added chlorine will oxidize the bromide rapidly (Farkas

et al., 1949) as follows:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad . \tag{5}$$

The rate constant for this reaction is pH dependent, since OCl^- does not oxidize Br^- at nearly the rate that HOCl does:

$$k_{obs} = \frac{k}{\frac{K_a}{[H^+]} + 1} \quad , \tag{6}$$

where K_a is the ionization constant for HOCl.

The rate constant for reaction (5) is $4.7 \times 10^{-4} \exp(-754.9/T)$ L mol^{-1} s^{-1}, where T is in Kelvin units (Inman and Johnson, 1979). For seawater with a natural bromide ion content of 65 mg/L and pH of 8, the rate constant would be 141 L mol^{-1} s^{-1} at 25°C (Haag and Lietzke, 1980). Hall et al. (1981) report computations that the reaction in seawater is complete in approximately 10 s.

In pure aqueous solutions, the chemistries of bromine and chlorine show qualitative similarities. The primary bromine species are molecular bromine (Br_2), hypobromous acid (HOBr) and hypobromite ion (OBr^-). The equilibria between these species are controlled by the following reactions:

$$Br_2 + H_2O = HOBr + H^+ + Br^-, \; K_h = 5.8 \times 10^{-9} \text{ at } 25°C \; ; \tag{7}$$

$$HOBr = OBr^- + H^+, \; K_a = 2 \times 10^{-9} \text{ at } 25°C \quad . \tag{8}$$

A primary difference between the chlorine and bromine systems is that there is a relatively high concentration of molecular Br_2 at near neutral pH values compared with very low concentrations of molecular Cl_2 (LaPointe et al., 1975). A second important difference is that for a given pH value, HOBr ionizes tenfold less than HOCl does. Since the un-ionized forms are more effective in disinfection or biofouling control, systems that contain bromide ion will respond very differently to any particular chlorination dosage.

While bromine and bromide ion can form tribromide ion, the equilibrium constant is about 15.9 at 25°C. Thus in natural waters, including seawater with a bromide concentration of 65 mg/L, the formation of

tribromide is insignificant. The relative fraction of Br_2 and HOBr can be calculated from the following relationship (Safe Drinking Water Committee, 1980):

$$\log \frac{(Br_2)}{(HOBr)} = \log (Br^-) - pH + 8.24 \ . \qquad (9)$$

Hypobromous acid is a weak acid with a dissociation constant of 2×10^{-9} at 25°C (see reaction (6); Farkas and Lewin, 1950). At pH 8.7 and 25°C, HOBr and OBr^- are present in equimolar concentrations. At higher pH, OBr^- becomes the major form of bromine; at lower pH, HOBr becomes dominant (Table 3). Lower temperature increases the pH range where HOBr is the dominant species. At pH values <6, halide species such as Br_3^- and BrCl may be present. However, these are not significant at the pH of natural waters (Hall et al., 1981).

The distribution of chemical species of bromine given in Table 3 were calculated from the equilibrium constants for the hydrolysis of bromine and dissociation of hypobromous acid. The principal reactive bromine species in chlorinated freshwater is probably HOBr at neutral pH. In seawater, HOBr is probably the most reactive species, although a significant fraction is made up of molecular bromine because of the relatively high concentration of bromide tending to displace the equilibrium of reaction (7) toward the left.

2.1.3 Iodine chemistry

The reaction of HOCl with iodide is very rapid (Lister and Rosenblum, 1963):

$$HOCl + I^- \rightarrow HOI + Cl^- \ . \qquad (10)$$

Molecular iodine (I_2) exists in equilibrium with the HOI oxidation product of free chlorine.

$$I_2 + H_2O = HOI + H^+ + I^- \ . \qquad (11)$$

The equilibrium constant for this reaction is 5.44×10^{-13} at 25°C (Burger and Liebhafsky, 1973). The average concentration of iodine in freshwater is estimated as 2 µg/L and that in seawater as 60 µg/L (Sengupta et al., 1978). The presence of HOI in some chlorinated freshwaters is shown by

Table 3. Distribution of principal oxidizing species of bromine produced by chlorination of bromide in natural waters at 25°C as a function of pH and bromide content

	Percentage of bromine species					
	Bromide (4 μg/L)[a]			Bromide (65 mg/L)[b]		
pH	Br_2	HOBr	OBr^-	Br_2	HOBr	OBr^-
5	3×10^{-3}	100	0.02	32	68	0.01
6	3×10^{-4}	100	0.2	4.6	95	0.2
7	3×10^{-5}	98	2	0.05	98	2
7.8	-	-	-	0.04	89	11
8	3×10^{-6}	83	17	0.04	83	17
9	3×10^{-7}	33	67	2×10^{-3}	33	67
10	3×10^{-8}	5	95	2×10^{-5}	5	95

[a]Assumed concentration for freshwaters based on molar ratio of bromide to chloride in seawater (1.6×10^{-3}) and assuming chloride concentration of 10 mg/L in freshwater.

[b]Approximate concentration of bromide in seawater.

the formation of dichloroiodomethane in many drinking waters (Thomas et al., 1980). In oxygenated seawater, iodine is probably present as iodate (Wong and Brewer, 1977) and relatively unreactive (thermodynamically stable) (Safe Drinking Water Committee, 1980).

The dissociation constant, K_a, for the dissociation of HOI [Eq. (12)] at 20°C is 4.5×10^{-13} (Safe Drinking Water Committee, 1980). The dissociation of HOI is expressed as

$$HOI = H^+ + OI^- \quad . \tag{12}$$

At pH 7, the concentration of HOI is about 10^5 greater than OI^-, and at pH 7.8 (seawater) the concentration of HOI is 10^4 greater than OI^-. Thus the dissociation of HOI occurs only at a high pH and is not of practical significance in the chlorination of natural waters and wastewaters. About pH 9, HOI disproportionates rapidly to iodate and iodide (Safe Drinking Water Committee, 1980):

$$3HOI + 2OH^- \rightarrow HIO_3 + 2I^- + 2H_2O \quad . \tag{13}$$

2.2 Combined Oxidant Chemistry

2.2.1 Chloramines

Hypochlorous acid (HOCl) reacts rapidly with ammonia to form monochloramine (NH_2Cl), dichloramine ($NHCl_2$), or nitrogen trichloride (NCl_3) as shown in reactions (14) through (16),

$$NH_3 + HOCl = NH_2Cl + H_2O \quad , \tag{14}$$

$$NH_2Cl + HOCl = NHCl_2 + H_2O \quad , \tag{15}$$

$$NHCl_2 + HOCl = NCl_3 + H_2O \quad . \tag{16}$$

The reaction products are dependent upon the pH, the relative concentrations of hypochlorous acid and ammonia, the reaction time, and the temperature (Morris, 1978b).

Usually monochloramine is the only chloramine that is observed (1) when pH values are >8, and (2) when the molar ratio of hypochlorous acid to ammonia is ≤ 1.0. At higher chlorine-to-ammonia ratios or at lower pH values, dichloramine and trichloramine (also called nitrogen trichloride)

are formed. At pH values <3, only nitrogen trichloride is ordinarily detected (Morris, 1978b). These and organic chloramines are produced during the chlorination of water containing ammonia or organic amines. Their presence may contribute to taste and odor problems in finished drinking water (Symons et al., 1975).

Drago (1957) described the general chemistry of monochloramine, and Theilacker and Wegner (1964) and Kovacic et al. (1970) reported its organic reactions in some detail. Most of these organic reactions occurred in nonaqueous media. Although extremely useful for organic syntheses, these experiments have only limited value for predicting reactions that may occur in chlorinated water.

Monochloramine has been the principal subject of several reviews. Its properties and chemistry have been described by Metcalf (1942), Colton and Jones (1955), Jander (1955a), Drago (1957), Theilacker and Wegner (1964), Czech et al. (1961), Gmelin (1969), and Kovacic et al. (1970). Monochloramine is a colorless, water-soluble liquid with a freezing point of -66°C. It may decompose violently above that temperature.

Relatively little is known about dichloramine. Chapin (1929) determined that its odor, volatility from aqueous solution, and relative solubility in various solvents are intermediate between those of monochloramine and nitrogen trichloride. He also found that dichloramine liberates iodine from acidified potassium iodide (KI) solution as do the other chloramines. Dichloramine solutions are reported to be unstable (Corbett et al., 1953). Recently, Gray et al., (1978) reported that aqueous dichloramine solutions are more stable than previously thought and, thus, may be more significant in water treatment processes.

Nitrogen trichloride is a bright yellow liquid with a strong irritating odor and lachrymatory fumes. Its melting point is below -40°C; its boiling point is 70°C. It is extremely explosive and, therefore, dangerous, except at very low concentrations. Its solubility in water is limited. In aqueous solutions it decomposes slowly to ammonia and hypochlorous acid (Remick, 1942). The hydrolysis reaction is pH dependent (Roscher et al., 1980). Corbett et al. (1953) observed that aqueous

solutions of nitrogen trichloride are stabilized by small amounts of acid. The compound is an effective chlorinating agent, particularly in non-aqueous media (Dowell and Bray, 1917; Houben and Weyl, 1962; Jander, 1955b; Kovacic et al., 1970).

Monochloramine is the principal chloramine that is encountered under the usual conditions of water and wastewater chlorination. The rate of its formation, shown in reaction (14), is extremely rapid at the concentrations and conditions of water treatment. At the pH range of most water and wastewaters, the reaction is usually 90% complete in ∿1 min. The reaction rate is maximum at pH 8.5 (Morris, 1978b; Weil and Morris, 1949). The reaction rate constant for the formation of monochloramine, assuming reaction between neutral molecules is 5.6×10^6 L mol^{-1} s^{-1} at 20°C (Saguinsin and Morris, 1975).

The specific rate of formation of dichloramine is much slower than that for monochloramine except at pH values <5.5 (Morris, 1978b). The reaction rate constant for the formation of dichloramine is 2.7×10^2 L mol^{-1} s^{-1} at 20°C (Saguinsin and Morris, 1975). The relative ratio of monochloramine and dichloramine is a function of the reaction kinetics. Because dichloramine forms much more slowly than monochloramine at near-neutral pH values, dichloramine does not constitute a large percentage of the available chlorine unless the waters are quite acid or when the molar ratio of chlorine to ammonia is >1. Assuming equilibrium conditions, the relative proportion of dichloramine and monochloramine for equimolar chlorine and ammonia from pH 4 to 9 are shown in Table 4.

At pH values of 5 or less, monochloramine is slowly converted to dichloramine (Morris, 1978b),

$$2NH_2Cl + H^+ \rightarrow NHCl_2 + NH_4^+ \quad . \tag{17}$$

Dichloramine is much less stable than monochloramine or nitrogen trichloride. The decomposition of dichloramine is simplified in reaction (18). The actual reaction is more complicated: more chlorine is reduced and some nitrate is formed (Morris, 1978b).

$$2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3H^+ + 3Cl^- \quad . \tag{18}$$

Table 4. Proportions of monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) formed at equilibrium conditions in water chlorination with equimolar concentrations of chlorine and ammonia as a function of temperature and pH (data selected from Safe Drinking Water Committee, 1980)[a]

pH	Proportion (%) at 0°C		Proportion (%) at 10°C		Proportion (%) at 25°C	
	NH_2Cl	$NHCl_2$	NH_2Cl	$NHCl_2$	NH_2Cl	$NHCl_2$
4	0	100	0	100	0	100
5	34	66	20	80	13	87
6	77	23	67	33	57	43
7	94	6	81	9	88	12
8	99	1	98	2	97	3
9	100	0	100	0	100	0

[a]Consideration of kinetic effects leads to calculated values with lower proportions of $NHCl_2$.

In acid solutions (pH 4 or less) or in solutions where chlorine concentrations far exceed those of ammonia, nitrogen trichloride is formed. Because nitrogen trichloride is formed from dichloramine [reaction (16)], the reaction occurs only under conditions in which the dichloramine is reasonably stable. Thus nitrogen trichloride is the only chloramine at pH values <3. At pH values below 3, monochloramine and dichloramine are converted to nitrogen trichloride by the following reactions:

$$3NH_2Cl + 2H^+ \rightarrow NCl_3 + 2NH_4^+ , \quad (19)$$

$$3NHCl_2 + H^+ \rightarrow 2NCl_3 + NH_4^+ . \quad (20)$$

At chlorine-to-ammonia molar ratios >2, nitrogen trichloride occurs in diminishing proportions up to pH values of 7.5. Above pH 7.5, no nitrogen trichloride is found regardless of the ratio of chlorine to ammonia (Morris, 1978b).

When chlorine is added to waters containing ammonia, the "breakpoint" phenomenon becomes significant in the pH range 6 to 9 (Fig. 2). At chlorine-to-ammonia molar ratios of 0 up to 1, monochloramine is formed, and the combined chlorine residual increases to a maximum. At chlorine-to-ammonia ratios >1, dichloramine is formed. Since it is unstable, it decomposes as indicated in reaction (18). Thus with the addition of chlorine, the apparent chlorine residual decreases from a chlorine-to-ammonia molar ratio of 1 up to $\sim$1.65 (the breakpoint) at which point the ammonia has been converted principally to nitrogen (N_2) and some nitrate. Chlorine that is added after the breakpoint exists as free chlorine [i.e., hypochlorous acid and the hypochlorite ion (Pressley et al., 1973; Wei and Morris, 1974; Morris, 1978b).

Reactions of chloramines. Few chemical studies have been designed to identify the products resulting from the reaction of chloramines with organic or inorganic constituents in water and wastewater. Monochloramine is a major constituent in chlorinated wastewaters, and it has been used as a disinfectant for drinking waters. In aqueous media, the principal reactions of monochloramine are probably due to hypochlorous acid formed by hydrolysis and to active chlorine transfer.

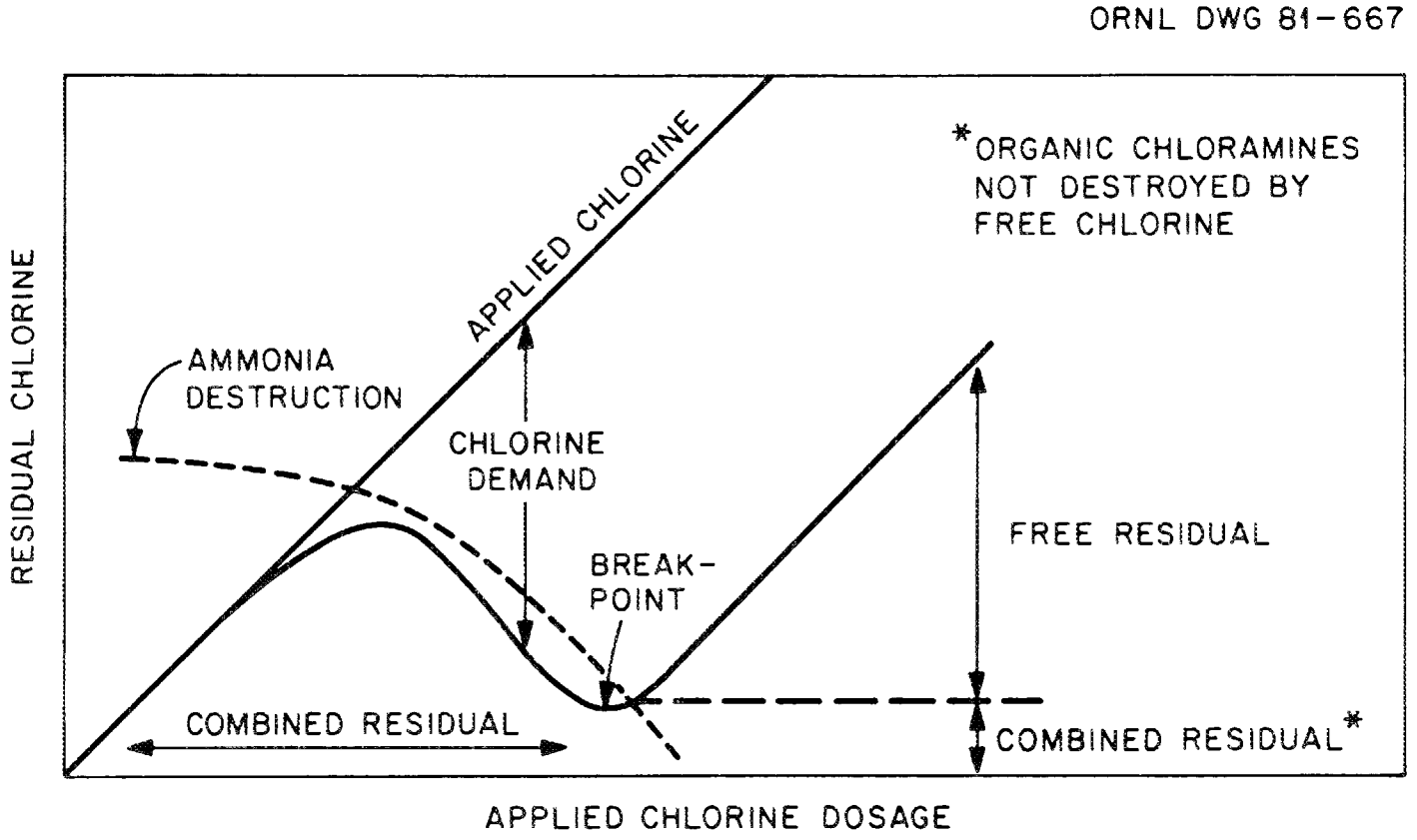

Fig. 2. Graphic description of the breakpoint phenomenon.

Monochloramine is less effective as a chlorinating agent than hypochlorous acid by a factor of approximately 10^4 (Morris, 1967). Presumably, many of the reaction products of chlorination of water with free chlorine will be produced by reaction with combined chlorine residual because of the hydrolysis of chloramines to hypochlorous acid; however, the products should occur in lower concentrations because of the low equilibrium concentrations of the acid. According to Margerum et al. (1979), the hydrolysis of monochloramine,

$$NH_2Cl + H_2O = HOCl + NH_3 \quad , \tag{21}$$

has a reaction half-time of 10 h. The equilibrium constant is $K = 6.7 \times 10^{-12}$ at 25°C.

Margerum et al. (1979) indicated that the formation of hydroxylamine (NH_2OH),

$$NH_2Cl + OH^- \rightarrow NH_2OH + Cl^- \quad , \tag{22}$$

at pH 8 and 25°C has a reaction half-time of 350 yr. Therefore, it probably does not occur in water treatment.

Stevens et al. (1978) determined that trihalomethane (THM) formation was minimized when chloramines (mostly monochloramine) were used to treat raw water. Thus during chlorination of water where the ammonia breakpoint is not achieved, THM production may not be great (Stevens et al., 1978).

Rickabaugh and Kinman (1978) determined that chlorination of Ohio River water with monochloramine at 10 mg/L, pH 7 to 9, and 25°C resulted in 90.7 to 99.9% less production of THM as compared with THM production from chlorination with 10 mg per liter of chlorine as hypochlorous and hypochlorite ion.

Although initially no chlorophenols are formed when low concentrations (milligram-per-liter range) of monochloramine and phenol are mixed, they appear after a reaction time of several days (Burttschell et al., 1959). This is likely a result of the hydrolysis of NH_2Cl and the subsequent reaction of HOCl with the phenols.

According to Margerum et al. (1979), monochloramine is a chlorinating agent for N-compounds in aqueous solutions. For example, with 10^{-4} M

glycine, the following reaction takes place:

$$NH_2Cl + H_2NCH_2COOH \rightarrow H(Cl)NCH_2COOH + NH_3 \ . \qquad (23)$$

The rate constant for this reaction is 1.5 L mol^{-1} s^{-1} at pH 5 to 9, making it or similar reactions probable in aqueous systems. This report also corroborates the observation of Ellis and Soper (1954) that monochloramine undergoes chlorine-exchange reactions with primary and secondary aliphatic amines. See also the research of Isaac and Morris (1980) in the following section.

Organic chloramines. Free chlorine also reacts with nitrogen-containing organic compounds (e.g., amino acids) to form organic chloramines (Calvert, 1940; Wright, 1926, 1936; Taras, 1950, 1953; Crane et al., 1946; Ellis and Soper, 1954; Mauger and Soper, 1946; Sandford et al., 1971; Edmond and Soper, 1949; Ingols et al., 1953; Wajon and Morris, 1980b). Morris (1967) concluded that the reaction rates of free chlorine with nitrogen-containing compounds were faster the higher the basicity (nucleophilicity) of the compound (Weil and Morris, 1949b). For example, the second-order reaction rate constant at 25°C for the chlorination of methylamine is 3.6 x 10^8 L mol^{-1} s^{-1}:

$$CH_3NH_2 + HOCl \rightarrow CH_3NHCl + H_2O \ . \qquad (24)$$

At 25°C and equimolar reactant concentrations, the rate of formation for *N*-chloromethylamine is 70 times faster than that for monochloramine. Morris (1967) analyzed data from the kinetic studies made by Mauger and Soper (1946) concerning chlorination of amides and concluded that at equimolar reactant concentrations the formation of monochloramine was much faster than the formation of N-chloramides.

Morris et al. (1980) state that knowledge about the nitrogen-containing organic compounds in natural waters or about the reactions of these compounds with aqueous chlorine and the properties of the products is very limited. This is unfortunate since the concentration of organic amino-N may greatly exceed that of ammonia in surface waters and some ground waters. Both ammonia chloramines and organic chloramines are formed when wastewater effluents are chlorinated. According to Isaac and

Morris (1980), the relative amounts depend on the concentration ratios of ammonia to organic amino-N and the relative rates of reaction. Assuming 20 mg/L NH_3-N and 2 mg/L amino-N and relative specific rates of reaction of 1 to 8.5 (NH_3 to amino-N), they calculate the combined chlorine would be 54% NH_2Cl and 46% N-chloroorganic within 0.3 s at pH 7 and 25°C. As time passes, transfer of chlorine from NH_2Cl to organic nitrogen is favored.

Isaac and Morris (1980) studied the reaction of monochloramine with amino acids (glycine, alanine, and serine), the secondary amines (sarcosine and dimethylamine), glyclglycine, and the ethyl ester of glycine. They demonstrated that monochloramine is an active agent for transfer of chlorine to other nitrogen atoms. The amino acids are of particular interest as chlorine receptors because of their relative abundance in natural waters. There are two plausible mechanisms for Cl^+ transfer from NH_2Cl to organic nitrogen -- hydrolysis and direct transfer. If the hydrolysis mechanism is valid, the transfer rate in the presence of excess nitrogenous organic compound should be equal to the hydrolysis rate of monochloramine and independent of the nature and concentration of nitrogenous organic reactant. Isaac and Morris found this was not the case when the initial concentration of nitrogenous organic compound was varied. Instead, the observed first-order rate constants were proportional to the initial concentration of N-compound. In addition, nearly a 20-fold variation in the reaction rate was observed for different N-compounds. The first-order reaction rate constants ranged from 2×10^{-3} to 3×10^{-2} s^{-1} at 25°C. These values are greater than the chloramine hydrolysis rate, 4×10^{-5} s^{-1} at 25°C. They concluded that NH_2Cl can react directly with such compounds to produce N-chloroorganics. At NH_2Cl and organic nitrogen concentrations (about 10^{-4} M) in wastewater effluents and in receiving waters at effluent discharge locations, direct reaction will occur between NH_2Cl and the organic nitrogen compounds to produce N-chloroorganics. They concluded that at reactant concentrations representative of freshwater (about 10^{-5} M), both direct transfer of Cl^+ to organic nitrogen compounds and NH_2Cl hydrolysis to HOCl with subsequent reaction of HOCl with organic nitrogen occur. The transfer of active chlorine from chloramines to produce organic chloramines may affect the toxic properties of the chlorinated water (Isaac and Morris, 1980).

2.2.2 Bromamines

Hypobromous acid reacts with ammonia and nitrogen-containing organics compounds to produce bromamines and organic bromamines. Galal-Gorchev and Morris (1965) and Johnson and Overby (1971) studied the formation of the inorganic bromamines:

$$HOBr + NH_3 = NH_2Br + H_2O \ , \quad (25)$$

$$HOBr + NH_2Br = NHBr_2 + H_2O \ , \quad (26)$$

$$HOBr + NHBr_2 = NBr_3 + H_2O \ . \quad (27)$$

By mixing dilute solutions of bromine with excess ammonia at pH $\geq$9, Galal-Gorchev and Morris (1965) prepared solutions of essentially pure monobromamine (NH_2Br) as indicated by uv spectra. With these reaction conditions, the reduction of bromine to bromide was quite rapid, and a large excess of ammonia was required to stabilize the NH_2Br solution. Dibromamine ($NHBr_2$) solutions as determined by uv spectra were prepared at pH $\leq$8.2, but there was a constant reduction of bromine to bromide, indicating the $NHBr_2$ is unstable. Reaction conditions leading to the best yield of $NHBr_2$ were pH 5.5 to 6.3, with a molar ratio of ammonia to bromine of 20. Tribromamine (NBr_3) formed readily at acidic pH even in solutions with a molar ratio of ammonia to bromine >1, indicated by uv spectra. At pH 4.5, the rate of reduction of oxidizing bromine was much slower, indicating that NBr_3 is considerably more stable than $NHBr_2$.

In contrast with chloramines, the proportion of bromamine species in solution depends on the pH and molar ratio of ammonia to bromine (i.e., the distribution is equilibrium controlled and rapidly established). In the chloramine system, equilibria are established slowly, and the proportion of NH_2Cl, $NHCl_2$, and NCl_3 depends on the kinetics of formation of each chloramine species (LaPointe et al., 1975).

Dibromamine is the predominant bromamine even under conditions with large excess of ammonia (e.g., 100 to 1 at pH 7). Monobromamine is present only at high pH and/or high ammonia concentrations. Tribromamine can be present up to pH 9 (see Fig. 3) (LaPointe et al., 1975).

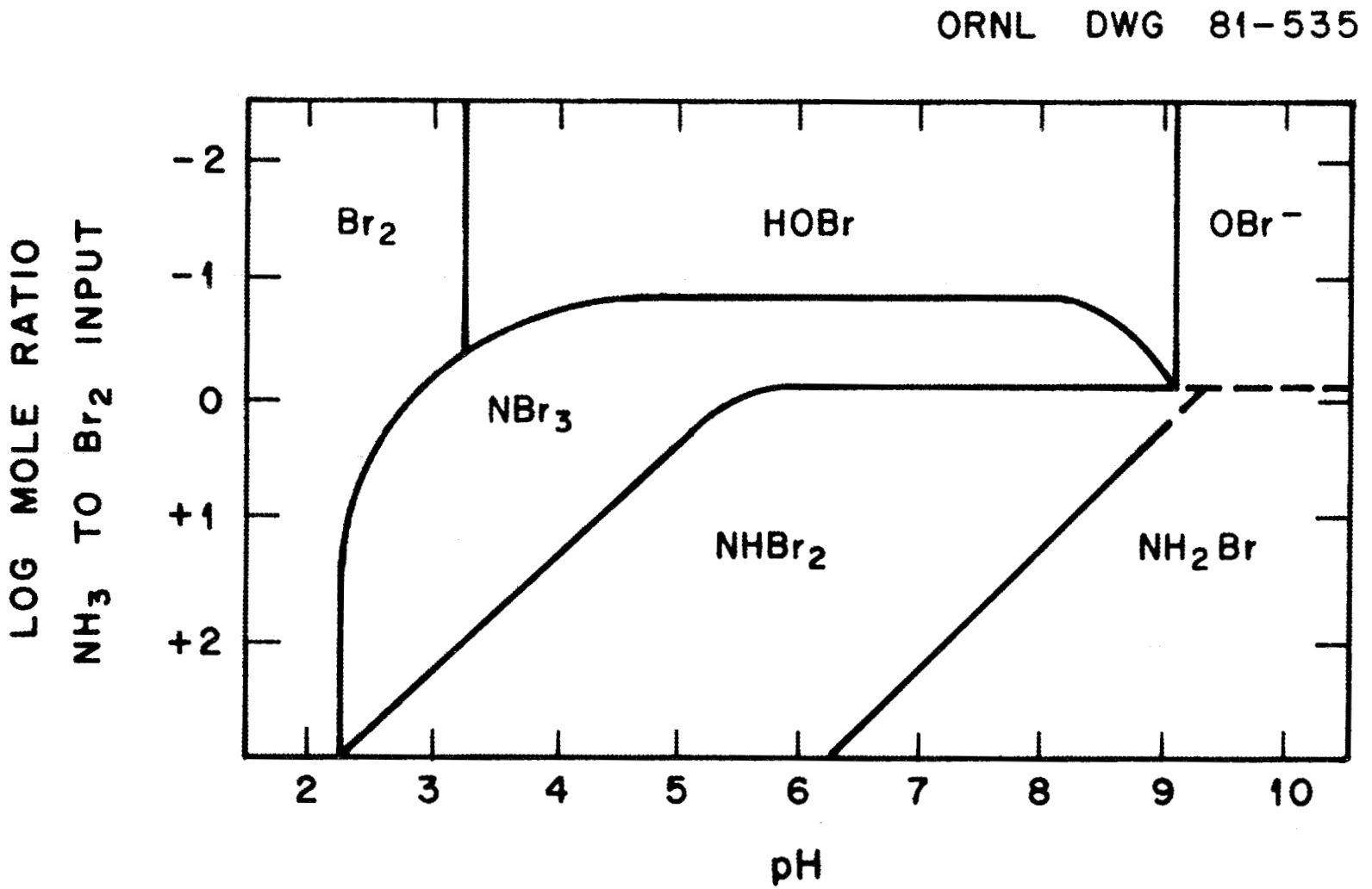

Fig. 3. Principal species of bromine and bromamine predominating after 1 to 2 min at various pH and ammonia-to-bromine ratios. Lines represent equivalent concentrations. Hypobromous acid separation from bromine given for 10^{-5} M bromide (LaPointe et al., 1975).

Galal-Gorchev and Morris (1965) and Johnson and Overby (1971) determined that, qualitatively, the kinetics of formation for bromamines were much faster than that for the analagous chloramines.

Wajon and Morris (1980a) determined that at pH 7 and 1 ppm NH_3-N, 90% of the aqueous bromine is converted to monobromamine in 0.2 s. Dibromamine is formed within 1 min at this pH, whenever the molar ratio of nitrogen to bromine is <100, indicating that the dibromamine formation is very rapid. In addition, dibromamine converts very rapidly to monobromamine when the pH changes. Bromine is, thus, a very labile atom, transferring rapidly from one attachment to another, whether it is oxygen, as in HOBr, or nitrogen. Johnson and Overby (1971) concluded that the distribution of N-bromo compounds is determined principally by equilibrium consideration, whereas that of N-chloro compounds is based on the relative rates of formation (Morris, 1967). This conclusion appears valid for reaction times from 1 min to 1 h.

Wajon and Morris (1980a) studied the reaction of aqueous bromine with ammonia and several amino acids for the pH range 9.5 to 12.7. According to their data, hypobromous acid is about 1000 times more reactive toward ammonia than is hypobromite ion. The overall rate of formation of NH_2Br at pH 7 is about 10 times that of NH_2Cl. The observed reaction rate constant at pH 7 and 20°C for NH_2Br formation was 2.9×10^5 L mol^{-1} s^{-1} and for NH_2Cl formation was 2.1×10^4 L mol^{-1} s^{-1}. At pH 9.5, the NH_2Br formation reaction was complete within 1.6 ms. Monobromamine formation was second order, first order each with respect to aqueous bromine and ammonia. Wajon and Morris determined that in contrast to the hypochlorite-ammonia reaction for which at a pH >10 the observed reaction rate constant decreased tenfold for each unit increase in pH, the hypobromite reaction exhibited a leveling off in rate at pH >11. The decrease with the hypochlorite-ammonia reaction has been attributed to a reaction mechanism in which the nonionic species, HOCl and NH_3, are the major reactants. This mechanism also appears to be the major pathway for the hypobromite-ammonia reaction at pH <11, but reaction with hypobromite ion itself probably accounts for the leveling off at pH >11.

The relative kinetics for the formation of bromamines and chloramines were evaluated by Galal-Gorchev and Morris (1965) based on kinetic data from Weil and Morris (1949a) and Farkas et al. (1949), and also experimentally. For equal concentrations of bromide and ammonia nitrogen, the calculated ratios of formation of monochloramine to hypobromous acid were 750 at pH 9, 110 at pH 8, 11 at pH 7, and 1.1 at pH 6. Using the following concentrations — HOCl at 2.3×10^{-4} M, ammonium ion at 4.6×10^{-4} M, and bromide at 4.6×10^{-4} M — Galal-Gorchev and Morris found only monochloramine at pH 8 and above, some bromamine formation at pH 7, and predominant bromamine formation with rapid loss of oxidizing halogen (90% loss in 7 min) at pH 6.

The decomposition of bromamines has been studied principally by Johnson and coworkers (Johnson and Overby, 1971; Cromer et al., 1978; Trofe et al., 1979; LaPointe et al., 1975; Inman et al., 1976; Inman and Johnson, 1978) and more recently by Wajon and Morris (1980a).

Dibromamine is the major bromamine in wastewater disinfected with bromine. The toxicity of the discharge of a brominated wastewater is directly related to the stability of dibromamine. Bromamines act as oxidizing agents and are reduced to bromide. Dibromamine is unstable in the absence of reducing agents and decomposes according to the following reaction when excess ammonia is present:

$$3NHBr_2 + NH_3 \rightarrow 2N_2 + 6HBr \ . \qquad (28)$$

Cromer et al. (1978) studied dibromamine decomposition kinetics and determined that from pH 6 to 8, the formation and decomposition rate of $NHBr_2$ became slower as the pH increased and also as the ammonia-to-bromine molar ratio increased. Cromer et al. (1978) postulated a possible change in reaction mechanism to explain the differences at pH 6:

$$3NHBr_2 = 2NBr_3 + NH_3 \ ; \qquad (29)$$

$$NHBr_2 + NBr_3 = N_2Br_4 + H^+ + Br^- \ ; \qquad (30)$$

$$N_2Br_4 + 2H_2O \rightarrow N_2 + 2H^+ + 2Br^- + 2HOBr \ ; \qquad (31)$$

with

$$v = \frac{-d[NHBr_2]}{dt} = k_a \frac{[NHBr_2]^{2.5}}{[NH_3]^{0.5}} \quad . \tag{32}$$

This reaction mechanism accounts for the observation that mixtures of $NHBr_2$ and NBr_3 are most unstable when equivalent amounts of each are present. Cromer et al. (1978) postulated a second decomposition pathway to explain the slower rate at pH 7 and 8:

$$NHBr_2 + NHBr_2 \xrightarrow{k_b} N_2HBr_3 + H^+ + Br^- \tag{33}$$

$$N_2HBr_3 + H_2O \rightarrow N_2 + 2Br^- + 2H^+ + HOBr \ ; \tag{34}$$

with

$$v = k_a \frac{[NHBr_2]^{2.5}}{[NH_3]^{0.5}} + k_b [NHBr_2]^2 \ . \tag{35}$$

Cromer et al. (1978) concluded that the dibromamine-tribromamine pathway was the preferred decomposition pathway. This mechanism also explains the slower decomposition rates at higher pH and ammonia-to-bromine ratios where there is less NBr_3. Because of the second-order and higher (2.5) dependence on dibromamine concentration, the rate of decomposition of dibromamine becomes quite slow at high dilution, high pH, and high ammonia concentration. They determined the half-life for $NHBr_2$ decomposition at pH 8 with a 100-fold excess of ammonia and 1 mg/L bromine at 20°C was ∿3 days.

Wajon and Morris (1980) concluded that dibromamine is considerably less stable than monobromamine. At pH 8 and 25°C, the half-life of 5 mg/L monobromamine is 19 h ($k_1 = 1 \times 10^{-5}$ s^{-1} from Galal-Gorchev and Morris, 1965) but the half-life of $NHBr_2$ is only 30 min ($k_2 = 17.5$ L mol^{-1} s^{-1} according to Johnson and Overby, 1971).

Inman et al. (1976) determined that tribromamine decomposes in acid solutions according to the reaction

$$2NBr_3 + 3H_2O \rightarrow N_2 + 3H^+ + 3Br^- + 3HOBr \ ; \tag{36}$$

and in basic solutions, according to the reaction

$$2NBr_3 + 3OH^- \rightarrow N_2 + 3Br^- + 3HOBr \ . \qquad (37)$$

They determined that tribromamine formed in 5 s under all conditions they studied. Decomposition of NBr_3 was approximately second order. The rate of NBr_3 decomposition increases with increasing pH. They postulated that NBr_3 is in equilibrium with $NHBr_2$, NBr_2^-, HOBr, and OH^- and that the decomposition of NBr_3 occurs by a rate-determining step in which NBr_3 reacts with NBr_2^-. The pH dependence of the reaction rates are accounted for by postulating hydroxide attack by either NBr_3 or $NHBr_2$ to form NBr_2^-. Decomposition rates are also dependent upon the bromide concentration. At pH 7 and 8 with low initial bromide and constant ionic strength, the rate equation for NBr_3 decomposition is

$$v = -\frac{d[NBr_3]}{dt} = k_a \frac{[NBr_3]^2[OH^-]}{[HOBr]} \ , \qquad (38)$$

where

$$k_a \sim 1.18 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25°C \ .$$

Galal-Gorchev postulated that tribromamine decomposes directly through dibromamine. LaPointe et al. (1975) state that this would explain the stabilizing effect of low ammonia-to-bromine ratios on NBr_3 (i.e., because the entire bromamine system exists in a state of equilibrium, low ammonia-to-bromine ratio shifts the equilibrium towards NBr_3). Similarly, high ammonia concentration in the region where monobromamine is the principal species will shift the equilibrium towards monobromamine (away from dibromamine) and reduce the likelihood of monobromamine hydrolysis to ammonia and free bromine. In addition, in the case of NBr_3, the probability of formation is increased with a large excess of bromine. LaPointe et al. (1975) state decomposition reactions for the entire bromamine system through dibromamine as governed by equilibria cannot be proven with the sparse data currently available, but the idea should not be dismissed.

Organic bromamines. Similar to the formation of organic chloramines, organic bromamines are formed by the reaction of HOBr with nitrogen-containing organic compounds (e.g., amino acids).

Wajon and Morris (1980a) determined that the formation of *N*-bromoglycine is more rapid than the formation of monobromamine. Observed reaction rate constants for the formation at pH 7 and 20°C of *N*-bromodimethylamine, *N*-bromoglycine, and *N*-bromoglutamate were $\geq 6 \times 10^4$, 4.6×10^5, and 3×10^5 L mol^{-1} s^{-1}, respectively. Comparable reaction rate constants for the formation of *N*-chlorodimethylamine and *N*-chloroglycine were 4.3×10^4 and 1.7×10^5 L mol^{-1} s^{-1}, respectively.

Wajon and Morris (1980a) conclude that glycine and glutamate react 2 to 3 times faster than ammonia with aqueous bromine. Dimethylamine reacts 10 times as fast. Other more basic nitrogeneous organic compounds may also react faster than ammonia with aqueous bromine. If transfer reactions of the type $NH_2X + RNH_2$ equal $NH_3 + RNHX$ are rapid, the distribution of active bromine in cooling water bromination will be determined by the position of equilibrium. With chlorine, the equilibria lie far on the side of the organic derivatives. If the same is true for bromine, most residual bromine will be in the form of N-bromoorganic compounds.

The decomposition of bromamines and *N*-bromoamino acids is quite rapid. At 25°C the half-life of *N*-bromoglycine at pH 8.4 has been found to be 100 min and that of *N*-bromoglutamate, about 10 min at pH 9.5.

2.2.3 Bromochloramines

The decomposition of monochloramine in the presence of bromide was studied by Trofe et al. (1979). Sugam and Helz (1977) had predicted that monochloramine could oxidize bromide, as expressed by

$$NH_2Cl + Br^- \rightarrow NH_2Br + Cl^- \quad , \tag{39}$$

but the reaction was expected to be slow. However, Trofe et al. (1979) concluded that the decomposition of NH_2Cl in the presence of bromide in saline waters proceeded according to the following overall reaction with the formation of a mixed halamine:

$$2NH_2Cl + Br^- \rightarrow NHBrCl + NH_3 + Cl^- \quad ,$$

where

$$k = 2.8 \times 10^{-6} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} \text{ at } 25°C \quad . \tag{40}$$

They postulated NHBrCl because of the formation of a peak at 218 nm in the uv spectra of the reaction products. Such a peak did not agree with known spectra for bromamines and chloramines. Haag (1980) conclusively proved the formation and existence of N-bromo-N-chloramines by isolating and characterizing *N*-bromo-*N*-chloromethylamine.

Trofe et al. (1979) concluded that the half-life for monochloramine at 1 mg/L chlorine in estuarine or marine waters will range from 2.5 to 60 h at salinity ranges from 5 to 35 parts-per-thousand (ppt) and pH from 7.5 to 8.0. The major chemical parameters influencing the rapidity of the decomposition reaction are salinity and pH.

Johnson and coworkers (Johnson, 1977; Inman and Johnson, 1978, 1979) first pointed out the competition between NH_2Cl formation and bromide oxidation when chlorine is added to seawater:

$$HOCl + NH_3 \xrightarrow{k_1} NH_2Cl + H_2O,\ k_1 \sim 2.8 \times 10^6\ L\ mol^{-1}\ s^{-1}\ at\ 25°C\ , \quad (41)$$

$$HOCl + Br^- \xrightarrow{k_2} HOBr + Cl^-,\ k_2 \sim 3.8 \times 10^3\ L\ mol^{-1}\ s^{-1}\ at\ 25°C\ . \quad (42)$$

Haag (1980) stated that the two reaction rates are highly pH dependent and will be equal at seawater pH 8.1 when the ammonia concentration is 60 µg/L. Haag concluded that bromide oxidation will predominate in most seawater, with the subsequent generation of bromamines. However, in seawater of high ammonia concentration or estuarine waters of lower bromide and higher ammonia concentrations, the rates for both reactions can be nearly equal. In such cases, a mixture of halamines ranging from monochloramine to bromochloramines to tribromamine would be expected, as indicated by

$$NH_2Cl + HOBr \rightarrow NHBrCl + H_2O\ , \quad (43)$$

$$NHBrCl + HOBr \rightarrow NBr_2Cl + H_2O\ . \quad (44)$$

Haag demonstrated that bromochloramines can be formed under environmental conditions by these reactions.

Courtot and Peron (1979) experimentally found NH_2Cl, NH_2Br, and $NHBr_2$ to be the predominant species in chlorinated seawater when the chlorine-to-ammonia molar ratio is <1.5. If the ratio is >1.5, NBr_3, HOBr, and OBr^- were predominant. They did not look for mixed halamines because they have only recently been reported.

Haag (1980) studied the decomposition kinetics of the mixed halamine CH_3NBrCl and determined its decomposition rate was similar to that of CH_3NBr_2 and CH_3NCl_2 at pH 8.2 and 25°C ($t_{1/2} \sim 170$ h). However, CH_3NBrCl decomposes much faster at pH 9.7 ($t_{1/2} \sim 13$ h) or under laboratory light at pH 8.2 ($t_{1/2} \sim 40$ h) than does CH_3NHCl under the same conditions (pH 8.2, ~69 days; pH 9.7, ~110 h; pH 8.2 with light, 27 days). He concluded that bromochloramines should be less persistent than chloramines in the environment. Johnson (1977) indicated that pure solutions of monochloramine are stable for months at pH 8.

2.2.4 Iodamines

Iodamines are unstable and do not form to a significant extent in aqueous solutions (Safe Drinking Water Committee, 1980).

2.3 Chlorine Demand

Hypochlorous acid is a strong oxidant and, consequently, reacts with many constituents in water. When chlorine is added to natural water or wastewater, the concentration of free and/or combined oxidant is observed to decrease with time. Typically, the rate of decrease is initially rapid and then becomes slower. The difference between chlorine dosage applied to the water and the measured available chlorine is called the chlorine demand of the water. The chlorine demand is principally due to inorganic oxidation reactions and reactions with organic constituents (Table 1).

2.3.1 Inorganic oxidation reactions

The principal inorganic constituents of natural waters and wastewaters that reduce free available chlorine (oxidant) are the following: ammonia, bromide, iron(II), manganese(II), nitrite, sulfide, and sulfite (Morris, 1978b). The complex reactions of chlorine with ammonia and bromide have been discussed above.

Oxidation of iron(II). Aqueous chlorine rapidly and stoichiometrically oxidizes iron(II). The reaction rate,

$$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3 + 5H^+ + Cl^- , \quad (45)$$

probably increases with pH (Morris, 1978b).

Oxidation of manganese(II). Two possible reactions occur with the oxidation to manganese(IV) predominating with excess chlorine:

$$2Mn^{2+} + HOCl + 3H_2O \rightarrow 2MnO(OH) + 5H^+ + Cl^- , \quad (46)$$

$$Mn^{2+} + HOCl + 2H_2O \rightarrow MnO(OH)_2 + 3H^+ + Cl^- . \quad (47)$$

The reaction rate increases with increasing pH and is effective for $MnO(OH)_2$ precipitation above pH 7.5. Manganese(IV) is the most common interfering material in chlorine residual measurement (Morris, 1978b).

Oxidation of nitrite. Nitrite oxidation is stoichiometric and rapid at neutral pH values, but slow above pH 9 (Morris, 1978b):

$$NO_2^- + HOCl \rightarrow NO_3^- + H^+ + Cl^- . \quad (48)$$

Oxidation of sulfide. The oxidation of sulfide constituents by chlorine is generally considered to occur by the following reactions:

$$HS^- + HOCl \rightarrow S + H_2O + Cl^- , \quad (49)$$

$$HS^- + 4HOCl \rightarrow SO_4^{=} + 5H^+ + 4Cl^- . \quad (50)$$

The first reaction is rapid and complete. With excess chlorine, sulfide is oxidized to sulfate ($SO_4^{=}$). The mechanism is not known. Chlorine demand because of sulfide is nonstoichiometric, and time, pH, and concentration dependent (Morris, 1978b).

Oxidation of sulfite. Sulfite may be used as a dechlorinating agent, but may also be found in wastes from treatment of wood-pulp and paper. The reaction of sulfite with aqueous chlorine is rapid and stoichiometric (Morris, 1978b):

$$HSO_3^- + HOCl \rightarrow SO_4^= + 2H^+ + Cl^- \quad . \tag{51}$$

When used for dechlorination, it is generally added as SO_2, which reacts according to the following reaction (Morris, 1978b):

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad . \tag{52}$$

2.3.2 Decomposition reactions

There are two major pathways for the decomposition of hypohalous acids or hypohalite ion, namely disproportionation (53) or decomposition (54);

$$3HOX \rightarrow 3H^+ + 2X^- + XO_3^- \text{ (or } 3OX^- \rightarrow 2X^- + XO_3^-) \quad , \tag{53}$$

$$2HOX \rightarrow 2H^+ + 2X^- + O_2 \text{ (or } 2OX^- \rightarrow 2X^- + O_2) \quad . \tag{54}$$

The pathway and rate of decomposition are determined by pH, concentration, temperature, ionic strength, and light (Downs and Adams, 1973). The main reaction in the decomposition of hypochlorite ion is the one to chlorate, with only a small fraction going to oxygen (Lister, 1956a).

Disproportionation. At basic pH values, the major decomposition pathway for hypohalite ions is disproportionation:

$$3OX^- \rightarrow 3X^- + XO_3^- \quad . \tag{55}$$

The equilibrium constants are very favorable with the reaction rate increasing in the sequence $OCl^- < OBr^- < OI^-$. For OCl^-, $K \sim 3 \times 10^{26}$, and the reaction rate is slow at 20°C, becoming rapid above 75°C. For OBr^-, $K \sim 8 \times 10^{14}$, and the reaction rate is moderately fast at 20°C. For OI^-, $K \sim 5 \times 10^{23}$, and the reaction rate is fast even at 20°C (Downs and Adams, 1973).

The disproportionation of OCl^- is a second-order reaction with the following mechanism:

$$2OCl^- \rightarrow ClO_2^- + Cl^- , \quad (56)$$

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^- . \quad (57)$$

The first step is slow, and the second step is relatively fast (Lister, 1956a). The reaction is not catalyzed by manganese, iron, cobalt, nickel, or copper oxides (Lister, 1956b). The halite (XO_2^-) ion is also an intermediate in the disproportionation of OBr^- and OI^-, which is autocatalyzed by the halide (X^-) ion (Downs and Adams, 1973). The effect of chloride ion on the disproportionation of OCl^- is unresolved. Lewin and Avrahami (1955) reported that the disproportionation of OCl^- alone was accelerated by the addition of chloride, whereas Lister (1956b) observed no catalytic effects due to chloride.

Hypohalous acids decompose more rapidly than the hypohalite ion and are more prone to yield oxygen especially when stimulated photochemically or in the presence of catalytic metal ions. Hypoidous acid decomposes exclusively by the pathway forming oxygen (Downs and Adams, 1973). In acid solutions, a parallel reaction to produce ClO_2 competes with the final oxidation of ClO_2^- to ClO_3^-:

$$H^+ + 2ClO_2^- + HOCl \rightarrow 2ClO_2 + Cl^- + H_2O \quad (58)$$

Increasing ClO_2^- concentration favors ClO_2 over ClO_3^- (Hall et al., 1981).

According to Morris (1978b), the disproportionation reaction producing ClO_3^- is strongly influenced by pH. The maximum rate occurs ~pH 6.7 and decreases rapidly in both acid and basic solutions. Solutions of HOCl are relatively stable at pH 4.5; OCl^- solutions are stable at pH 13.

Because the disproportionation reaction rate is highly dependent on reactant concentrations, it may be the cause of deterioration of stock hypochlorite solutions. However, disproportionation to ClO_3^- is probably not significant at the milligram-per-liter levels of chlorine used for water treatment (Morris, 1978b).

In the pH range 7 to 10 with equal concentrations 0.02 to 0.05 M and temperatures, hypobromite solutions disproportionate to bromate at a much higher rate than hypochlorite solutions. Consequently, because both OCl^- and OBr^- disproportionate by passing through the slow rate-determining halite step, it is apparent that HOBr is much more reactive than HOCl in the pH range 7 to 10 (Lewin and Avrahami, 1955). The disproportionation of hypobromite to bromate follows second-order kinetics. The rate constant for OBr^- disproportionation increases slightly with increasing HOBr-OBr^- or bromide ion concentration, decreases strongly with increasing pH, and is independent of chloride concentration up to 0.5 M (Lewin and Avrahami, 1955; Engel et al., 1954).

Macalady et al. (1977) determined that sunlight induced the formation of bromate in seawater at 40°C that had been chlorinated to 4.2 to 4.9 mg/L chlorine dosage. The rate and extent of bromate formation depended on the sunlight intensity. They observed no bromate formation in the dark. They concluded that the fact that they observed no bromate formation in the absence of light was not at variance with Lewin and Avrahami (1955) because the solutions Macalady and coworkers used were 1000 times more dilute. Calculations using rate constants from Lewin and Avrahami indicated conversion to bromate of <1% after 24 h. Wong (1980) also observed that sunlight induces the decomposition of free oxidant (chlorine dose of 5 mg/L) in seawater to bromate. He postulated the formation of an unknown oxidant species to account for differences between titrations at pH 4.0 and at pH 1.4. It is not clear whether this is an artifact. Hostgaard-Jensen et al. (1977) concluded that sunlight accelerated the decay of oxidant residual in a chlorinated marine cooling water system (pH 8.0 and 20 to 28°C).

Lewin and Avrahami (1955) studied the oxidation of bromide by hypochlorite (see reaction 5). They determined that in the pH range 7 to 10, mixtures of OCl^- and OBr^- were unstable, and chlorate and bromate were formed. The rate of decomposition of OCl^- to ClO_3^- was increased approximately three orders of magnitude in the presence of bromide.

Haag (1981) determined that both bromate and chlorate are products of the decomposition of free oxidants in seawater for molar ratios of >1

for applied chlorine to bromide. Using initial chlorine concentrations of 200 and 320 mg/L as Cl_2, he determined that bromate and chlorate are essentially the only products of hypohalite decomposition in the dark (i.e., no detectable evolution of oxygen). The solutions containing mixtures of hypobromite and hypochlorite disproportionate to form halates much faster than separate solutions of pure hypohalites. No chlorate was formed when the chlorine dosage was less than the equivalent bromide in the seawater; however, bromate was formed. Haag concluded this was not at variance with Carpenter and Macalady (1978) or Wong and Davidson (1977) who had detected no bromate in seawater after decomposition of oxidant residual in the dark because of the longer times and much higher concentrations that he used. Haag determined that no rate enhancement exists for mixed hypohalite systems exposed to sunlight, although halate formation is much more rapid than in the dark. Haag (1981) concluded that rate enhancement in the formation of chlorate and bromate could occur in the chlorination of cooling waters from the upper reaches of an estuary where approximately a 1:1 mixture of HOCl and HOBr might exist after satisfaction of demand reactions.

Decomposition to oxygen. Hypohalous acid and hypohalite decomposition to oxygen is slow in the dark, as indicated by

$$2OX^- \rightarrow 2X^- + O_2 \quad (59)$$

Lister (1956b) found copper, nickel, and cobalt catalyzed the production of O_2. In 1 M sodium hypochlorite solution at 50°C using 10^{-4} moles of metal the rates of oxygen production were: Cu, 7.4 mL/min; Co, 4.0 mL/min; Ni, 2.0 mL/min. Manganese and iron do not catalyze the reaction.

In a later study, Lister and Petterson (1962) determined that the rate of oxygen evolution is second order with respect to hypochlorite. The rate constant is 1.25×10^{-7} L mol^{-1} s^{-1} at 60°C.

The significance of photochemically accelerated decomposition of oxidant residuals to oxygen is not known.

2.3.3 Reactions with organic compounds

A large variety of reactions may occur between free available chlorine (HOCl, OCl^-) and the complex mixtures of organic constituents present in natural waters and wastewaters. The following treatment is merely designed to highlight possible organic reactions and is not intended to be exhaustive.

The types and concentrations of organic products of chlorination reactions are a function of the reactant concentrations, reaction kinetics, pH, temperature, and presence of other halides or ammonia. Some products (e.g., trihalomethanes) appear to be ubiquitous. The possible reactions of chlorine with organic constituents in natural waters and wastewaters and products have been extensively summarized and reviewed (Jolley, 1973, 1978; Jolley et al., 1978b, 1980; Morris, 1975; Symons et al., 1975; Dienzer et al., 1978; Pierce, 1978; Morris et al., 1980; Safe Drinking Water Committee, 1980; Hall et al., 1981). Only major reaction types and selected specific examples will be reviewed below.

The possible chemical reactions of free chlorine with organic constituents in aqueous solution may be grouped into several general types (Table 1): (1) oxidation, (2) addition, and (3) substitution (i.e., the formation of both N-chlorinated compounds and C-chlorinated compounds).

Oxidation. Oxidation may be the predominant type of reaction occurring between HOCl and organic constituents in natural waters and wastewaters (Jolley, 1973, 1978; Christman et al., 1980). The carbohydrates and carbohydrate-related compounds are examples of organics which are subject principally to oxidative reactions (see Crane et al., 1980).

Addition. Hypochlorous acid will react with organics containing reactive double bonds to produce chlorohydrin products. For example, oleic acid reacts with HOCl at pH 2 to 10 to produce 9-chloro-10-hydroxystearic acid (Carlson and Caple, 1978).

Substitution. Chlorine may react with aromatic compounds and amino compounds to replace a hydrogen substituent producing C-chlorinated or N-chlorinated compounds. The formation of N-chloroorganics has been

discussed in some detail elsewhere in this review. The production of trihalomethanes and reactions with humic substances and aromatic constituents are examples of substitution reactions in which carbon-chlorine bonds are produced.

Since Rook (1974) and Bellar et al. (1974) reported the presence of chloroform and other trihalomethanes (THM) in drinking water, THMs have been shown to be essentially ubiquitous in chlorinated waters including seawater (Helz and Hsu, 1978). Much data are now abailable concerning THM precursors, THM production, and analysis (Jolley, 1978; Jolley et al., 1978a,b; Hoehn et al., 1978; Morris and Baum, 1978; Minear and Bird, 1980; Safe Drinking Water Committee, 1980). Numerous studies indicate that temperature, season of the year, pH, organic content of the water, chlorine dose, and chlorine contact time can influence the concentration levels of trihalomethanes in the chlorinated water. In general, the trihalomethane concentration is directly dependent upon the chlorine dose, the organic content of the water, the contact time, and the temperature. This conclusion can probably be extrapolated to the nonvolatile chlorinated by-products.

Humic materials have been implicated as being THM precursor material. In addition to THM, nonvolatile chlororganics may be produced by chlorination of humic materials. Research in this area is increasing (see Jolley, 1978; Jolley et al., 1978b, 1980; Glaze et al., 1980; Helz et al., 1978). Space permits citing only selected examples of current research.

Christman et al. (1980) studied the chlorination at pH 12 of aquatic humic material separated from Black Lake, North Carolina, with the objectives of gaining insight into the types of compounds present in chlorinated drinking water as well as structural information about the humic acid molecule. Three main classes of compounds were detected in the reaction mixture in which humic acid had a concentration of 420 mg carbon per liter and chlorine at a chlorine-to-carbon mol ratio of 1.5. These classes were nonchlorinated substituted aromatic constituents, nonchlorinated straight-chain acids, and chlorinated straight-chain acids.

Rook (1980) examined the chlorination of humic materials from two points of view: (1) the influence of functional groups on the reactivity

of chlorine and bromine with aromatic constituents using appropriate model compounds; and (2) degradation pathways for humic material by examination of the reaction products of resorcinol. Results from these two approaches were then used to formulate a proposed pathway for the degradation of humic acids by chlorination. The reaction pathways proposed account for most of the major degradation products found in reaction mixtures of chlorine and humic materials. After breakpoint chlorination, two classes of chlorinated and brominated by-products are found in finished drinking water: (1) volatile trihalomethanes, and (2) nonvolatile halogenated compounds. Rook stated that the majority of the chlorinated aliphatic and aromatic degradation by-products formed on chlorination of humic acid containing waters are of the nonvolatile halogenated class.

Some aromatic compounds such as phenols are readily chlorinated in aqueous solution by free chlorine. Some nitrogenous organic compounds also undergo chlorination substitution reactions. For example, the pyrimidine uracil reacts with aqueous HOCl to form 5-chlorouracil (Jolley, 1973).

Wajon and Morris (1980b) have studied the chlorination of many nitrogenous compounds and found the reaction products to be quite varied. For example, some amino acids and heterocyclic bases react readily to form N-chloroamino acids and N-chloroheterocyclic compounds which are detectable analytically as free available chlorine; other amino acids and heterocyclic bases may react with chlorine, but the reaction product is not detectable as available chlorine. This phenomenon has considerable significance for the interpretation of analytical results obtained on chlorinated waters containing nitrogenous organic compounds. Presumably, the reaction products not detectable as either free or combined available chlorine may include chloroorganics and oxidized organics. Because of the observed different behaviors of the individual compounds, no generalizations about this group can be made.

3. ANALYTICAL METHODS FOR OXIDANT SPECIES IN CHLORINATED WATERS

Chlorine present in aqueous solution as hypochlorous acid and hypochlorite ion is called "free chlorine" (free residual chlorine). Although generally of little consequence in waters at near-neutral pH values, molecular chlorine and nitrogen trichloride are also usually analyzed as free chlorine. Chlorine present as monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and N-chloroorganic compounds in which the chlorine-containing compound has a lower oxidation potential than free chlorine or slow reaction rate is called "combined chlorine" (combined residual chlorine). These compounds frequently react slower than the free chlorine species in disinfection processes and chemical reactions involved in analytical determinations. Iodide can accelerate some of the chemical reactions of combined species in analysis procedures. "Total chlorine" (total residual chlorine) is the sum of the free and combined available chlorine.

Bromide and iodide, when present at even trace concentrations, are oxidized by chlorine to HOBr and HOI and, consequently, will be detected by the usual analytical methods as free available chlorine. Hypobromous acid will also react with ammonia to produce bromamines. Thus the terms free oxidant and combined oxidant are more appropriate than free chlorine and combined chlorine when such solutions (e.g., seawater) are the subject of analysis. However, present analytical methods may not differentiate between free and combined bromine species.

Analytical results are customarily reported as nominal chlorine mass units (e.g., as mg/L chlorine). Hall et al. (1981) believe a convenient and more general unit is microequivalent per liter or micronormality (μN) particularly when chemical reactions are considered.

The basic questions underlying all analytical determinations concern the meaning of the measurement. Can the measurement be related to the real world situation? Can cause-effect relationships be deduced from observed phenomena associated with the analytical measurement? Can action be predicated based on such association and analyses?

The difficulty of quantitative determination of chlorine-containing species or other halogen or oxidant species resulting from the chlorination of waters is a function of the chemical complexity of the water system. The real meaning of such measurement is dependent upon the inherent limitations of the analytical technique or method, the water quality (chemical composition of the sample), the specific history of the sample being analyzed (i.e., how and when collected, method of preservation, and time-frame of analysis), and the experience, knowledge, and technique of the analyst. Critical analysis of extant literature must be cognizant of such factors. For example, results from the use of the most accurate and precise analytical method may be rendered of no value by poor technique, such as faulty equipment or deteriorated reagents. Conversely, an analytical technique with inherently poorer accuracy and precision may yield acceptable data in the hands of a skilled, knowledgeable operator, or if high-quality water is analyzed. Sorber et al. (1977) have stated that most published procedures perform well in relatively clean systems free from interferences. Sollo et al. (1970) examined the data reported by Lishka et al. (1969), comparing nine analytical methods for free and total chlorine. From the data Sollo and coworkers concluded that each method when used properly and according to specified instructions can be acceptable. They concluded the failures were due to poor laboratory procedure and not to prescribed methodology.

Voluminous literature exists concerning analysis of chlorine- and other halogen-containing species in aqueous solution. This literature has been well reviewed (Opresko, 1980; Hall et al., 1981; Marks, 1972; Helz, 1980; *Standard Methods*, 1975; White, 1972) and many analytical methods have been compared with respect to accuracy and precision (Sengupta et al., 1978; Johnson, 1978; Liska et al., 1969; Sollo et al., 1970; Sorber et al., 1977; Lishka and McFarren, 1971; Bender, 1978; Nicolson, 1965; Guter and Cooper, 1972). This literature and selected papers concerning specific procedure development have been reviewed with two principal objectives in mind, namely: (1) determination of the accuracy and precision of the analytical method relative to toxicity tests; and (2) determination of the sensitivity, accuracy, and reliability of

the analytical method relative to analysis of low concentrations of chlorine or oxidant.

This report only reviews the analytical methods for determining available chlorine, "Cl^+", and other oxidant species formed by chlorination of water (e.g., HOBr). The analysis of both inorganic and organic reaction products (e.g., bromates, trihalomethanes, nonvolatile haloorganics, etc.) is beyond the scope of this review.

A large number of analytical methods are available for determining the available chlorine or oxidant in waters. *Standard Methods* (1975) lists several methods accepted for use in the control of disinfection of drinking water and wastewaters. Helz (1980) has grouped the methods into three major types: colorimetry, potentiometry, and amperometry. However, this misses the important distinction between measurement of some property of the free or combined oxidants and the alternative of titrimetric oxidant estimation using some property for equivalence point detection. The critical point is that, for the direct measurement approach, standards covering the whole range of analyte concentrations need to be prepared to verify that the sensing system is performing as expected; whereas, for titrimetric techniques, only the titrant strength needs to be standardized against some reference substance.

For this review, the analytical methods have been grouped into the following categories:

1. Direct property measurement
   a. Potentiometry
   b. Amperometry
   c. Spectrophotometry
2. Colorimetry
3. Chemiluminescence
4. Titrimetry

3.1 General Analytical Considerations

Several compounds may be present in water or formed on chlorination of water that are falsely measured as chlorine by most of the analytical

methods. These compounds may thus be incorrectly interpreted as available chlorine in either the free or combined chlorine fractions. Johnson (1978) stated that the most common interference in free chlorine measurements is manganese(IV) oxide formed by chlorine oxidation of soluble manganous(II) ion. In general, all strong oxidants will interfere in chlorine measurements. Sengupta et al. (1978) presented a list of possible strong interfering oxidants. Many, such as O_2 and IO_3^-, will react only slowly under normal analytical conditions. Of most importance on an abundance basis are Fe and Mn. Copper(II) may be of importance in power plants with copper/nickel condenser tubes and high corrosion rates. In waters highly polluted by agricultural runoff and wastewaters, nitrite and nitrate may be important. Most interferences may be controlled by compensatory manipulation of reagent concentrations if the analyst is aware of their presence.

Most methods that measure total available chlorine (chlorine produced oxidants) utilize iodide salts at some stage of the analysis because of the following chemical reaction:

$$R\text{-}X + 2I^- + H^+ \rightarrow I_2 + R\text{-}H + X^- , \qquad (60)$$

in which X represents a relatively labile halogen atom. The reaction goes spontaneously to the right at relatively low I^- concentrations and neutral pH range (6 to 8) with strong oxidants such as HOCl, HOBr, and monochloramine (NH_2Cl). For less strong oxidants [e.g., dichloramine ($NHCl_2$)], the reaction is enhanced by increasing the I^- concentration and acidity (Sengupta et al., 1978). The iodine (I_2) produced from reaction (60) can be measured in a variety of ways and such measurements form the basis for many of the analytical methods discussed in this chapter.

Bromine oxidant species that might be present in chlorinated fresh or estuarine waters are capable of reacting quantitatively with I^- to form I_2, I_3^-, and IO_3^-. The proportion of I_2 to I_3^- is controlled by the concentration of I^-, as indicated in reaction (61):

$$I_2 + I^- = I_3^- . \qquad (61)$$

Iodate (IO_3^-) can be converted to I_2 by increasing iodide concentration and acidity, as shown in reaction (62) (Sengupta et al., 1978),

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O \ . \qquad (62)$$

Seawater contains ∿60 µg/L total iodine that is present in oxygenated surface waters as IO_3^-. (Sengupta et al., 1978; Wong and Brewer, 1977). If oxidant analysis is performed using conditions permitting the detection of IO_3^-, then IO_3^- may contribute to a background oxidant level. Freshwater rivers and lakes contain on the average 2 µg/L elemental iodine. Thus, similarly to the seawater situation, iodine may contribute to small background oxidant level to the extent it is present as IO_3^-. Mixtures of freshwater and seawater as in estuarine areas possess intermediate background oxidant levels in such analyses. Iodate will not be detected by most of the available chlorine (oxidant) analyses. However, IO_3^- can be converted to I_2 according to reaction (62). The reaction rate is directly proportional to I^- and H^+ concentration (Sengupta et al., 1978).

The oxidation of I^- by oxygen [reaction (63)] during the course of the analysis or during shelf storage of the reagent solution is a potentially serious interference with low-level oxidant analyses:

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O \ . \qquad (63)$$

This reaction is slow at neutral pH but is accelerated by increasing acidity (decreasing pH), by light, and by traces of Cu(II) and nitrogen oxides. Sengupta et al. (1978) indicated this may be the source of reported background oxidant levels >10 µg/L as chlorine in unchlorinated water. They recommended using KI reagent prepared fresh each day. Ridgon (1978) used KI in 0.025 M NaOH which eliminated background oxidant levels and the need for daily reagent preparation.

Sengupta et al. (1978) thoroughly discuss potential negative errors. The most frequently cited error is volatilization of I_2 or other halogen species during the course of analysis. The magnitude of this error is limited to only a few percent if the analysis is accomplished within a

few minutes after KI addition. However, this is a significant problem for amperometric titration of low concentrations of chlorine. They indicate adsorption of I_2 on glassware is usually only a minor error, but adsorption on suspended inorganic or organic particles may be more significant. An important loss of I_2 during the analysis of highly polluted water (e.g., sewage treatment plant effluents) is the reaction of I_2 with organic matter. However, the most serious potential negative error may be the formation of oxidative chlorine by-products that may be undetected during the time period of the analysis (Carpenter and Macalady, 1978; Macalady et al., 1977; Carpenter et al., 1977).

A serious potential problem created by the use of iodide is that many oxidants will oxidize iodide to iodine. Therefore, analytical methods using iodide are not specific; for example, more substances will interfere with total chlorine determinations than with free chlorine measurements.

Another potential analytical error is the change in chemical speciation of the oxidant due to changing the pH of the water sample prior to fixation of the species during the chemical analysis. Most analytical methods for specific chemical species take this factor into consideration.

Water samples collected for available chlorine or oxidant analysis must be analyzed soon after collection because of the instability of available oxidant species and degradation reactions. The practice of "fixing" the available oxidant by adding a known amount of reductant in stoichiometric excess then back titrating with a standard oxidant can be a useful technique. Such techniques require considerable precision and care, knowledge of the storage stability of the added reductant, and reasonably accurate knowledge of the oxidant concentration so that the quantity of added reductant does not greatly exceed the oxidant.

3.1.1 Definition of Terms

As applied to methods of chemical analysis, precision refers to the reproducibility of a method when it is repeated on a sample under controlled conditions. Precision can be expressed as the standard deviation (σ) according to the following equation:

$$\sigma = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}, \tag{64}$$

where x is the observed value, and $\bar{x}$ is the average observed value in n observations (*Standard Methods*, 1975).

Accuracy refers to the agreement between the observed value and the amount of measured component actually present in the sample. The relative error expresses the difference between the measured or observed value and the actual amount, as a percentage of the actual amount (*Standard Methods*, 1975).

The minimum detectable concentration or limit of detection is a function of the reproducibility of the blank value. If the blank value were perfectly reproducible, the limit of detection would be determined by the smallest discrimination obtainable with the instrument or method being used (Nicolson, 1965). For purposes of this review, the limit of detection for colorimetric or spectrophotometric methods is defined as the concentration of component that gives an absorbance of 0.001 using a 1-cm path length (Nicolson, 1965). This may be calculated from molar absorptivity (ε) using the following relations:

$$C = \frac{A \times MW}{\varepsilon \times b}, \tag{65}$$

where C is concentration, A is absorbance, MW is the molecular weight (e.g., 70 for chlorine), ε is the molar absorptivity, and b is the optical path length.

The minimum limit of detection for amperometric and potentiometric methods is usually defined as two times the noise level of the measurement. Because this is customarily not reported for such methods, the limit of detection used is that reported by the investigators.

3.1.2 Sampling

In analytical chemistry there is an axiom that the result of any analytical procedure can be no better than the sample on which it is

performed. The objective of sampling is to collect a representative sample and to handle it in such a way that no significant change in composition occurs prior to the analysis. See *Standard Methods* (1975) for general sampling considerations.

Because of the labile nature of chlorine and oxidant species in water samples, the samples must be analyzed expeditiously. Exposure to sunlight or other strong light or agitation will accelerate the loss of chlorine. Therefore, chlorine determinations should be started immediately after sampling, thus avoiding extensive light and agitation. *Standard Methods* (1975) recommends to not store samples that are to be analyzed for chlorine. Therefore, samples to be analyzed for chlorine must be either grab samples analyzed immediately after sampling or must be continuously analyzed by on-line monitors. However, several analytical procedures use addition of excess reductant (e.g., phenylarsine oxide) to reduce the chlorine and other oxidant species immediately upon the collection of the sample, thus permitting analysis by "back titration" later at the laboratory. These methods presumably are as accurate as the "forward" methods; however, judging the amount of reductant to add may require taking more samples in order to bracket the stoichiometric amount of reductant required. See *Standard Methods* (1975) for specific details regarding back titration procedures. Decisions regarding sampling methodology must be made on a site-specific basis taking into consideration the analytical methodology to be used.

3.2 Potentiometry

Potentiometry involves the measurement of the spontaneous electrical potential generated between two dissimilar electrodes in a solution. One electrode is chosen to be insensitive to the solution composition (the reference electrode), and the other electrode ideally responds exclusively to the concentration of the analyte (Willard et al., 1965). For free oxidants produced by chlorination, the sensing electrode is commonly made of platinum or some other noble metal. Because noble-metal electrodes are prone to surface poisoning and sometimes fail to achieve stable potentials, potentiometric methods have not been widely used. According

to Helz (1980), a patient, experienced analyst can produce valuable data using noble metal electrodes.

Precision with potentiometric methods can be expected to be roughly 5% and is limited by the logarithmic (Nernstian) response of the electrode. At low concentrations (ppb range), even a plot of log concentration vs electrode potential is not linear. These methods are commonly used only for "total oxidant," as defined by the formation of I_2 from I^-, and all chemical species that can participate in this reaction are included in the analytical results. Standardization is based on solutions of known iodine content, rather than standard chlorine solutions.

Because of relative ease of operation, potentiometry was used by Eppley et al. (1976) for available chlorine measurements. The initial electrode potential varied with the available chlorine concentration of the sample and, after addition of potassium iodide solution at pH 4.0, the potentials were stable. They concluded that the potentiometric method has advantages of speed, sensitivity (10 µg/L), and can possibly be adapted to on-line instrumentation (Eppley et al., 1976).

The Orion chlorine electrode instrument measures the redox potential generated by the iodine produced by the reaction between available chlorine and iodide at pH 4. The electrode potential is a logarithmic function of the iodine concentration and therefore proportional to the total available chlorine concentration. The electrode consists of a platinum-sensing electrode and an internal iodide reference. The instrument is small and portable, permitting rapid analysis at sampling sites. The calibration curve of the electrode potential vs log of chlorine concentration is linear from 0.05 to 1.0 mg/L as chlorine. The approximate detection limit of this potentiometric electrode is 50 µg/L chlorine (Sengupta et al., 1978). Oxidizing agents (e.g., bromine, iodate, Cu(II), and MnO_2) interfere with the measurement. Dissolved oxygen may also oxidize iodide to iodine and give erroneously high results for low-ppb concentration samples (Scarano and Saroglia, 1980).

Seaman et al. (1980) evaluated a potentiometric electrode for on-line automated monitoring of total chlorine in cooling-water effluents (freshwater). They concluded from both field and calibration data that the

potentiometric electrode measurements of total chlorine were significantly lower than the values obtained by amperometric titration. The instruments were calibrated by the manufacturer. However, Olson and Williams (1980), in a comparative study of the amperometric titration method and potentiometric electrode method for determining total available chlorine, concluded the values obtained by the two methods at different laboratories were not significantly different ($p<0.05$).

Helz (1980) stated that a major difficulty in low-level analysis using the potentiometric method is the calibration curves cease to be linear below 50 µg/L (i.e., the solutions at those concentrations do not follow Nernst's law). The nonlinearity requires greater care in calibration and reduces sensitivity. In addition, at ultralow concentrations the time required to achieve equilibrium increases significantly.

Rigdon et al. (1978) developed a computer-based system that compensates for the problems associated with potentiometric analysis of ultralow concentrations of oxidants. They reported determinations of chlorine in water in the concentration range 3 to 100 µg/L, with an accuracy of 2 µg/L. The method uses Orion Model 97-70 chlorine electrodes and the standard addition potentiometric technique to measure the potential difference between the iodide reference electrode and iodine that is generated by the active chlorine. The technique is computer-automated to perform the multiple additions of standards, measure the potential, and carry out the computations to determine the concentrations of active chlorine and error functions. The method yielded linear calibration curves in the concentration range 3.5 to 35,000 µg/L. The method uses standard techniques of the addition of iodide to assay solutions at pH 4. The hypochlorous acid and hypochlorite ion convert the iodide to iodine, and the potential difference between iodide and iodine is measured. Consequently, oxidizing agents such as bromine, iodate, cupric ion, and manganese dioxide interfere with the assay because they convert iodide to iodine. In addition, oxygen dissolved in the sample or absorbed from the atmosphere can oxidize the iodide and contribute significantly high results in the assay of low microgram-per-liter range samples. Also, loss of gaseous iodine may occur,

resulting in erroneously low results. Thus it is desirable to minimize the effect of oxygen oxidation of iodide and volatilization of the iodine by operating under conditions where their magnitudes are comparable. Rigdon et al. determined that the interference by oxygen in aerated water was an average of 0.16 µg/L, with relative standard deviation of 0.1 µg/L using their methodology. They studied the effect of stirring both gently and vigorously and determined that these errors after stirring 6 min were in the range of 0.6 and 20 µg/L chlorine, respectively. By standardizing their measurement techniques and using computer calibration, they were able to compensate for these errors. Another error that they evaluated was air oxidation of the iodide reagents. Adding potassium iodide crystals to the sample was a satisfactory means of correcting the problem of iodide reagent oxidation. However, the initial potential varies with the amount of iodide added. Therefore, the iodide concentration must be the same for electrode calibration. Consequently, Ridgon and coworkers used a reagent sample of 10% potassium iodide in 0.025 M sodium hydroxide and determined that such reagent was stable for several weeks. They also evaluated the error due to volatilization or loss of iodine gas and determined that this error was in the range of 0.04 to 0.06% after 6 min in measurements of 10 to 80 µg/L chlorine using their standard methodology. They determined that the lower limits of the assay is probably governed more by absorption of oxygen than by the sensitivity of the chlorine electrode (Rigdon et al., 1978).

3.3 Amperometry

Amperometry measures the current generated when a constant external potential is applied across the indicator and reference electrodes. The magnitude of the current is proportional to concentrations of dissolved constituents which are oxidized and reduced at the electrode surfaces. The current is generally measured on the diffusion-current region of the current-voltage curve. In this region the current is independent of the potential because of polarization of the indicator electrode. The constituents reacting at the electrode surface are maintained at a concentration near zero. Consequently, the current is limited by diffusion of

the fresh reactants to the electrode surface. The rate of diffusion and, therefore, the current is proportional to the concentration of diffusing substance in the solution (Willard et al., 1965).

Several investigators have used amperometry to measure free and total available chlorine in aqueous solution as summarized by Opresko (1980). The current in an electrolytic cell is proportional to the oxidants in solution if pH and temperature are held constant. Monochloramine interferes with the free-chlorine analysis and electrode surface contamination can contribute to instability and decrease in sensitivity (Johnson, 1978). A common operating practice is to thoroughly rinse the electrodes after the determination of total oxidant and prior to the determination of free oxidant to reduce the effect of excess iodine (adsorbed on the electrode surfaces) on the free oxidant measurement.

3.3.1 Chlorine-flux monitor

Marienko and coworkers have developed a chlorine-flux monitor that uses amperometry to determine available chlorine and has an internal coulometric iodine generator for periodic calibration. The system may be used for continuous monitoring. Laboratory tests indicated that in the range of 10 to 100 µg/L chlorine the standard deviation was 1 µg/L. Field tests were comparable to results achieved by amperometric titration (Marienko, 1976; Marienko et al., 1975, 1976).

Sengupta et al. (1978) evaluated the chlorine-flux monitor. They determined a linear calibration curve for the coulometric-iodine generator over the concentration range of 12 to 270 µg/L chlorine and estimated a lower detection limit of 2 µg/L. In the continuous mode of operation, some difficulty was experienced with maintaining constant flow rates. Iodate, bromate, Cu(II), Fe(III), and Mn(IV) interfered in this technique less than in the amperometric titration. The flux monitor calibration is made on the sample matrix itself and, consequently, interferences are minimized. The analytical data generated by Sengupta et al. (1978) showed linearity for tapwater over the range 0 to 1.20 mg/L chlorine. They concluded the instrument is potentially superior to other electrochemical methods for onsite chlorine analyses.

Johnson et al. (1978) stated that continuous amperometric monitors are much less selective for free chlorine than the amperometric titration procedure. Morrow and Roop (1975) concluded that chloramines interfered significantly (85%) in the techniques using normal bare-electrode amperometric cells even when KI is not added.

3.3.2 Membrane electrode

Johnson and Edwards (1974) developed a membrane electrode for the analysis of active halogen. They determined that a microporous fluorinated polymer permitted diffusion of molecular chlorine and bromine and their hypohalous acids. Incorporation of this membrane into an amperometric electrode permitted determination of these halogen species in water solution. Johnson et al. (1978) stated that the interference from combined available chlorine, monochloramine, and dichloramine was 1.3 to 3.0%. A principal advantage of the membrane electrode, as cited by Johnson (1978), is that it is selective for HOCl.

Soderberg et al. (1980) compared free available chlorine analyses using the membrane-covered polarographic electrode with the following methods: amperometric titration, DPD-colorimetric, DPD-titrimetric (DPD-FAS), and FACTS. The effect of sample concentration, pH, ionic strength, temperature, and interferences on the different methods was compared. The membrane-covered polarographic electrode has a limit of detection greater than 50 µg/L as Cl_2. Precision is ±2% and accuracy is ±5% at 0.5 ppm. The membrane electrode was unresponsive to OCl^-, monochloramine, and ionic oxidants. It responded significantly to trichloramine (∿50% of the response to HOCl). It was also sensitive to HOBr and iodine, and thus could not be used directly for estuarine or saline water applications. Soderberg et al. (1980) stated that the overall relative standard error of the membrane electrode method compared to the standard methods used in this test was <10%. They stated that the overall standard error compared favorably to the precision and accuracy obtained for free available chlorine analysis by Lishka and McFarren (1971) and Nicolson (1965).

3.4 Spectrophotometry

Opresko (1980) reviewed the use of ultraviolet spectrophotometry to evaluate chemical speciation and degradation reactions of chlorine and bromine compounds. These types of studies have generally been limited to laboratory research applications. For example, Haag (1980 a,b) used ultraviolet absorbance spectra and measurements in his study on the formation of N-bromo-N-chloramines in chlorinated saline waters.

Carpenter and coworkers developed a method using ultraviolet photometric titration for determining total residual oxidant concentrations in seawater. In this procedure, the water samples are treated at pH 2.0 with potassium iodide (2.4×10^{-4} M). The oxidants are converted to I_2, which is detected as the I_3^- complex ion by measuring the absorbance at 350 nm (Carpenter, 1965; Carpenter et al., 1977; Carpenter and Macalady, 1978; Carpenter and Smith, 1978). According to Carpenter and Smith (1978) the standard deviation (precision) for photometric titration of replicate determinations was 2.5 µg/L as chlorine, and the method appeared to be a viable alternative to amperometric titration. Interferences noted were background levels of iodate which slowly reacted with the iodide to form iodine and loss of iodine by reaction with organic compounds (Opresko, 1980). As in other iodometric methods, it measures all strong oxidants capable of oxidizing iodide.

3.5 Colorimetry

The principal advantages of colorimetric analysis of chlorine or oxidant residuals are simplicity and convenience. Visual colorimetry, however, is primarily useful for oxidant concentrations greater than 0.1 mg/L as chlorine. The color intensity at λ_{max} of the oxidant reaction products may be measured with simple hand-held color comparators or with spectrophotometers. Colorimetric methods may suffer from interferences caused by turbidity and natural organic coloring constituents (marine gelbstoff) or humic compounds in the water being analyzed. This material creates problems because its light absorbance changes on reaction with chlorine, thus preventing the use of an unchlorinated control (blank).

Although usually relatively unimportant at active chlorine concentration above 0.1 mg/L (except in highly polluted water), this problem may be significant at low to trace concentrations of chlorine, even in high-quality waters.

3.5.1 Orthotolidine (OT) method

There is presently a trend away from orthotolidine methods because (1) the indicator is a suspected carcinogen (Helz, 1980) and (2) the acid-orthotolidine method is less accurate than other methods (Johnson, 1978; *Standard Methods*, 1975).

Acid-orthotolidine. Ellms and Hauser (1913) developed the orthotolidine method as a substitute for the starch-iodide method. Because of its simplicity, it has become the most widely and accepted colorimetric method (White, 1972).

The acid-orthotolidine method is based on the oxidation of the colorless benzidine compound, orthotolidine, to a highly yellow-colored holoquinone structure at low pH values (Marks, 1972). At slightly higher pH values, the oxidation product is the blue unpaired electron semiquinone imine dimer (Johnson and Overby, 1969). If insufficient orthotolidine is used, an unstable red holoquinone product is produced (Marks, 1972).

The yellow-colored complex is formed in direct proportion to chlorine oxidant if the test is carried out at pH 1.3 or lower and with a ratio (by weight) of three parts orthotolidine to one part chlorine (Chamberlin and Glass, 1943; Palin, 1975). The total chlorine is measured by comparing the color intensity of the test sample with color standards. This method has been used primarily in the chlorine concentration range 50 µg/L to 10 mg/L. Nicolson (1965) reported the lower limit of detection of the acid-orthotolidine method was 1.4 µg/L as determined by the concentration calculated to produce an absorbance of 0.001. The molar extinction coefficient of the acid-orthotolidine yellow reaction product is 5.03×10^4 L mol^{-1} cm^{-1} as calculated from the Nicolson (1965) data.

Black and Whittle (1967b) observed that the orthotolidine colorimetric test is unsatisfactory for the determination of free chlorine, and

chloramines interfere in the test. According to Johnson (1978), the yellow color of the orthotolidine oxidation product fades rapidly. Nitrite and Fe(III) interfere as well as MnO_2, which interferes stoichiometrically.

Details of the analytical procedures for the orthotolidine methods are given by Marks (1972) and White (1972). It is not included in *Standard Methods* (1975).

Orthotolidine-arsenite (OTA) method. Hallinan (1944) developed an orthotolidine-arsenite (OTA) procedure designed to differentiate between free chlorine (HOCl and OCl^-) and chloramine based on their different reaction rates with orthotolidine. In the OTA procedure, the water sample containing available chlorine is reacted with orthotolidine, and arsenite is added immediately, thus reducing the chloramines and thereby preventing their development of additional color with the reagent. The developed color is compared with a sample that has first been treated with arsenite and subsequently reacted with orthotolidine. This control permits compensation for (1) interfering substances such as manganese, iron, or nitrite, and (2) turbidity. The test does not completely eliminate interference of monochloramine in the determination of the free-chlorine residual.

According to Hallinan (1944), the OTA test is restricted to the following concentrations: chlorine, 3 mg/L; chloramine, 3 mg/L in the test for chloramine and 25 mg/L in the test for chlorine; nitrite, saturated solution of $NaNO_2$; iron, 25 mg/L as $FeCl_3$; and manganese, 2.5 mg/L as colloidal MnO_2. Below these limits, no false residuals were observed. Temperatures had to be below 60°F (Connell, 1947) to avoid chloramine interferences.

Sollo and Larson (1965) stated that the orthotolidine-arsenite (OTA) test was probably the most widely used method for the determination of free chlorine in water at that time. Chloramine interferences are minimized by chilling the water sample to 1°C.

Johnson (1978) stated that the free-chlorine test had a high combined-chlorine (NH_2Cl) interference of 3%/s at 20°C. Nicolson (1965) found that

below 100 µg/L chlorine, that OTA solution did not obey Beer's law, thus making the lower limit of detection difficult to determine.

Details of analytical methodology are given by Marks (1972), and White (1972). This method is no longer in *Standard Methods* (1975).

Stabilized neutral orthotolidine (SNORT) method. Johnson and Overby (1969) developed a neutral orthotolidine method for free chlorine in which the orthotolidine and blue quinhydrone imine product are stabilized by bis(2-ethylhexyl)sulfosuccinate. The authors stated that chloramine interference is minimized by maintaining a neutral pH and that interference by iron and nitrite is eliminated. The rate of monochloramine interference at pH 7.0 was 40 L mol^{-1} min^{-1}, and first order in monochloramine and orthotolidine with a first-order catalytic dependence on hydrogen ion concentration. The dependence on hydrogen ion (pH) explains why methods of analysis involving lower pH, required because of the instability of the chromogenic oxidation products, have significant chloramine interference. Anionic surface-active agents stabilize the color developed by free chlorine and orthotolidine at pH 7.0. The optimum concentration of Aerosol OT [bis(2-ethylhexyl)sulfosuccinate] was found to be 0.4 mg per milliliter of sample plus reagents (*Standard Methods*, 1975). The ratio (by weight) of orthotolidine dihydrochloride to chlorine must be at least 8 to 1, and the pH between 6.5 to 7.5.

Johnson and Overby (1969) indicated that the molar absorptivity at λ_{max} 625 nm of the blue quinhydrone imine was 3.41×10^4 L mol^{-1} cm^{-1} at pH 7.0. Thus the sensitivity (defined as that concentration producing 0.001 absorbance per cm) of SNORT is 2.1 µg/L as chlorine. They found the relative standard deviation was 0.39% for 10 measurements at 0.98 mg/L chlorine and remained good up to 7 mg/L chlorine. Johnson and Overby (1969) reported the interference of combined chlorine in the free-chlorine analysis by the SNORT method to be low (i.e., 0.1%/min interference by NH_2Cl). The blue color fades slowly, for example, at 25°C and 0.7 mg/L chlorine, fading produces an error of ∿0.1%/min. At higher temperatures, fading is more rapid (Johnson and Overby, 1969). Manganese dioxide interferes stoichiometrically with the free chlorine analysis. They found no measurable interference due to dichloramine ($NHCl_2$) up to 10^{-4} M. Fe(III)

up to 10^{-3} M and nitrite up to 2×10^{-3} M did not interfere. *Standard Methods* (1975) reports that the minimum detectable concentration of SNORT is 10 µg/L free chlorine. Details of analytical methodology are given in *Standard Methods* (1975).

3.5.2 *N,N*-Diethyl-*p*-phenylenediamine (DPD) methods

Palin (1957) described a method for analysis of free chlorine, monochloramine, dichloramine, and nitrogen trichloride using *N,N*-diethyl-*p*-phenylenediamine (*p*-aminodiethylamiline) as the indicator. At neutral pH (6.2 to 6.5), DPD gives a red color (λ_{max} 515 nm) on reacting with chlorine. Addition of a small amount of KI causes monochloramine to react with the iodide, producing free I_2 which forms a red color. Further addition of KI causes a reaction of dichloramine without pH adjustment. Nitrogen trichloride is included in the dichloramine fraction but may also be included with the free-chlorine fraction by changing the order of reagent addition.

In the DPD colorimetric method, the solutions are compared against standard color solutions prepared from potassium permanganate after the several analytical steps (Opresko, 1980). To avoid interfering reactions, colorimetric measurements must be made immediately after the free-chlorine and monochloramine steps. For the slower dichloramine reaction step, a period of 2 min is required (White, 1972).

Several significant problems are associated with the DPD methods: (1) the DPD reagent is not very stable in aqueous solution [i.e., discoloration occurs on standing (Palin, 1957; Johnson, 1978; Sengupta et al., 1978], and (2) the oxidized colored products show fading within a few minutes. The color developed with DPD is also reported to be temperature sensitive (Palin, 1957; Marks et al., 1951; Sengupta et al., 1978).

Manganese(IV) interferes with free-chlorine measurements but may be corrected for by separate tests according to Palin (1957). However, Johnson (1978) states manganese dioxide interferes stoichiometrically in the free-chlorine measurement. Interferences from Fe(III) and nitrite are minimal (Sollo and Larson, 1965). Copper and nitrite will interfere with dichloramine measurements. Dissolved oxygen causes faint color development with

time [e.g., fully saturated water at 18°C gave an error of 10 µg/L as free chlorine (Palin, 1957)]. Interference by copper up to 10 mg/L is overcome by incorporating ethylenediaminetetracetic acid (EDTA) into the reagents. The EDTA enhances the stability of the DPD solution by (1) retarding oxidation, and (2) suppressing (almost completely) the dissolved oxygen errors by preventing trace metal catalysis *(Standard Methods*, 1975).

Johnson and Overby (1969) reported that the combined chlorine (NH_2Cl) interference in the DPD free chlorine measurement is 3.6%/min at 25°C. Because monochloramine slowly reacts with the DPD reagent (monochloramine breakthrough), Palin (1957) emphasizes that readings must be taken rapidly.

The DPD method has been most recently evaluated by Sengupta et al. (1978). They concluded that for measurement in distilled water or water with low interference the DPD concentration, temperature, and pH have limited effects on the analytical response. However, with monochloramine present, temperature and pH will have a significant effect. Serious errors can be caused by reagent instability. Using fresh DPD solutions at pH 6 minimized drift error. In the presence of iodide, the compounds IO_3^-, Cu(II), Fe(III), $S_2O_8^{2-}$, and H_2O_2 were shown to cause DPD color development. Bromate did not interfere.

Nicolson (1965) found the DPD colorimetric method to be the most accurate of the nine older colorimetric methods he evaluated for solutions containing free and combined chlorine.

Nicolson (1965) reported a sensitivity or lower limit of detection for the DPD-colorimetric method of 4 µg/L chlorine, and for the DPD-titrimetric, 11 µg/L chlorine. Sengupta et al. (1978) reported a 16 µg/L lower detection limit with the DPD-colorimetric method and estimated that a 5 µg/L lower limit could be achieved with instrument modifications. Johnson reported the molar extinction coefficient (ε) of the DPD reaction product was 7.5×10^3 L mol^{-1} cm^{-1} (Johnson, 1981). Therefore, using this value, the calculated lower limit of detection is 9.5 µg/L.

Recently Palin (1978, 1980) has added a step that decreases the interference of monochloramine during the free-chlorine measurement using the DPD-colorimetric procedure. The step involves the immediate addition of thioacetamide after DPD has been added to the sample. This appears to act in two beneficial ways to increase the selectivity of the procedure: (1) the thioacetamide immediately reduces any combined chlorine present, but the free residual will have already reacted with the DPD reagent because of its rapid reaction rate; (2) thioacetamide reverses the monochloramine-DPD reaction. The reaction reversal is selective for monochloramine because when DPD is oxidized by free chlorine the addition of thioacetamide has no effect on the color reaction product (Snead et al., 1981).

Analytical methodologies are given in detail in *Standard Methods* (1975). The DPD-colorimetric method has been approved by EPA for analysis of chlorine in water samples (*Federal Register*, 1976).

3.5.3 Leuco crystal violet (LCV) method

Black and Whittle (1967b) developed an analytical method for separately measuring free and total available chlorine using leuco crystal violet, 4,4',4"-methylidynetris(*N-N*-dimethylaniline). The chlorine oxidants are determined by visual comparison of the blue-colored oxidation product with the color developed by chlorine standards or by reference to a standard calibration curve. The combined available chlorine is determined by the difference between measurements for the free chlorine and the total available chlorine (*Standard Methods*, 1975).

The indicator solution proposed by Black and Whittle (1967b) consists of a dilute leuco crystal violet solution and a saturated mercury(II) chloride solution which enhances color development and retards dichloramine interference (Black and Whittle, 1967a). Free-chlorine measurements in the range of 0.1 to 2 mg/L are made at pH 4 by measuring the absorbance of the developed color at λ_{max}, 592 nm. Total available chlorine measurements are made by adding KI to the sample before colorimetric determination (Black and Whittle, 1967b). Proper color development is dependent upon pH (3.6 to 4.3), ratio of indicator to oxidant

(≥30:1 by weight), sample temperature (≤40°C), and the proper timing (test must be completed within 5 min) (*Standard Methods*, 1975).

The indicator reacts rapidly with free chlorine but only slowly with combined chlorine (Opresko, 1980). Johnson (1978) indicated that the monochloramine interference is only 1.0%/min in the free-chlorine analysis. Interference from chloramines in free-chlorine determinations is minimized if measurements are completed quickly. Interference from iron and nitrate up to 20 mg/L is negligible. Alkalinity values up to 150 mg/L and total hardness up to 300 mg/L did not interfere. Chloride concentration over 600 mg/L gave lower absorbance values. Manganese(IV) interferes at very low concentrations (Black and Whittle, 1967b). Johnson (1978) indicates MnO_2 interferes stoichiometrically in the free-chlorine measurement.

This procedure has not been widely used for routine analyses due to the large number of reagents and complex mixing procedure (Palin, 1975; Johnson, 1978; Opresko, 1980). However, the procedure is accurate and suppresses the hydrolysis (interference) of organic chloramines (Lishka et al., 1969). Whittle and Lapteff (1975) reported a modified LCV method for determining total available chlorine, free available chlorine, monochloramine, dichloramine, and nitrogen trichloride.

The minimum detectable concentration by the LCV method is 10 µg/L free available chlorine and 5 µg/L total available chlorine (*Standard Methods*, 1975).

Details of the analytical methodology are presented in *Standard Methods* (1975) and Marks (1972).

3.5.4 Methyl orange method

Sollo and Larson (1965) reported a procedure based on the quantitative bleaching of methyl orange by free chlorine. The oxidant concentration is determined by measuring the change in absorbance of the solution at 510 nm. At pH 2, the test is specific for free chlorine, and chloramine interference is minimized by measuring the absorbance in <2 min. Chloramine interference is increased by bromide and, also, by concentrations of chloride >500 mg/L.

Manganese(IV) quantitatively interferes. The concentration of Mn(IV) may be determined by measuring the bleaching of a control sample in which the free chlorine has been reduced by arsenite. Interferences of Fe(III) and nitrite up to 10 mg/L are negligible. (Sollo and Larson, 1965; *Standard Methods*, 1975; Opresko, 1980).

The methyl orange method, because it depends on bleaching rather than color development, requires precise measurement of reagents and precise control of temperature (Sollo and Larson, 1965). For this reason and because the method lacks in precision, it is no longer included in *Standard Methods* (1975). Nicolson (1965) excluded the methyl orange method from his comparative study because it gave (1) nonlinear calibration curves, and (2) the order and rate of mixing the reagent and sample affected the extent of bleaching.

Details of the analytical method are given by Sollo and Larson (1965).

3.5.5 Syringaldazine (FACTS) method

The syringaldazine test for free chlorine was developed by Bauer and Rupe (1971) and modified by Cooper et al. (1975). At pH 7 syringaldazine reacts with free chlorine to produce a red color (λ_{max}, 530 nm), but it is very insensitive to chloramines. The precision (reproducibility) of the test was good, with relative standard deviations ranging from ±1 to ±20% for concentrations having from 1.056 to 0.055 mg/L chlorine, respectively. In a series of tests with tap water, the results obtained by the syringaldazine method compared very closely with those obtained by both the orthotolidine test and orthotolidine-arsenite tests. The color developed in the test is maximum after 30 s at pH 7 and is stable for at least 5 min for concentrations <5 mg/L chlorine. At high chlorine concentrations, color fading is observed (Cooper et al., 1975).

Guter et al. (1972) and Sorber et al. (1977) evaluated several analytical methods and concluded that the DPD method was most accurate and precise, but the syringaldazine method was most specific for free chlorine. Thus they developed a modified method called FACTS (free available chlorine test with syringaldazine) designed for two ranges of free chlorine: FACTS I, to 5 mg/L; FACTS II, to 10 mg/L (Cooper et al., 1975).

In the FACTS method, very high concentrations of monochloramine (>35 mg/L), oxidized manganese (>2.6 mg/L), and ferric iron (>10 mg/L) will produce color but at a slow rate. Nitrite, nitrate, sulfate, and chloride (≥1 g/L) do not interfere (*Standard Methods*, 1975). Bromine, bromamines, iodine, and ozone will react with syringaldazine (Sengupta et al., 1978; Ryan et al., 1980). Consequently, this method like all others would not be specific for free available oxidants in seawater.

Lieberman et al. (1978, 1980) modified the FACTS procedure to yield a colorimetric method for the analysis of total chlorine, total combined chlorine, and the various forms of combined chlorine. The reactions of the various forms of free and combined available chlorine with potassium iodide are quantitative at pH 4 and can be used for FACTS analysis of total available chlorine. Efforts at differentiating between mono- and dichloramine by pH adjustment of the potassium iodide reaction were unsuccessful. Beers law data obtained with this method demonstrate that the reaction is linear in the range 0.2 to 10 mg/L as chlorine. Color development occurred in <1 min, and fading was appreciable only at high chlorine concentration. The method was shown to be simple, accurate, and precise for analysis of total available chlorine.

Standard Methods (1975) reports the FACTS procedure is sensitive to free available chlorine concentrations of ≤0.1 mg/L. Sengupta et al. (1978) reported a lower limit of detection of 12 µg/L using a spectrophotometer with a 1-cm length but that the lower practical limit could be extended to 5 µg/L with a 10-cm path length. Johnson (1981) reported the molar extinction coefficient (ε) of the syringaldazine reaction product is 2.3×10^4 L mol^{-1} cm^{-1}. Therefore, the calculated lower limit of detection is 3.1 µg/L.

Details of analytical methodology are given in *Standard Methods* (1975).

3.5.6 Cyanogen chloride-barbituric acid method

Nicolson (1965) concluded that the cyanogen chloride-barbituric acid method was most selective of the colorimetric methods evaluated for

the measurement of free chlorine in the absence of chloramines. In this method HOCl reacts with cyanide ion to form cyanogen chloride which, in turn, reacts with pyridine by opening the ring to form a dialdehyde. The dialdehyde reacts with an amine to produce an intensely colored anile, the color intensity of which provides a quantitative measure of the free chlorine (Marks, 1972). Although amines such as benzidine and sulfanilic acid have been used, barbituric acid has given better reagent stability, sensitivity, and reliability. The method is considered very specific for free chlorine.

Nicolson (1965) found the cyanogen chloride-barbituric acid method to be virtually free from serious interference. In this test, Mn(III) at 0.5 mg/L (as chlorine) was detectable as 0.01 mg/L. Bromine interfered partially. The limit of detection was 0.6 µg/L free chlorine. The relative standard deviation (precision) was 3.5% and 1.8% for free chlorine concentrations of 0.1 and 0.5 mg/L, respectively. The method is reproducible, sensitive, relatively specific, and independent of temperature. However, the reagent was found to be unstable in storage, and the method had the disadvantages of (1) responding only partially to combined chlorine; and (2) being a complex procedure, thus restricting its practical use (Nicolson, 1965).

3.6 Chemiluminescence

The oxidation of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) is accompanied by intense blue chemiluminescence (Seitz, 1975). Isacsson and Wettermark (1976, 1978) have used this reaction to develop a very sensitive analytical method for HOCl. Isacsson et al. (1978) postulated that both HOCl and $Cl_2(aq)$ oxidize luminol to azaquinone and produce a slow and rapid light emission, respectively. They concluded that HOCl was the reacting species at pH 8.9 to 11.5, and the pseudo-first-order rate constant for the oxidation of luminol by HOCl was approximately 10^2 s^{-1}.

The chemiluminescence reaction is conducted at alkaline pH by mixing the luminol solution (6.5×10^{-3} M in 0.01 M NaOH), carbonate buffer, and aqueous chlorine solution. Emitted light, λ_{max}, 425 nm, is measured by

a fibre optics-photomultiplier-recorder system. Hydrogen peroxide may be used to intensify the light emission (optimum concentration, 3.4×10^{-4} M H_2O_2). Luminol shows chemiluminescence only in an alkaline environment. The optimum pH for maximum light intensity from the hypochlorine-luminol reaction is 8.9 (Isacsson and Wettermark, 1976, 1978; Isacsson et al., 1978). Isacsson and Wettermark (1976) determined a linear calibration curve in the hypochlorite concentration range 10^{-4} to $10^{-6.5}$ M. In a set of eight measurements, the relative standard deviation (precision) of free chlorine at 10^{-5} M was 6%. A principal difficulty in measurements of 0.05 ng hypochlorite or less was the instability of the chlorine solution.

The chemiluminescence method has much potential for ultralow-level detection of free chlorine but has received very limited application in the water treatment field (Hall et al., 1981).

3.7 Titrimetry

In contrast to the analytical methods that are based on direct measurement of some property of the total oxidants or an induced colorimetric or chemiluminescence property, the titrimetric methods (by definition) involve the reaction of the oxidants with a reducing reagent that is added to the sample to the exact extent required to just completely react with the sample constituents. An important parameter in these methods is the choice of a technique for sensing the progress of the titrimetric reaction and estimating when the equivalence point has been reached. The reaction equivalence point may not be identical with the titration "endpoint," and this discrepancy becomes more significant in analyses for low concentrations (<1 mg/L) of total oxidants. Potentiometry, amperometry, spectrophotometry, or visual colorimetry may be used to follow the course of the titration. Given adequate sensitivity for the endpoint detection, titrimetric methods are inherently precise since it is relatively simple to measure the volume of the titrating solution with a precision better than 1%.

3.7.1 Iodometric method

The reaction of iodine with thiosulfate,

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} , \quad (66)$$

is one of the most important in chemical analysis and is used in analyses for a variety of substances. It provides a general method for the determination of oxidizing agents by the addition of excess iodide and titration of the resulting iodine with thiosulfate. Soluble starch is used as an endpoint indicator for this titration, giving a deep blue color as long as an "appreciable" concentration of iodine is present (Latimer and Hildebrand, 1940). It should be realized that this statement applies to titrations of fairly high concentrations, for example, in the standardization of solutions; but for very dilute solutions the visual endpoint is reached considerably in advance of the equivalence point. Also, since it measures all reagents capable of oxidizing iodide, it is inherently lacking in selectivity.

When chlorine was first used for water treatment, the only method available for analysis of free and combined available chlorine was the iodometric (starch-iodide) method (White, 1972). The method is based on the production by chlorine of free iodine from potassium iodide solutions at pH 8 or less (preferably pH 3 to 4). The iodine is subsequently titrated with a standard solution of sodium thiosulfate with starch as the indicator. Titration at neutral pH minimizes interference from Fe(III), Mn(IV), and nitrite; but titration at acidic pH is necessary for accurate determination of total available chlorine. For analysis of wastewaters or waters containing relatively high concentrations of organics, a standard reducing agent is added to react with the oxidant species in stoichiometric excess and the unreacted reducing agent is "back-titrated" with a standard oxidant. This method avoids loss of iodine through reactions with organics. For analytical methodology details refer to *Standard Methods* (1975) and *Annual Book of ASTM Standards* (1976). The iodometric method with starch-iodine or amperometric endpoint detection has been approved by EPA for analysis of chlorine in water solution (*Federal Register*, 1976).

It should be noted that all the analytical methods for free or combined oxidants require standards or reference solutions of known strength for calibrations of the measuring system. Commonly, commercial hypochlorite solutions (household bleach) are used, and iodometric titrations with the visual starch endpoint indicator are a convenient method for assaying the strength of these materials. Since errors in this assay will be reflected in all the data collected with whatever method is calibrated with the "standard" solutions, high confidence that this step has negligible errors is quite important.

Hallinan and Thompson (1939) studied in detail the influence of pH over the range 1.3 to 7.47 and iodide concentration over the range of 0.1 to 1.25 g/L on the titration of total available chlorine and evaluated the effects of certain interfering substances such as manganese. They determined that the reaction stoichiometry was affected by increasing pH. At lower pH, iodine reacts with thiosulfate to form iodide and tetrathionate ion [reaction (5)]. At higher pH values, however, tetrathionate ion may be further oxidized by iodine to sulfate [reaction (67)].

$$7I_2 + S_4O_6^{2-} + 10H_2O \rightarrow 4SO_4^{2-} + 14I^- + 20\ H^+ \qquad (67)$$

Increasing iodide concentration partially suppresses this reaction. The slower the titration is performed, the more sulfate is formed, with correspondingly lower chlorine titer. The effect of increasing pH is to reduce Mn(IV) interference. The authors present a nomogram of pH, time, and KI concentration to permit optimization of the thiosulfate titration.

Carpenter (1965) listed several sources of error in iodine titrations using thiosulfate: (1) air oxidation of iodide, (2) volatilization of iodine, (3) oxygen contributed by the reagent solution, (4) iodate contamination of the iodide solutions, (5) consumption or production of iodine by reagent contaminants, and (6) difference between titration endpoint and the equivalence point. In iodine titration with thiosulfate, he indicated that air oxidation of iodide to iodine is minimized by using pH of 2 or greater and that the loss of iodine by volatilization was minimized by the formation of the triiodide complex with high iodide concentrations. The error produced by iodate contamination of the iodide reagent

could be reduced by careful selection of chemicals. Reducing impurities in the iodide reagent may contribute to a negative blank. Such impurities were caused by dark and discolored particles in the sodium iodide reagent and were removed manually by using tweezers and a hand lens.

The iodometric (starch-iodide) procedure is useful only in determining total available chlorine. *Standard Methods* (1975) gives the minimum detectable concentration as 40 µg/L.

Iodometry forms the basis for the amperometric titration and other total oxidant analysis methods discussed below. The sensitivities of several iodine endpoint techniques, as indicated by Carpenter (1965), were visual starch, 10 microequivalents/L (350 µg/L as Cl); colorimetric starch, 2 microequivalents/L (70 µg/L as Cl); amperometric technique, 0.02 microequivalent/L (0.7 µg/L as Cl) in 0.001 N iodide or 0.08 microequivalent/L (2.8 µg/L as Cl) in 1 N iodide; ultraviolet absorption at 350 nm, 0.015 microequivalent/L (0.5 µg/L as Cl) in 0.01 N iodide.

3.7.2 Amperometric titration

Amperometric titration is performed by observing changes in the current as the titration proceeds. The electrode potential is not varied during the titration. The endpoint is best determined graphically, although it is sometimes indicated by a nonmeasured abrupt current increase or decrease (Stock, 1965).

The amperometric titration method is currently preferred for precise, low-level analyses of available chlorine (Helz, 1980); Sengupta et al., 1978; Hall et al., 1981; Opresko, 1980; Bender, 1978; Utility Water Act Group, 1979; Rice et al., 1980; Brooks and Seegert, 1979; Payne, 1979; Sugam et al., 1981; Olson and Williams, 1980; Scarano and Saroglia, 1980). Marks and Glass (1942) pioneered in the development of amperometric titration for chlorine residual analysis, and many investigators have contributed to its development (Haller and Listek, 1948; Marks et al., 1951; Morrow, 1966; Manabe, 1974; Morrow and Roop, 1975; Sengupta et al., 1978; Brooks and Seegert, 1979). *Standard Methods* (1975)

presents accepted analytical methodology details. In general, the standard amperometric titration method is based on the titration of free chlorine or iodine by a standard solution of phenylarsineoxide (or sodium arsenite),

$$C_6H_5AsO + X_2 + 2H_2O \rightarrow C_6H_5AsO(OH)_2 + 2H^+ + 2X^-, \quad (68)$$

where X = chlorine, bromine, or iodine (Helz, 1980).

This titrant can be used also to advantage in the visual starch iodometric titration. Marks et al. (1951) modified the method to permit differentiation between the various oxidant species based on their ability to react with phenylarsine oxide (PAO) or iodide. In nonsaline waters, only free oxidant is reduced directly to PAO at pH 7. Monochloramine reacts with KI to form I_2 at neutral pH, which is titrated by PAO. Dichloramine reacts with KI to form I_2 at pH 4. If present, nitrogen trichloride will titrate partly as free chlorine and partly as dichloramine. Thus by appropriate adjustment of pH and addition of KI, free chlorine, free chlorine plus monochloramine, and total chlorine residuals may be determined.

The application of this method to seawater analyses is being investigated (Helz, 1980; Carpenter et al., 1977; Sengupta et al., 1978).

As currently developed, the lower limit of detection by amperometric titration is 1.5 µg/L in estuarine waters (Helz, 1980) and 1.8 µg/L in freshwater (Brooks and Seegert, 1979). According to Helz (1980), this is approximately one order of magnitude lower than the detection limit of standard commercial titrators. For example, the detection limit for one standard commercial amperometric titrator is 20 µg/L. Sengupta et al. (1978), Sugam et al. (1981), and Brooks and Seegert (1979) present details concerning ultralow available chlorine analyses with amperometric titration.

Manabe (1974) indicated that the primary disadvantages of amperometric titration are (1) loss of chlorine during analysis due to photodecomposition or volatilization, and (2) incomplete reaction of the PAO with the chlorine residual. He determined that Cu(II) at concentrations as low as 50 µg/L gave a false chlorine residual and reduced analytical

sensitivity by poisoning the electrode. Iron(III) at 5 mg/L caused a similar loss in sensitivity. Manganese oxide does not interfere with free-chlorine determinations, and monochloramine had only a low interference [i.e., 0.1%/min, Johnson (1978)]. Free chlorine apparently causes a film-type polarization to occur at the surface of the measuring electrode (Morrow and Roop, 1975). This requires careful cleaning between titrations. Morrow and Roop (1975) recommended the addition of bromide to the cell and adjustment of electrode potential to permit free chlorine to be measured without significant interference. Sengupta et al. (1978) found negligible interference from IO_3^-, $S_2O_8^{2-}$, and Fe(III) at 1 mg/L, but when iodide was added, H_2O_2, BrO_3^-, and ClO_3^- gave nonquantitative, but measurable, responses.

Phenylarsineoxide solution is very stable, and amperometric titrations are relatively unaffected by color, temperature, and turbidity (Opresko, 1980).

The accuracy and precision of the amperometric titration method as developed by Brooks and Seegert (1979) compared favorably with that reported by Lishka and McFarren (1971). For example, for a solution containing free chlorine at 0.695 mg/L, Brooks and Seegert (1979) found a relative error of -10.8% and a relative standard deviation of 1.1%. Because of consistently low results, they questioned the use of the iodometric method as the standard for comparison. Helz (1980) reported a detection limit of 1.5 µg/L in natural estuarine waters. This is about an order of magnitude lower than the detection limit of commercial titrators. Payne (1979) determined that the lower limits of detection by amperometric titration were 5 to 10 µg/L as chlorine. He calculated relative errors of -4 to -16% for free-chlorine residuals of 1.92 to 0.42 mg/L,with relative standard deviation of 2.5 to 12%. Nicolson (1965) reported the lower limit of detection by amperometric titration to be 12 µg/L.

Rice et al. (1980) conducted a comparative study of the accuracy and precision of amperometric titration at several power plant locations with different operators and made the following conclusions: (1) the "ASTM D1253 Method C, back titration, would not work as written;"

(2) for the concentration range 0.0 to 0.2 mg/L chlorine, the average overall precision (standard deviation) was 33 µg/L for free chlorine and 28 µg/L for total chlorine using ASTM D1253 Method A, forward titration; and (3) for the range 0.0 to 0.2 mg/L chlorine, the average single operator standard deviation was 12 µg/L for both free and total available chlorine. Rice and coworkers conclude from their study using operators familiar with approved amperometric methods and possessing a level of skills representative of industry practice for monitoring chlorine in power plant discharges (river, lake, estuarine, and ocean water sources) that the use of 20 µg/L total chlorine as a minimum effluent concentration is inappropriate for plant control, compliance monitoring, and enforcement purposes.

For analytical methodology details refer to *Standard Methods* (1975) and *American Society for Testing and Materials* (1976). The iodometric method with amperometric or starch-iodine endpoint detection has been approved by EPA for analysis of chlorine in water solutions (*Federal Register*, 1976).

3.7.3 Ferrous-orthotolidine titrimetric method

Palin (1954) developed the ferrous-orthotolidine method for determining free chlorine, monochloramine, dichloramine, and nitrogen trichloride. Free chlorine is determined by mixing sample, phosphate buffer (pH 7) and orthotolidine, and titrating with ferrous ammonium sulfate (FAS) solution until the blue color disappears. Addition of potassium iodide solution and retitration until the blue color again disappears determines the monochloramine present. Errors may be introduced by the fading of colors but are minimized by rapid titration and a temperature of near 0°C. Dichloramine is determined by adjusting the pH to acidic values (∿2) and titrating with FAS.

Nitrogen trichloride is determined by either extraction of a portion of the original sample with carbon tetrachloride and titrating the aqueous layer for HOCl and OCl^- using FAS, or destroying the HOCl and OCl^- by reaction with oxalic acid and titrating the relatively unreactive nitrogen trichloride with FAS.

Nicolson (1965) reported the lower limit of detection of the ferrous-orthotolidine method was 43 µg/L.

3.7.4 Ferrous-DPD titrimetric method

The titration of samples with a ferrous ammonium sulfate solution using *N*,*N*-diethyl-*p*-phenylenediamine (DPD) as an indicator was developed by Palin (1957). Presumably the titrimetric technique overcomes the problems associated with the DPD instability that impair the use of this compound in colorimetry (Johnson, 1978; Sengupta et al., 1978). Titration of replicate samples with and without KI and at different pH values provides a basis for distinguishing the various oxidants in the samples.

Marks et al. (1951) studied the DPD titration method. They determined that for HOCl, the method is accurate and reliable. At lower temperatures for the determination of monochloramine, the precision and reliability of the DPD method is satisfactory. However, at higher temperatures, the method is unsatisfactory. The method gives erratic results for dichloramine at low temperatures and is unsatisfactory at temperatures near 25°C.

Nicolson (1965) reported the lower limit of detection for this method to be 11 µg/L.

For analytical methodology details refer to *Standard Methods* (1975). The ferrous-DPD titrimetric method has been approved by EPA for analysis of chlorine in water solutions (*Federal Register*, 1976).

3.8 Comparative Studies

3.8.1 Nicolson Study

Nicolson (1965) evaluated nine colorimetric and three titrimetric methods used at that time for determining free chlorine in water. Criteria used for comparing the methods were stability of colored reaction products, precision of analysis, accuracy, sensitivity, specificity, linearity of the calibration curve, effect of temperature, stability of reagents, and simplicity of the method.

In the absence of combined chlorine (monochloramine), Nicolson (1965) determined that the cyanogen chloride-barbituric acid method was the best

of the methods evaluated for determining free chlorine. In the presence of monochloramine, the DPD-colorimetric method was more satisfactory. Nicolson did not evaluate the methyl orange method because of nonlinear calibration curves. Nicolson found the titrimetric methods were less reproducible than the spectrophotometric methods.

The precision and limit of detection as determined by Nicolson (1965) for several methods are listed in Table 5.

3.8.2 Analytical Reference Service Water Chlorine (Residual) No. 1

The Analytical Reference Service of the Consumer Protection and Environmental Health Service conducted an evaluation of nine methods for determining free and total chlorine (Lishka et al., 1969). Seventy-two participating laboratories analyzed three samples that when prepared properly were to contain the following: sample one, 0.83 mg/L free chlorine and 1.0 mg/L combined chlorine; sample two, 0.80 mg/L free chlorine; and sample three, 0.64 mg/L combined chlorine. The samples were analyzed by two referee laboratories using the amperometric titration method, and the values obtained agreed well with results obtained by a third referee laboratory using SNORT, ferrous-DPD, and iodometric methods. Statistical data are available in Lishka et al. (1969). They concluded the following: "The best overall accuracy and precision was shown by the ferrous-DPD method, followed closely by the methyl orange, SNORT, and amperometric methods. The leuco crystal violet method produced poor results for sample 1 but was quite acceptable for samples 2 and 3. ...The lack of accuracy of the orthotolidine and orthotolidine-arsenite methods make them least acceptable, although all methods (with the possible exception of ferrous-DPD) appear to have comparable precision."

Sollo et al. (1970) state the data gathered by Lishka et al. (1969) do not justify the conclusions reached. Sollo and coworkers contend there is not enough evidence to support any "rating" of the nine methods: "Each method evaluated for the determination of chlorine when used properly and according to specified instructions can be quite acceptable" Sollo et al., 1970). In their critical review they state that 16 of the 72 participating laboratories reported results that deviated from those

Table 5. Precision and limit of detection of analytical methods for determining free chlorine (Nicolson, 1965)

	Precision, %		Limit of detection (µg/L)
	Chlorine (0.1 mg/L)	Chlorine (0.5 mg/L)	
Cyanogen chloride–barbituric acid	3.48	1.85	0.47
DPD-colorimetric	4.04	1.95	3.6
Acid-orthotolidine	4.14	3.01	1.4
Amperometric titration	7.28	3.94	12
Ferrous-DPD-titrimetric	7.20	4.53	11
Ferrous-orthotolidine titrimetric	16.40	2.76	43

of the reference laboratories by only 0.08 to 0.15 mg/L on all methods tested. The average relative deviation for these 16 laboratories was <20%. Sollo et al. contend that the use of the values determined by these consistently competent laboratories is more objective than using the values determined by all the laboratories. For example, 12 laboratories consistently had relative deviations >50%, and inclusion of the results from these laboratories in the statistical analysis biased the results toward poorer precision and accuracy. Thus Sollo and coworkers believe the methods should be rated by consistently competent laboratories. Table 6 shows the data recalculated by Sollo et al. (1970) using this criterion.

Sollo et al. (1970) conclude the following: "It is clear that the methods are satisfactory, and the failures lie with astonishingly poor laboratory performance, which has nothing to do with the prescribed methodology."

3.8.3 Analytical Reference Service Water Chlorine (Residual) No. 2

It was concluded from the previous study (Lishka et al., 1969) that the precision of all methods evaluated was poorer than anticipated because of the variability in sample preparation from dry mixtures. Therefore, the Analytical Reference Service of the Environmental Protection Agency conducted a subsequent evaluation of analytical methods for which the chlorine-containing samples were prepared from strong chlorine solutions sealed in glass ampoules stored in the dark. Seventy-one laboratories participated in the study by analyzing three samples: sample 1, 0.44 mg/L free chlorine; sample 2, 0.98 mg/L free chlorine; sample 3, 0.05 mg/L free chlorine and 0.66 mg/L total chlorine. Stock solutions were standardized by iodometric titration, and the diluted samples were checked amperometrically by EPA staff and a referee laboratory (Lishka and McFarren, 1971).

Lishka and McFarren (1971) concluded from this study that the best accuracy and precision was obtained by the leuco crystal violet and SNORT procedures, followed by the DPD-titrimetric, amperometric titration, DPD-colorimetric, and methyl orange procedures. The poorest procedure was

Table 6. Analysis of Analytical Reference Service Water Chlorine (Residual) No. 1 (Sollo et al., 1970)

Method	Sixteen selected laboratories		All laboratories	
	Average deviation (mg/L)	Number of laboratories	Average deviation (mg/L)	Number of laboratories
SNORT	0.062	4	0.126	17
Ferrous-OT	0.080	3	0.330	19
Ferrous-DPD	0.083	6	0.178	19
Amperometric	0.095	8	0.213	24
Iodometric	0.120	7	0.251	32
Methyl orange	0.125	6	0.276	28
Orthotolidine	0.145	2	0.390	17
Orthotolidine-arsenite	0.167	5	0.480	23
Leuco crystal violet	0.213	5	0.313	18

the orthotolidine-arsenite. However, the relative mean error of the leuco crystal violet method is low compared to the other methods because of the small number of laboratories doing the analysis. Selected data from the Lishka and McFarren (1971) study are presented in Tables 7 and 8. The data reported by the individual laboratories show considerable variation in determined values thus indicating that laboratory experience and competency may play a significant role in the relatively poor precision and accuracy found for the methods in this comparative study.

3.8.4 Bender Study

Bender (1978) evaluated eight methods for determining total chlorine — all based on the iodide-iodine reaction using four sample matrices (drinking water, river water, secondary effluent from a wastewater treatment plant, and untreated wastewater). Seven replicate determinations were used to determine the precision of the methods. Accuracy was determined in terms of percent yield as compared with the iodometric (starch endpoint) method. Bender (1978) concluded that each of the methods worked well in certain matrices,but not in others. He concluded that comparison should be made of each method with the iodometric titration (amperometric or starch-iodine endpoint), DPD-colorimetric, or DPD-titrimetric method as recommended in the *Federal Register* (1976) to ensure the method is compatible with the sample matrix. Tables 9 to 11 present the precision and accuracy of the methods as determined for drinking water, river water, and secondary effluents.

3.8.5 Comparative studies of amperometric techniques

Seaman et al. (1980) have compared three on-line monitoring instruments for measuring the chlorine residual with the amperometric titrator. The on-line monitoring instruments were a total residual chlorine-membrane electrode (polarographic-membrane electrode), the iodometric method for total chlorine using a specific ion electrode for iodine, and an amperometric-type analytical instrument. Factors of concern in the study were accuracy, precision, sensitivity to changes in feed rate, time-of-day behavior, minimum detectability, and baseline drift. The

Table 7. Comparison of analytical methods for determining free and total chlorine in aqueous solution containing 0.98 mg/L free chlorine (Lishka and McFarren, 1971)

Method	Precision				Accuracy	
	Free		Total			
	Standard deviation (mg/L)	Relative standard deviation (%)	Standard deviation (mg/L)	Relative standard deviation (%)	Free, relative mean error (%)	Total, relative mean error (%)
Methyl orange	0.315	32.1	0.301	30.7	-0.6	+2.9
Leuco crystal violet	0.042	4.3	0.015	1.5	-5.1	-0.7
SNORT	0.120	12.2	0.142	14.5	-4.9	-3.3
Ferrous-DPD titrimetric	0.298	30.4	0.205	20.9	-3.9	-3.2
DPD-colorimetric	0.171	17.4	0.152	15.5	-1.4	+10.5
Amperometric	0.206	21.0	0.137	14.0	-1.2	-11.0
Orthotolidine-arsenite	0.335	34.1	0.325	33.2	+11.6	-9.3

Table 8. Comparison of analytical methods for determining total chlorine in aqueous solution containing 0.66 mg/L total chlorine (Lishka and McFarren, 1981)

Method	Precision		Accuracy, relative mean error (%)
	Standard deviation (mg/L)	Relative standard deviation (%)	
Methyl orange	0.143	21.7	+4.4
Leuco crystal violet	0.089	13.5	-1.1
SNORT	0.110	16.7	-4.8
Ferrous-DPD titrimetric	0.121	18.3	-4.7
DPD-colorimetric	0.210	31.8	+15.6
Amperometric	0.171	25.9	-16.4
Orthotolidine-arsenite	0.218	33.0	-13.9

Table 9. Determination of total chlorine in drinking water (Bender, 1978)

Method	Total chlorine		Precision		Accuracy (% recovery)
	True value[a] (mg/L)	Measured value (mg/L)	Standard deviation (mg/L)	Relative standard deviation (%)	
Iodometric	--	0.68	0.04	5.2	--
Iodometric (back titration)	0.85	0.84	0.04	4.3	98.8
Amperometric	0.94	0.97	0.03	2.6	103.2
Amperometric (back titration)	0.83	0.82	0.05	5.9	98.8
Ferrous-DPD-titrimetric	0.91	0.98	0.01	1.2	107.7
DPD-colorimetric	0.86	0.94	0.008	0.8	109.3
Chlorine flux monitor	0.91	0.84	0.02	1.9	92.8
Orion electrode	0.84	0.88	0.03	3.1	104.8

[a]Determined by iodometric method.

Table 10. Determination of total chlorine in river water (Bender, 1978)

Method	Total chlorine		Precision		Accuracy (% recovery)
	True value[a] (mg/L)	Measured value (mg/L)	Standard deviation (mg/L)	Relative standard deviation (%)	
Iodometric	--	0.30	0.03	9.7	--
Iodometric (back titration)	0.78	0.84	0.02	2.7	107.7
Amperometric	0.56	0.57	0.02	3.0	101.8
Amperometric (back titration)	0.66	0.68	0.06	9.4	103.0
Ferrous-DPD-titrimetric	0.73	0.79	0.01	1.4	108.2
DPD-colorimetric	0.70	0.86	0.02	1.9	122.9
Chlorine flux monitor	0.50	0.39	0.07	17.1	78.0
Orion electrode	0.96	0.72	0.02	3.3	78.0

[a]Determined by iodometric method.

Table 11. Determination of total chlorine in secondary effluent from wastewater treatment plant (Bender, 1978)

Method	Total chlorine		Precision		Accuracy (% recovery)
	True value[a] (mg/L)	Measured value (mg/L)	Standard deviation (mg/L)	Relative standard deviation (%)	
Iodometric	--	1.11	0.06	5.9	--
Iodometric (back titration)	1.00	0.87	0.07	7.6	87.0
Amperometric	0.50	0.41	0.03	6.9	82.0
Amperometric (back titration)	1.45	1.10	0.09	8.3	75.9
Ferrous-DPD-titrimetric	1.20	1.08	0.02	1.8	90.0
DPD-colorimetric	1.01	1.07	0.03	2.4	106.0
Chlorine flux monitor	0.75	0.74	0.02	2.6	98.7
Orion electrode	0.95	0.71	0.03	3.8	75.0
Orion electrode	0.80	0.83	0.04	4.7	103.8

[a]Determined by iodometric method.

total residual chlorine-membrane electrode was found to be reliable, accurate, and precise in the field. The investigators determined that there was no statistically significant difference between the total chlorine-membrane electrode and the amperometric titration. They did note, however, that significant differences did exist between both the iodometric method with specific ion electrode and the amperometric-type analytical instrument when compared with the amperometric titration.

Four chlorine monitoring techniques were evaluated by Sugam et al. (1981): manual amperometric titration, automatic amperometric titration, amperometric back titration, and chlorine-flux monitor. The instruments were tested under field operating conditions, with field operators having no previous experience with the methods. Three field locations were used: (1) a freshwater site, (2) a brackish-water site, and (3) a seawater site. The study focused on analysis of the total residual oxidant. However, free residual "chlorine" was found to be a significant part of the total oxidant at the freshwater and seawater sites and was present in only trace amounts at the brackish-water site.

Sugam et al. (1981) found no interference at any of the locations that was attributable to natural oxidant background. They found the back titration method yielded slightly less oxidant than the forward titration in seawater. They recommended the use of either the manual or automatic forward amperometric titration for utility applications. They determined that either can be used with acceptable accuracy and precision down to concentrations of 0.036 (manual) and 0.021 (automatic) mg/L chlorine. Over a range extending to at least 1.0 mg/L chlorine, relative precision (95% confidence level) was +20%, -17% for the manual method, and +30%, -23% for the automatic methods. The chlorine-flux monitor cannot be used at levels below 0.021 mg/L chlorine, but Sugam and coworkers did question its reliability for analyses in brackish water and seawater.

3.8.6 Comparative study on chlorinated seawater

In January 1980, an ASTM Intercomparison Workshop was held at Rosenstiel School of Marine and Atmospheric Science, University of Miami, as described in ASTM Report No. RR:D19-1067 (Marinenko, 1980).

Six different operators participated in the workshop, representing five different methods designed as follows:

A - PAO (phenylarsine oxide) back titration using spectrophotometric endpoint

B - Chlorine Electrode

C - Chlorine Flux-Monitor

D - Chlorine Flux-Monitor

E - Amperometric Forward Titration

F - Polarographic Electrode

In Table 12, the first column designates chlorine solution numbers 2-5. The initial chlorine demand in Gulf Stream water was satisfied by chlorination and the resulting water of relatively low chlorine demand was used for preparation of known concentration sodium hypochlorite solutions. Solution 1 was the "blank" Gulf Stream water used for preparation of all solutions. As may be seen from the data in Table 12, the results from the use of the various methods are discordant to an extent that greatly exceeds the presumed accuracy and precision of the methods.

3.9 Summary of Analytical Methods

The voluminous literature concerning analytical methodology for active chlorine-containing species in aqueous media has been reviewed with two major objectives: (1) to assist in evaluating toxicity data relative to the meaning of reported analytical concentrations of available chlorine, and (2) to assist in evaluating methodology for the analysis of low concentrations of chlorine or oxidant. Table 13 summarizes the principal techniques currently in use, their applicability, and the lower limits of detection.

Additional research is needed to determine the limitations of the several "best" analytical methods. With the currently available data, it is difficult to draw conclusions regarding selection of an analytical method most suitable for analysis of the water sample being analyzed. A review of the comparative studies of existing methods indicates the need for a comprehensive evaluation of the methods in several sample

Table 12. Chlorine concentration in seawater[a] (measured by six different experimentalists and five different methods)

Solution No.	Nominal concentration of Cl	A	B	C	D	E	F
2	0.011	0.019	0.065	0.016	0.009	0.012	0.013
2	0.090	0.072	0.100	0.050	0.032	0.074	0.045
4	0.451	0.409	0.372	0.282	0.228	0.317	0.306
5	4.508	4.414	5.90	3.514	3.352	3.072	3.79

[a]The values in the table were corrected for decay.

Table 13. Summary of applicability of analytical methods for available chlorine (free and combined oxidant species). For definition of lower limits of detection, see Sect. 3.1.1.

Method	For more details see below section	Approximate lower limit of detection (µg/L as Cl)		Available chlorine (oxidant species)					
		Laboratory standards	Natural water sample	Total	Free	Combined	NH_2Cl	$NHCl_2$	NCl_3
Potentiometry	5.2	50[a], 3[b]			x				
Amperometry	5.3	2[a]	21[c]		x				
Spectrophotometry	5.4	0.5[d]		x	x				
Colorimetry	5.5								
Acid-orthotolidine	5.5.1.1	1.4[e]		x	x				
OTA	5.5.1.2			x	x	x			
SNORT	5.5.1.3	2.1[f]		x	x	x	x	x	
DPD-colorimetric	5.5.2	4[e], 9.5[g], 16[a]		x	x	x	x	x	x
LCV	5.5.3	5[h]		x	x	x			
Methyl orange	5.5.4			x	x	x			
FACTS	5.5.5	3.1[g], 12[a]		x	x	x			
Cyanogen chloride-barbituric acid	5.5.6	0.5[e]			x				
Chemiluminescence	5.6	30[i]			x				
Titrimetry	5.7								
Iodometric	5.7.1	40[h], 0.5-350[d]		x					
Amperometric	5.7.2	12[e], 5-10[k]	1.5[j], 21-36[c]	x	x	x			
Ferrous-orthotolidine	5.7.3	43[e]		x	x	x	x	x	x
Ferrous-DPD-titrimetric	5.7.4	11[e]		x	x	x	x	x	x

[a] Sengupta et al. (1978).
[b] Rigdon et al. (1978).
[c] Commercial equipment, Sugam et al. (1981).
[d] Carpenter (1965).
[e] Nicolson (1965).
[f] Johnson and Overby (1969).
[g] J. D. Johnson, personal communication (1981).
[h] *Standard Methods* (1975).
[i] Isacsson et al. (1978).
[j] Modified equipment, Helz (1980).
[k] Payne (1979).

matrices including seawater. This evaluation should include, besides accuracy and precision, a determination of the limit of detection using (to the extent possible) a standard frame of reference. Research should continue on the analysis of chlorine and chlorine-produced oxidants at the parts-per-billion concentration and lower.

3.9.1 Selection of method

For analysis of chlorine in water solution, the EPA recommends the iodometric titration (amperometric or starch-iodine endpoint), DPD-colorimetric or the DPD-titrimetric methods (*Federal Register*, 1976). Bender (1978) suggested that methods selected for analysis of oxidants in a particular sample matrix should be compared with these EPA recommended methods to ensure the selected method is compatible with the sample matrix. The following discussion concerning the selection of methods relates principally to sample matrix and does not deal with the analysis of trace or parts-per-billion concentrations.

Natural and treated waters. For natural and treated waters the amperometric titration method is accepted as a standard of comparison for free and combined chlorine. It is minimally affected by turbidity, color, temperature variations, and common oxidizing agents. The iodometric method (forward or back-titration) with starch-iodine endpoint detection is suitable for chlorine concentrations greater than 1 mg/L. The ferrous-DPD-titrimetric method is suitable for free chlorine determinations and for mixtures of free and combined chlorine. Free chlorine may be determined by the SNORT and DPD-colorimetric, but increasing concentrations of monochloramine may produce increasing interference with this determination. Combined fractions may be estimated using SNORT and DPD-colorimetric. Free chlorine, total chlorine, and combined chlorine may be determined by the LCV method with minimal monochloramine interference in the free chlorine determination. Oxidized manganese interferes with SNORT, DPD-colorimetric, and LCV determinations. Dichloramine (0 to 9 mg/L as chlorine) does not affect free chlorine determinations by amperometric, SNORT, DPD, or LCV methods. However, nitrogen trichloride reacts partially as free chlorine in all except the LCV method. The FACTS method was developed specifically

for free chlorine and is unaffected by significant concentrations of combined chlorine and oxidized manganese. All colorimetric procedures are subject to interferences by sample color and turbidity (*Standard Methods*, 1975).

Polluted waters. In polluted waters, chlorine will exist principally in the combined state as chloramines and organic chloramines. At the same time unsatisfied chlorine demand may exist such that addition of reagents for chlorine determination may permit loss of chlorine through continued reaction with the chlorine demand. Thus in wastewater the differentiation between free and combined chlorine is not ordinarily made. *Standard Methods* (1975) recommends the amperometric titration method for determining free chlorine in wastewater because it is not subject to interferences from color, turbidity, iron, manganese, or nitrite. The SNORT and DPD methods require addition of arsenite immediately after reagent addition to avoid interference by monochloramine. The LCV method is less affected by monochloramine, and arsenite addition minimizes this effect. However, the combination monochloramine and nitrite seriously interferes with free chlorine determinations using the LCV method. The FACTS free chlorine determination is unaffected by combined chlorine, nitrite, iron, and manganese (*Standard Methods*, 1975).

Standard Methods (1975) recommends the iodometric back titration method with either the amperometric or starch-iodine endpoint detection for determining total chlorine in the presence of significant concentrations of organic matter. The amperometric endpoint is inherently more accurate and not affected by color and turbidity although some metals may interfere. Color and turbidity in the sample may cause difficulty with the starch-iodine endpoint. SNORT, DPD-titrimetric and colorimetric, and LCV methods are applicable to the determination of total chlorine in polluted samples.

Seawater. The analysis of oxidant species in chlorinated seawater is a subject of currently active research. The methods currently used are spectrophotometry, potentiometry, amperometry, and amperometric titration (Table 12). Definitive conclusions have not been made regarding recommended procedures.

Sengupta et al. (1978) compared DPD-colorimetric oxidant determinations in freshwater and artificial seawater. They found there was either a large chlorine demand by the seawater or that the apparent sensitivity of the DPD method was reduced significantly. They attributed the effect to the high chlorine demand of the seawater. They concluded that the method was feasible for determination of chlorine-produced oxidant in seawater if the amount of other oxidizing ions are present only in trace amounts.

Sengupta et al. (1978) determined that bromamine samples reacted with syringaldazine to produce an orange color. They concluded that the formation of bromamines in chlorinated seawater would decrease the sensitivity of the FACTS colorimetric method for oxidant determinations in seawater as compared with freshwater.

3.9.2 Analytical measurements/toxicity data

Judgments concerning reported concentrations of chlorine or oxidant concentrations in toxicity studies must be made for each individual study based on the following criteria.

1. *Water quality.* Determinations made on high-quality water, free from pollution and ammonia, may be interpreted with a higher degree of confidence than those made on highly polluted waters. Most published procedures perform well in relatively clean systems free from interferences (Sorber et al., 1977). Values reported on highly polluted waters (e.g., wastewater effluents) may be low, as discussed in *Standard Methods* (1975). Conclusions regarding the effect of water quality on analytical data are best made by the researcher reporting the data.
2. *Analyst expertise.* Analytical results are highly dependent on the level of expertise and knowledge of the analyst.
3. *Methodology.* Analytical methodology must be reported to permit data evaluation.
4. *Statistical significance.* Statistical treatment of data and reports on significance facilitate evaluation of reported concentrations. This includes replicate analyses and rigorous quality assurance/quality control procedures.

3.9.3 Analysis of low concentrations

Accurate and precise analysis of chlorine and chlorine-produced oxidant species is highly dependent upon the skill and expertise of the analyst. This is especially true for analysis of oxidant concentrations in the parts-per-billion range. The analyst must be cognizant of the limitations of the analytical method and the possible interfering substances in the water sample. Although accurate and precise analyses at the parts-per-billion level may not currently be achievable with commercial analytical equipment and operators possessing the level of skills representative of the industry practice for monitoring chlorine in power plant discharges (Rice et al., 1980), analyses at that parts-per-billion level are achievable by highly competent chemists with modified analytical instruments (Helz, 1980).

Sengupta et al. (1978) conclude that optical methods (colorimetric) will not be able to provide reliable data for analysis of chlorine or oxidant residuals at parts-per-billion levels in natural waters. They base this conclusion on an evaluation of most accurate and precise analytical methodologies currently in use and on interferences present in natural waters. Most scientists concerned with analyses at the parts-per-billion level now recommend electrochemical techniques, principally amperometric techniques using analysts with a high degree of expertise.

Other techniques are being developed and may prove equally reliable in the future. The choice of method and the significance of the data generated by the method are a function of the nature and quality of the water being analyzed. Increased knowledge concerning the chemistry of systematic errors (Helz, 1980) and interferences is needed before ultra-low-level analyses can become routine.

4. ENVIRONMENTAL FATE

Relatively little information exists concerning the environmental fate, transport, and distribution of chlorine and chlorination products in natural waters receiving chlorinated discharges such as cooling waters, process waters, and wastewaters. The chemistry and interrelationship of free oxidant (HOCl, OCl^-, HOBr, OBr^-), combined oxidant (chloramines, organic chloramines, bromamines, organic bromamines, mixed halamines), and reaction products (chloro- and bromoorganics, oxidized organics, chlorate and bromate ion, oxidized metal ions, nitrogen, and oxygen) are schematically shown in Fig. 4. The chemical products and pathways are principally controlled by reactant concentrations, pH, temperature, salinity (including bromide concentrations), and sunlight, in addition to the chemical kinetics and equilibria for the many possible reactions.

The ultimate decomposition products of free chlorine in natural waters are chloride, oxidized organics, chloroorganics, oxygen, nitrogen, and possibly chlorate and nitrate. Depending upon the bromide content of the chlorinated waters, other possible products are bromate and bromoorganics. The chlorine consumed in these reactions represent what has been termed chlorine demand. Only a few percent of the chlorine added to the water are found in the many possible haloorganic products (e.g., trihalomethanes). A larger fraction of the added chlorine is probably consumed in the oxidation of organics. The fractions disproportionating to halates, decomposing to oxygen, or oxidizing metal ions and other materials are relatively unknown. However, the decomposition of oxidant to oxygen and halate ion is presumed to be considerably less than the available oxidant consumed in the decomposition of chloramines and bromamines. Consequently, very little is known concerning the concentrations of these products in receiving waters and their ultimate distribution and fate. For specific details concerning chlorine chemistry and possible chemical reactions, see Sect. 2.

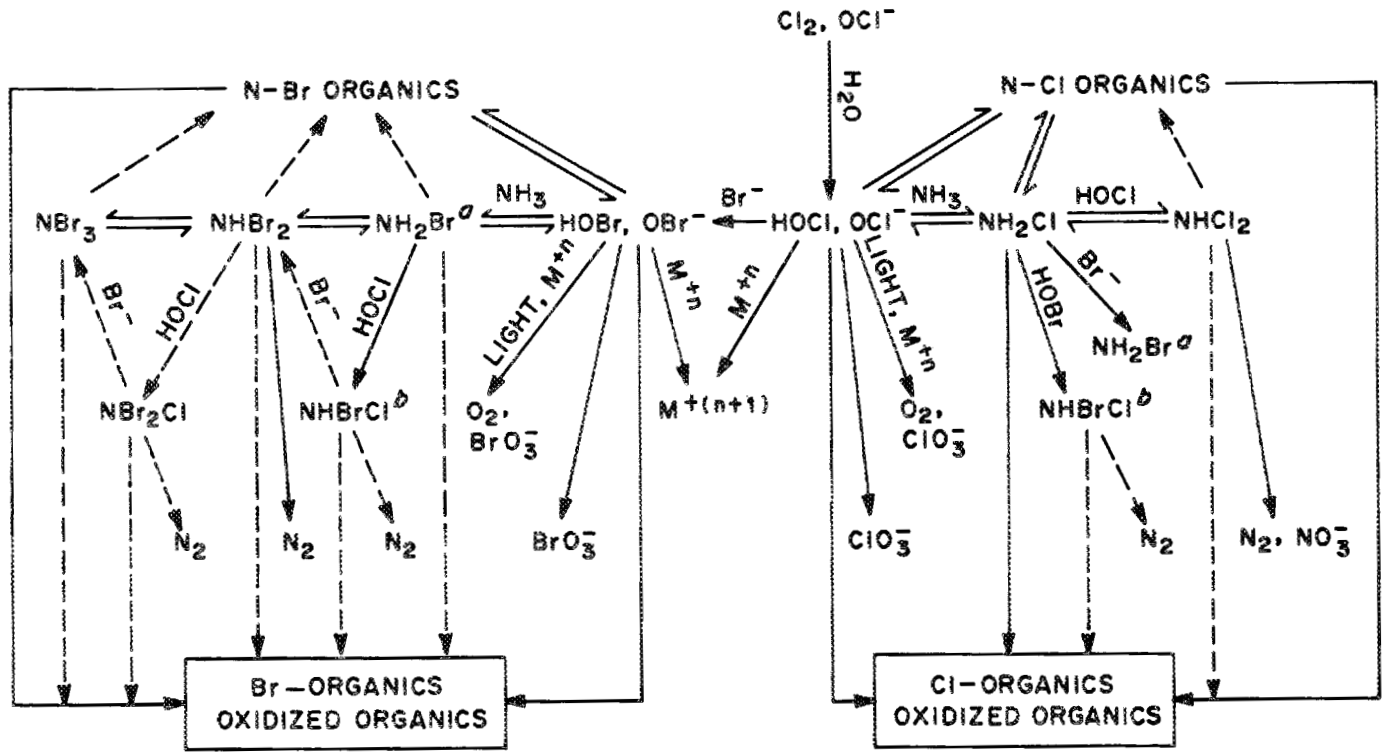

Fig. 4. Principal chemical pathways for reaction, degradation, and environmental fate of free available chlorine in the aquatic environment. Presumed pathways (not yet proven) are given by dashed arrows. Compounds formed at different places in the reaction scheme are designated with superscripts *a* and *b* to assist in understanding interrelationships. Halides (Cl^- and Br^-) are not depicted but are products of many of the chemical pathways.

4.1 Freshwater System

The reactions on the right side of Fig. 4 represent the principal chemical reactions of chlorine in freshwaters and wastewaters. The relative concentrations of ammonia, chlorine, and pH are the principal parameters determining the products. If the chlorinated water contains bromide (as in some freshwaters and estuarine waters), then the remaining reactions may become increasingly important as the bromide concentration increases.

According to Johnson (1978), the stability of free chlorine in natural water is very low because it is a strong oxidizing agent (at pH 7, E° = 1.28 v). Consequently, it rapidly oxidizes inorganic compounds and more slowly oxidizes organic compounds. In the presence of ultraviolet light, HOCl oxidation of water to O_2 proceeds at a significant rate (Johnson, 1978; Hancil and Smith, 1971). According to Johnson (1978), Snoeyink and Marcus determined that free chlorine (HOCl, OCl^-) in nitrified secondary effluents dosed with 3.1 mg/L chlorine and subjected to prevailing sunlight and wind gave first-order decay rates of 2.1 to 7.4 h^{-1}, with half-lives of 8 to 28 min. For similar chlorinated effluents kept in the laboratory, without stirring and ultraviolet light (sunlight) present in the outdoor samples, a tenfold greater persistence was measured (i.e., first-order decay constants of 0.19 to 0.77 h^{-1} after an initial rapid decay with half-lives of 10 to 30 min) with a half-life of 1.3 to 5 h.

Monochloramine, the principal chloramine formed in chlorinated natural and wastewaters at neutral pH, is much more persistent in the environment. According to Johnson (1978), Snoeyink and Marcus measured first-order decay rate constants of 0.03 to 0.075 h^{-1} for NH_2Cl in the laboratory and higher rate constants of 0.28 to 0.31 h^{-1} outdoors using chlorinated effluents. These decay rates are approximately tenfold slower than the decay of free chlorine. If discharged into receiving waters containing bromide, NH_2Cl will decompose faster probably through the formation of NHBrCl and decomposition of the dihalamine (Trofe et al., 1980). The rate of monochloramine disappearance is primarily a function of pH and salinity. For example, at pH 7 and 25°C, the half-life of

monochloramine is 6 h at 5 ppt (parts-per-thousand) salinity and 0.75 h at 35 ppt salinity; at pH 8.5 and 25°C, the half-life of monochloramine is 188 h at 5 ppt salinity and 25 h at 35 ppt salinity. Monochloramine would be expected to decompose, also in receiving waters via chlorine transfer to organic nitrogen-containing compounds (Isaac and Morris, 1980).

Several investigators have developed equilibrium or empirical models attempting to predict the concentration-time relationship of the several chlorine-containing species in chlorinated freshwaters and wastewaters (Draley, 1972; Hostgaard-Jensen et al., 1977; Khalanski, 1980; Sugam and Helz, 1981). However, equilibrium is probably not established in the chlorine-ammonia-water system. Thus equilibrium models have limited significance. Empirical models lack adaptability to changing ammonia concentrations and chlorine demand conditions and may not be valid outside the chlorine dose ranges and time periods studied.

Consequently, Lietzke (1978a, 1978b) and Haag and Lietzke (1980) have developed a kinetic model for calculating the concentration-time relationship for the chlorine-containing species. Their model for freshwater was based principally on the reactions leading to the production of the chloramines and on an assumed chlorine demand reaction. The mathematical formulation of the model involved the solution of five simultaneous differential equations representing kinetic data for the several chemical reactions. The kinetic model was validated by using actual chlorine residual measurements for the cooling system of an electric-power plant (Lietzke, 1978b). The predicted values for the chlorine residual compared favorably with actual measured values. The relative standard error for the predicted value was 20%.

Haag (personal communication, 1981) modified the Haag and Lietzke kinetic model to include amino acids. Typical results for halogen species in chlorinated freshwater as a function of time resulting from chlorination (2.0 mg/L chlorine) of a sample containing 0.4 mg/L ammonia-nitrogen are given in Table 14.

Refinements of the kinetic model are needed to predict the concentrations of chloroorganics, oxidized organics, and inorganic constituents such as chlorate.

Table 14. Concentration of active halogen species for chlorination of freshwater (mol/L)[a,b]

Time (min)	HOCl	NH_2Cl	$NHCl_2$	RNHCl[c]	NH_3	RNH_2[d]	Chlorine demand	Total chlorine residual
0	2.8×10^{-5}	0	0	0	2.9×10^{-5}	7.1×10^{-6}	2.1×10^{-5}	2.8×10^{-5}
17	3.0×10^{-10}	8.9×10^{-6}	2.7×10^{-9}	4.8×10^{-6}	2.1×10^{-5}	8.6×10^{-7}	8.3×10^{-6}	1.4×10^{-5}
38	2.4×10^{-10}	6.9×10^{-6}	2.0×10^{-10}	3.4×10^{-6}	2.4×10^{-5}	8.3×10^{-7}	6.3×10^{-6}	1.0×10^{-5}
60	2.3×10^{-10}	6.7×10^{-6}	1.4×10^{-10}	2.4×10^{-6}	2.5×10^{-5}	8.0×10^{-7}	6.1×10^{-6}	9.0×10^{-6}

[a] Initial conditions: pH, 7.0; temperature, 25°C; chlorine added as Cl_2, 2.0 mg/L; chlorine demand as Cl_2, 1.5 mg/L; NH_3 concentration as nitrogen, 0.4 mg/L; RNH_2 (amino acid) concentration as nitrogen, 0.1 mg/L.

[b] Personal communication, W. R. Haag (1981).

[c] *N*-chloroalanine, representing *N*-chloroamino acids.

[d] Alanine was used to model amino acids.

4.2 Saline Water System

In open oceans, seawater contains little ammonia, thus the principal chemical reactions of chlorine in seawater are the formation of HOBr and associated demand reactions (reactions in the center of Fig. 4). In estuarine waters or seawaters containing relatively high concentrations of ammonia, the reactions represented on the right and left sides of Fig. 4 also become increasingly important.

Johnson (1977) first pointed out the importance of ammonia in the chemistry of seawater chlorination. According to Inman and Johnson (1978) at low ammonia concentrations in seawater, bromamines are formed from the hypobromous acid produced by the reaction of free chlorine (HOCl, OCl^-) with bromide (present at 65 mg/L in most seawater). The degree of halogen substitution on the nitrogen is governed by the pH and the halogen-to-ammonia ratio. If the ammonia concentration is sufficiently high, the rate for the formation of monochloramine may become competitive with bromide oxidation to hypobromous acid. Consequently, a mixture of halamines will be produced, including N-bromo-N-chloramines (Trofe et al., 1980; Haag, 1980).

Bongers et al. (1978) determined that in the chlorination of estuarine waters at 1 to 8 parts-per-thousand salinity, the rate of oxidant decay will decrease with increasing ammonia concentration at constant salinity (i.e., with increasing monochloramine formation), but the rate of oxidant decay will increase with increasing salinity (i.e., with increasing bromide concentration) at constant ammonia concentration. Helz et al. (1978) determined that in the chlorination of estuarine water, the oxidant decay was initially very rapid (90% decay while in the cooling water system) but entered a slow phase in which the decay was apparently first order in total oxidant concentration with a half-life of 30 to 100 min. Other investigators have also determined that the oxidant produced by the chlorination of seawater first decays rapidly, then decays at a much slower rate. For example, Wong (1980) dosed seawater with 5 mg/L chlorine and detected residual oxidant concentrations up to 2 mg/L as chlorine after 3.5 days. The compounds HOBr and OBr^- appear to be the predominant

oxidant species in these long-term studies (Wong and Davidson, 1977). Eppley et al. (1976) in their studies on chlorinated seawater found an initial rapid decline in both free and combined oxidant, followed by a slower decline. Their observations suggested that the initial oxidant demand may involve organic reactions or oxidation of metal ions.

Experiments were conducted by Inman and Johnson (1978) to determine the variation in halogen-containing species as a function of chlorine-to-ammonia ratio in chlorinated seawater. They concluded that at a 1.5 to 1.7 molar ratio of halogen to ammonia, conditions were favorable for oxidation rather than substitution reactions and that the total oxidant concentration decreases rapidly with time. At low ammonia concentrations and halogen-to-ammonia ratios >3, NBr_3 is the principal bromamine present. A mixture of dibromamine and monochloramine will form when the chlorine dose is <2.5 mg/L and the ammonia concentration is >0.5 mg/L as nitrogen in chlorinated seawater. With longer time and higher ammonia concentration, NH_2Cl becomes the predominant species due to more rapid bromamine decay. For relatively large chlorine doses and with ammonia <0.4 mg/L as nitrogen, NBr_3 and HOBr are the major products.

As long as the breakpoint for ammonia oxidation is not exceeded, the relative rates of HOBr and NH_2Cl formation are independent of the chlorine dosage and dependent only on the salinity (Br^- concentration), ammonia concentration, and pH. Inman and Johnson (1978) concluded that at pH 8.1 and ammonia-nitrogen of 50 µg/L decreasing salinity tenfold would decrease the rate of HOBr formation so that NH_2Cl would become the predominant halogen species. However, a decrease in pH would tend to decrease NH_3 concentration and, consequently, decrease the rate of NH_2Cl formation. Large variations of ammonia and bromide concentrations are encountered in estuarine waters.

Inman and Johnson (1978) concluded that at pH 8.1, the critical weight ratio of ammonia nitrogen to bromide is 0.008. At higher ratios, after 30 to 60 min, NH_2Cl should be the predominant species. For lower ratios, the major oxidant species would be dibromamine. However, the small fraction of monochloramine present would persist after the bromamine decayed.

Haag and Lietzke (1980) developed a kinetic model for predicting halogen-containing species involving 21 chemical reactions leading to the formation and disappearance of the most important halamines and hypohalous acids likely to be encountered in chlorinated seawater. Accurate kinetic data exist for five of the chemical reactions. Haag and Lietzke estimated rate constants for the remaining reactions by comparisons with similar reactions. The model requires the solving of 15 simultaneous differential equations. Typical results are presented in Table 15. This model predicts that bromochloramines are the predominant species.

The Haag and Lietzke model gives an estimate of the trihalomethane production at low salinities based on an empirical relation derived by Peters et al. (1980). The model does not address the effect of light, which may significantly increase the decay rate of halamines (Haag, personal communication, 1981).

4.3 Distribution and Transport

Little information was found regarding the distribution and transport of chlorination products in receiving waters. The diffusion or spread of available oxidant has been measured by several investigators in cooling water discharge plumes [e.g., see Grieve et al. (1978)]. Principal factors affecting distribution and transport of the products of water chlorination are water quality, water flow (dilution), wind, sunlight, and temperature. In particular, much of the active halogen is lost to the "chlorine demand" of the receiving waters. The total oxidant concentration is always considerably less than if only dilution is considered. The chemical and physical properties of the chlorination product will govern its environmental fate. For example, the major environmental fate of many low-molecular-weight chloroorganics such as the trihalomethanes will be volatilization from the chlorinated water and receiving waters (Jolley et al., 1978; Smith et al., 1980). Dilution and reaction of the oxidants with the receiving waters are of major importance in reducing available oxidant concentrations. The fate of residual oxidants in receiving waters may include such reactions as chloramine oxidation of bromide, halogen transfer to organic nitrogen-containing compounds, and reaction with

Table 15. Concentrations of active halogen species in a test case for chlorination of seawater (mol/L)[a,b]

Time (min)	HOCl	NH_2Cl	$NHCl_2$	RNHCl	HOBr	NH_2Br	NHBr	NBr_3
0	1.1×10^{-5}	0	0	0	0	0	0	0
1	6.7×10^{-9}	1.5×10^{-7}	3.5×10^{-10}	6.5×10^{-8}	3.6×10^{-6}	6.6×10^{-12}	1.5×10^{-8}	2.6×10^{-7}
10	1.2×10^{-13}	4.1×10^{-10}	3.5×10^{-10}	8.1×10^{-12}	1.5×10^{-6}	4.6×10^{-11}	3.1×10^{-8}	2.4×10^{-7}
30	2.6×10^{-15}	1.3×10^{-12}	3.5×10^{-10}	1.7×10^{-11}	6.7×10^{-7}	3.2×10^{-10}	5.5×10^{-8}	2.2×10^{-7}
60	2.5×10^{-15}	1.2×10^{-13}	3.5×10^{-10}	3.0×10^{-11}	3.7×10^{-7}	1.1×10^{-9}	7.5×10^{-8}	2.0×10^{-7}

Time (min)	RNHBr	$RNBr_2$	NHBrCl	RNBrCl	NH_3	RNH_2	Chlorine demand	Total residual halogen
0	0	0	0	0	7.1×10^{-7}	7.1×10^{-7}	4.2×10^{-6}	1.1×10^{-5}
1	2.0×10^{-9}	1.4×10^{-7}	2.9×10^{-7}	5.2×10^{-7}	6.2×10^{-14}	0	2.6×10^{-9}	6.5×10^{-6}
10	9.6×10^{-11}	1.5×10^{-7}	3.9×10^{-7}	5.7×10^{-7}	2.3×10^{-15}	0	0	4.5×10^{-6}
30	8.2×10^{-11}	1.5×10^{-7}	3.1×10^{-7}	5.7×10^{-7}	3.1×10^{-14}	0	0	3.5×10^{-6}
60	8.9×10^{-11}	1.5×10^{-7}	2.2×10^{-7}	5.7×10^{-7}	2.2×10^{-13}	0	0	3.0×10^{-6}

[a] Initial conditions: pH, 8.2; temperature, 25°C; chlorine added as Cl_2, 0.8 mg/L; chlorine demand as Cl_2, 0.4 mg/L; NH_3 concentration as nitrogen, 0.01 mg/L; RNH_2 concentration as nitrogen, 0.01 mg/L. Note: Loss of inorganic halamines will be faster in the final version of the model because of the incorporation of breakpoint reactions.

[b] Reference: Haag and Lietzke (1980).

organic constituents. In general, the rates for such reactions will be lowered due to dilution.

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