

THE AMMONIA-CHLORINE TREATMENT OF WATER:
A STUDY OF SOME REACTIONS OF FREE CHLORINE AT HIGH DILUTIONS
AS AFFECTED BY AMMONIA AND CERTAIN OTHER SUBSTANCES

by

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The Ammonia-Chlorine Treatment of Water:

A Study of Some Reactions of Free Chlorine at High Dilutions as Affected by Ammonia and Certain other Substances

Introduction.

The disinfection of water by the use of chlorine or calcium hypochlorite has been practiced almost as long as the germicidal power of chlorine has been recognized. Bleaching powder, which was formerly widely used, has now been largely replaced by chlorine gas for disinfection of water on a plant scale. Within the last few years, the use of ammonia in conjunction with the regular chlorination has been receiving increasing attention, and where this process has been tried with success its advantages may be summarized as follows:

- (1). Tastes and odors which do not yield to chlorine treatment alone, or are even increased by it, have been eliminated.
- (2). The effectiveness of sterilization has been increased, with the use of less chlorine.
- (3). The ability to increase the chlorine dosage without objectionable tastes or odors allows the use of a heavier dosage to aid in the control of algae.
- (4). The maintainance of residual chlorine throughout the distribution system insures against aftergrowths or subsequent contamination.

The first application of the ammonia-chlorine process of water treatment on a plant scale was made by Race (1) at Ottawa Canada in 1916. The treatment was undertaken principally in the interest of economy, since bleaching powder, which was used as a source of chlorine, had advanced greatly in price. Ammonia and bleaching powder were mixed in dilute solution, with a very short contact period before being added to the water. A ratio of 2 parts by weight of chlorine to 1 part by weight of ammonia, was found to give good results. Race's records show practically the same percentage reduction in number of bacteria per cc. with "bleach" and ammonia as with "bleach" alone, but by using 0.13 part per million of ammonia, the available chlorine required was reduced from 1.1 ppm to 0.25 ppm. For the same period, the cost per million gallons of water treated using "bleach" alone was \$1.26, while that using "bleach" and ammonia was \$.54.

Recent work by Harold (2) has dealt with the chloro-amine treatment of field water supplies for the British Army in India. Liquid chlorine added to pre-ammoniated water was found to be a very effective sterilizing agent, even for highly polluted waters.

McAmis(3) in 1926, began the use of ammonia at

Greenville Tennessee, to correct tastes which had been prevalent in the local water supply since the introduction of chlorination in 1912, and his success has lead to a renewed interest in its use in the United States.

Spaulding (4) reports that the ammonia-chlorine treatment has been successfully employed in the Springfield Illinois plant, being especially effective in the prevention of chloro-tastes.

Harrison (5) says that the process, when used at Bay City Michigan, has not proven effective for the tastes encountered in that water, but is suited for the removal of odors. Experiments there have extended over a period of 2 years.

A series of tests made by Braidech (6) at the Baldwin filtration plant of Cleveland Ohio, serves to establish the value of pre-ammoniation in the prevention of tastes and odors and increased efficiency of chlorination.

Because of its chemical activity, chlorine will unite readily with many substances occurring in surface waters and produce compounds of objectionable taste or odor. In this connection, Runow and co-workers(7) state that not more than 2% of the applied chlorine is used for the destruction of bacteria, the most of it being used by other

organic matter and salts in the water. This "chlorine demand" of the water must be satisfied before disinfection becomes effective.

Industrial trade wastes from coke ovens, gas works, and oil refineries, which may find their way into a water supply, contain substances especially likely to produce tastes in the water upon chlorination. These impurities, chiefly phenols, have been found to cause tastes when present to the extent of as little as 1 part per billion. By adding ammonia to the water first, the taste producing compounds no longer are formed upon the addition of chlorine, which reacts instead with the ammonia presumably with the production of chloroamines. These exert a toxic action on bacteria, so that destruction of pathogenic bacteria and taste prevention are both accomplished.

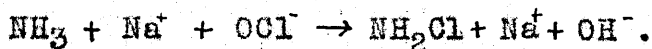
The reactions between chlorine and ammonia have been studied by a number of investigators. Noyes and Lyon (8) have shown that the reaction between gaseous chlorine and concentrated ammonia solution is:

$12\text{NH}_3 + 6\text{Cl}_2 \rightarrow \text{N}_2 + \text{NCl}_3 + 9\text{NH}_4\text{Cl}$, when the two are allowed to react in these proportions. With an excess of ammonia, further reactions may occur:



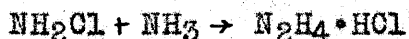
A few years later, Raschig (9) succeeded in prepar-

ing and isolating for analysis, an intermediate product in the reaction between chlorine and ammonia. This compound, NH_2Cl , monochloroamine, was obtained in the form of pale yellow oily drops by distillation in vacuo from a cooled mixture of strong hypochlorite and ammonia solutions, zinc chloride being added to bind any excess ammonia. As is well known, when solutions of hypochlorite are diluted with water, a blue color is produced upon the addition of a solution of aniline. Raschig found that when ammonia was used for the dilution of the hypochlorite solution, no blue color was produced with aniline. He further found that the blue color, when once formed from diluted hypochlorite and aniline, could not be destroyed by ammonia. Since evolution of nitrogen did not immediately occur upon the addition of ammonia to the hypochlorite solution, and since the property of coloring aniline solution was destroyed, Raschig was lead to believe that an intermediate product had been formed. By mixing hypochlorite solutions of known strength with varying amounts of ammonia, he found that the power to color aniline solution was lost when 1 mol of hypochlorite and 1 mol of ammonia were present, indicating the following reaction:



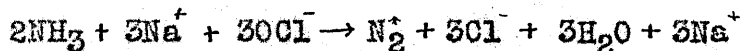
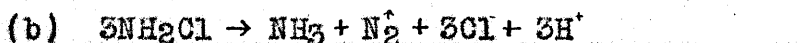
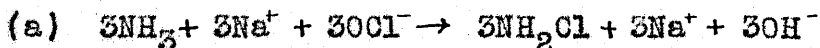
In the same paper, Raschig points out that monochloro-

amine will react with ammonia to form hydrazine:

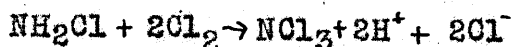
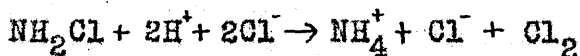
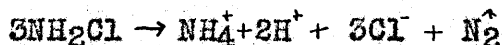


For this to occur, the presence of from 10 to 30 times the theoretical amount of ammonia is required. By mixing equal volumes of tenth normal sodium hypochlorite and normal ammonia solutions and heating rapidly to boiling, he states that a 20% to 25% theoretical yield of hydrazine was obtained. With egg albumin, casein, or animal glue added to the mixture, the yield was as high as 70%.

Later work, by Bray and Dowell (10) lead them to believe that, in alkaline solution, the formation of monochloroamine takes place as a rapid primary reaction, (a) which is subsequently followed by its slower decomposition(b):



Experiments by Marckwäld and Wille (11) upon concentrated aqueous solutions of NH_2Cl show it to be very unstable, since even at 0 degrees it soon begins to evolve nitrogen and form NCl_3 . The changes occurring are represented as follows:



In a recent paper, Chapin (12) states that di-chloro-amine, NHCl_2 , as well as mono-chloroamine, may result from the ammonia-chlorine reaction, the pH of the solution determining which compound is formed. He found that if the solution is more alkaline than pH 8.5 nothing but mono-chloroamine is formed, while below pH 4.4 nitrogen tri-chloride is formed almost exclusively. Between pH 4.4 and 8.5, the 2 chloroamines may co-exist. In the interval of pH 4.5 to 5.0, dichloroamine predominates.

The possible reactions between ammonia and chlorine are well summarized by Berliner (13), as follows:

"In the interaction of the substances, chlorine may replace every atom of hydrogen in ammonia to form NH_2Cl , NHCl_2 , or NCl_3 ; or the chlorine in solution may first form hypochlorous acid which will react with ammonia to form ammonium hypochlorite. This will, in turn, decompose into monochloroamine and water. The chloroamines themselves may unite with more ammonia to form hydrazine and hydroxyl amine. Other side reactions have been noted or suspected. For all practical purposes, however, we may consider that chlorine reacts directly with ammonia to form monochloroamine, NH_2Cl . This in turn may be subject to subsequent slow reactions involving its decomposition into nitrogen and hydrochloric acid."

Rideal (14) was the first to note an increase in the germicidal power of chlorine when used in conjunction with ammonia. He found that the phenol coefficient of chlorine was increased from 2.18 to 6.36 when used with ammonia. Since the phenol coefficient of ammonia itself is only 0.7 and that of ammonium chloride negligible in these concentrations, the other ammonia-chlorine compounds formed must be highly effective sterilizing agents. Rideal found, as have several later investigators, that the germicidal action of chlorine alone is more rapid than it is when ammonia is present. In the presence of ammonia, however, sterilizing action persists over a period of several hours, ultimately producing better results than when chlorine is used alone.

Hinman and Beeson (15) found that the previous addition of ammonia retarded the germicidal action of chlorine upon a clear water of low organic content. In a turbid water of high organic content, however, the germicidal power of chlorine was increased by the presence of ammonia.

The chemical properties of free chlorine and the chloramines are so similar that, as yet, no completely satisfactory method has been devised for their differentiation when they exist in the same very dilute solution.

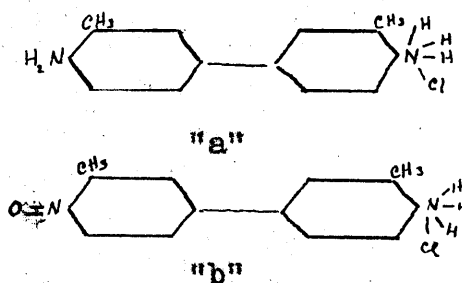
Harold(2), in titrating a pre-ammoniated chlorinated water with sodium thiosulfate in the presence of KI and

starch, found he could detect and determine two fractions of available chlorine. The first fraction liberated iodine from KI in a neutral solution and could be titrated. After acidifying, the solution again became blue, indicating the existence of a second substance, capable of freeing iodine from KI in acid but not in neutral solution. This second titration fraction was noted in ammonia-chlorine solutions which showed increased germicidal power, over that of similar solutions containing no ammonia. From these facts, Harold concluded that the presence of a compound of chlorine and ammonia was indicated and that this compound was readily decomposed, giving up its chlorine upon acidification.

Besemann (16) briefly describes a method for distinguishing between free chlorine and the chloramines formed from ammonia, by the use of methyl orange. He found that in acid solution chlorine decolorized methyl orange, but in the presence of alkali the reaction between methyl orange and an aqueous solution of chlorine was slowed down or stopped completely. Upon acidifying, however, the color was rapidly lost. He concluded from this that salts of hypochlorous acid do not react with (decolorize) methyl orange, while the free acid does produce decolorization. He also noted that the addition

of ammonia stopped the methyl orange and chlorine reaction, presumably due to the combination of the chlorine with the ammonia. Consequently, when the solution was acidified, the characteristic red color of methyl orange persisted, indicating that all the free chlorine had been removed by combination with ammonia. However, he could still obtain a positive test for chlorine with starch-iodide solution. Besemann also noted a similar binding of chlorine in solutions which contained other nitrogenous compounds, such as aniline, urea, and asparagine.

Since the work described below was begun, Berliner⁴ has announced a method for the determination of chloroamine by means of the standard ortho-tolidine reagent. In HCl solution, ortho-tolidine is present as a salt having the formula "a". According to Ellms and Hauser (17), oxidation of this compound by free chlorine produces a yellow dye of formula "b", the depth of color serving as a means for quantitatively determining small amounts of chlorine in water.



When chlorine alone is present, the color develops at once, reaching its maximum intensity in about 1 minute.

*Private communication

and gradually fading out on standing, but when the chlorine is present as chloroamine, the color develops much more slowly, reaches a maximum intensity in 15 to 20 minutes, and does not fade out as rapidly as does the chlorine color. Freedom from nitrites is essential for correct results, since they also produce a yellow color with ortho-tolidine. Chlorine, being a strong oxidizing agent, readily oxidizes nitrites. Hence, if the excess of chlorine is sufficient, nitrites and free chlorine cannot co-exist. Chloroamine, however, is not a strong oxidizing agent and will not completely react with nitrites. Therefore, nitrites and chloroamine may be present in the same sample and unless the nitrite content be reduced by oxidation, the ortho-tolidine reagent will indicate too high a chlorine residual. Berliner recommends removal of excess nitrite as follows:

Treat a 100 cc sample with 1 cc of 0.75% HCl.

Add 0.5 cc of commercial 3% H_2O_2 . After 4 minutes, add 1 cc of o-tolidine reagent and let stand 20 minutes. Compare with chlorine standards.

Jenne and Welsford (18) routinely used the above method of nitrite removal and chloroamine determination to control the disinfection of swimming pools in Philadelphia, and Berliner's directions for it are included in their paper. They emphasize the importance of the removal of nitrites before making the o-tolidine test, so that true

residual chlorine readings may be made.

The results of Besemann and Berliner suggest two possible analytical differences between chlorine and chloroamine which might serve to distinguish them: first, other dyes or indicators may show decolorizing effects similar to methyl orange; second, an excess of nitrite added to a solution of free chlorine or to a mixture of chloroamine and free chlorine, may destroy the chlorine and not the chloroamine. After oxidation of the excess nitrite with peroxide, the color developed upon the addition of ortho-tolidine would be due solely to chloroamine.

In order to determine the reliability of these methods, the following experimental work was carried out.

Experimental Work, part I.

Preliminary tests were made upon a number of dyes to select those which would give a distinct, but not too deep, color when present in amounts which would be decolorized or appreciably faded by a chlorine solution of 0.5 part per million, in a reasonably short period of time. The dyes were prepared in .002% solutions and 1 cc of the dye was added to 100 cc of the chlorine solution. All tests were carried out in 100 cc, tall, cylindrical glass bottles about 13.5 cm high to the neck, which are commonly known as oil sample bottles.

The chlorine was prepared by gently warming a mixture of powdered $K_2Cr_2O_7$ and concentrated HCl . The gas evolved was washed through 2 Woulff bottles containing small amounts of water, and collected in distilled water in a brown bottle surrounded by cold water. After saturation, the solution was kept in the refrigerator. From this main solution, stock solutions were prepared as needed, and their chlorine content determined by iodometric titration with $N/100 Na_2S_2O_3$. From the standardized stock solutions, test solutions containing any amount of chlorine could be prepared by dilution, and checked by the ortho-tolidine method.

Tabulated results of the dye reactions with .5 ppm chlorine solution are found in Table #1. Controls containing no chlorine were run on each dye. All tests were made in distilled water. The various time intervals shown, indicate the time required for complete decolorization of the dye.

Table #1. Reaction of Various Dyes with 0.5 ppm Chlorine.

Dye	Reaction in acid sol'n	Reaction in alk. sol'n.	Reaction in neut. sol'n
Crystal violet	35 minutes	Color too light to be used	
Phenolphthal- ein (A)	no color	too light	no color
Neutral red (H)	10 minutes	" "	30 minutes
Acid Fuchsin	35 "	Color too light to be used	
Dimethylamino- azobenzene (H)	30 "	no change	no change
Aniline red	15 "	Color too light to be used	
Gentian violet	48 hours	Control also decolorized	no change
Rosolic acid	48 "	no change	48 hours
Brilliant green	48 "	48 hours	no change
Phenol red (K)	48 "	no change	48 hours
Safranin	48 "	no change	no change
Methyl Orange	10 minutes	too light colored to be used	
Methylene blue	48 hours	Control also decolorized	no change

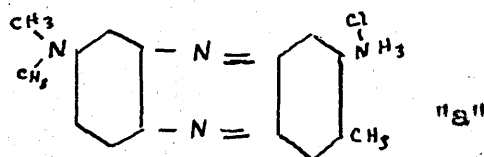
(A) indicates an alcoholic solution of the dye.

(H) indicates a hydrochloric solution of the dye.

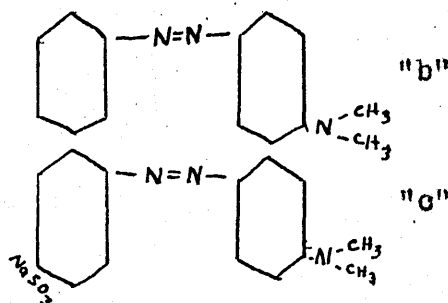
(K) indicates a potassium hydroxide solution of the dye.

In addition to the above dyes, alizarin S, azolitmin, congo red, erythrosine, hematoxylin, schlarlach R, bismark brown and methyl red were tried, but gave too light a color in the concentrations used.

From the list of dyes tested, neutral red ("a"), dimethylaminoazobenzene ("b"), and methyl orange ("c"), were chosen for further consideration



since their original color was of a readable depth, and their decolorization was rapid and definite. Aniline red, crystal violet, and acid fuchsin were



eliminated since their original color was too indefinite, even though they were rapidly decolorized by the chlorine solution. Since the reactions in acid solutions produced the most definite color changes, the further experiments on decolorization were done in solutions acidified with 0.5 cc of dilute HCl per 100 cc.

The dyes selected were next tried in acid solutions containing decreasing amounts of chlorine. The lower limit was a concentration of 0.1 ppm of chlorine, which failed to decolorize any of the dyes within 24 hours.

Table #2. Time of decolorization of dyes by chlorine.

<u>Concentration</u> <u>of chlorine</u>	<u>Methyl</u> <u>Orange</u>	<u>Dimethylam.</u> <u>azobenzene</u>	<u>Neut.</u> <u>Red</u>
0.5 p.p.m.	10 minutes	30 minutes	10 minutes
0.4 "	15 "	30 "	15 "
0.3 "	25 "	40 "	20 "
0.2 "	45 "	55 "	20 "
0.1 "	No change within 24 hours		slight dec. in 24 hrs.

The time of decolorization of the dyes can not be stated more accurately than to the nearest 5 minutes, because the final stages of the decolorization take place very slowly.

After determining the effect of chlorine alone upon the dyes selected, the effects of ammonia-chlorine mixtures were next studied. Ammonium hydroxide solution of sp.gr. 0.9 was diluted to make a stock solution of 100 parts per million of ammonia, from which further dilutions were made as needed. Varying concentrations of chlorine and ammonia were used, with the results shown in the following tables.

Table #3 Chlorine and chlorine-ammonia mixture in distilled water, in contact with the dye 30 minutes, before acidifying with .5 cc HCl.

Dye	3 ppm of chlorine	3 ppm of Cl_2 . and .75 ppm NH_3
Meth. orange	no color	no color
Neut. red	" "	" "
Dimethylan.	" "	" "

Table # 4 Chlorine and chlorine-ammonia mixture in tap water, in contact with dye 30 minutes, before being acidified with .5 cc HCl.

Dye	2 ppm Cl_2 only	2 ppm Cl_2 . and .5 ppm NH_3
Meth. orange	no color	color (faded)
Neut. red	" "	no color
Dimethylan.	" "	color (faded)

Table #5 same procedure as above, in tap water.

Dye	1 ppm Cl_2 only	1 ppm Cl_2 . and .25 ppm NH_3
Meth. orange	no color	slight color(faded)
Neut. red	no color	no color
Dimethylan.	no color	slight color(faded)

Table #6 Chlorine and chlorine-ammonia mixture in tap water, in contact with dye 30 minutes before being acidified with .5 cc HCl.

Dye	0.5 ppm Cl_2 only	0.5 ppm Cl_2 . and 0.12 ppm NH_3
Meth. orange	no color	slight color(faded)
Neut. red	" "	no color
Dimethylam.	" "	slight color(faded)

Table #7 Same procedure as above, in distilled water.

Dye	0.5 ppm Cl_2 only	0.12 ppm NH_3 and 0.5 ppm Cl_2
Meth. orange	decol. in 25 min.	decol. in 25 min.
Neut. red	" " 15 "	" " 15 "
Dimethylam.	" " 40 "	" " 40 "

In the more concentrated solutions, tables 4 and 5, the presence of ammonia apparently slows up the decolorizing action of the chlorine, since a slight color is obtained upon acidifying the ammonia-chlorine solution, while no color results upon acidifying a chlorine solution of the same concentration, containing no ammonia. In no case, however, is the reaction between the dye and chlorine stopped completely, since the color in the ammonia-chlorine solution slowly fades out. For the bleaching of the dye by the chlorine to be completely inhibited, a longer contact period would probably be needed.

No difference in the time of decolorization of the dyes is noted in the dilute chlorine and ammonia-chlorine solutions. Since the usual chlorine concentration encountered is much less than the lowest dilution of chlorine used above (0.5 ppm), it is evident that none of these dyes would be suited for the differentiation of free chlorine from chloroamine, in the average public water supply.

A series of solutions containing varying amounts of chlorine and ammonia in the ratio of 2 parts of chlorine to 1 part of ammonia gave similar results.

Since natural waters and water in swimming pools may contain traces of nitrogenous organic substances, a series of them was studied in connection with the ammonia-chlorine reaction to determine their effect on chlorine, as evidenced by the decolorization of dyes. These are not intended as the identical compounds occurring in water, but the list was selected to include an aliphatic and an aromatic amine, an amide, an amino acid, etc. Aniline, ammonium chloride, phenol, acetamide, ammonia, methyl amine hydrochloride, asparagine, bacto-peptone*, aspartic acid and urea were used. Phenol was included in the list because

*A water soluble nitrogenous bacteriological nutrient product marketed under that name by the Digestive Ferments Company.

of its well known property of uniting with chlorine to produce troublesome chlorophenol compounds.

In all the experiments on the binding of chlorine by the various nitrogenous compounds, the same concentrations were used and the same procedure followed throughout. One cc of a 100 ppm stock solution of the test substance was added to 5 cc of a solution containing 10 ppm of chlorine and left in contact for a given time. The mixture was then diluted to 100 cc, making the final concentrations when the indicator and acid were added, 1 ppm of the test substance and 0.5 ppm of chlorine. In all the series of tests run, two bottles of each nitrogen compound and chlorine mixture were set up. One bottle was allowed a brief contact period, 10 to 15 minutes, and the other, a 24 hour period. Controls of 0.5 ppm chlorine with no nitrogen compound, were run under parallel conditions. Controls containing 1 ppm of the nitrogen compound and no chlorine, were run to show that no decolorization of the indicator was produced by the nitrogen compound alone.

In the following tables, the time required for complete decolorization of the dye in the solution is shown. When complete decolorization did not occur, the tables indicate roughly the depth of the color at the end of 24 hours.

Table # 8 Effect of 1 ppm of test substance upon .5 ppm of free chlorine indicated by time required for decolorization of dyes. O-tolidine values show amount of chlorine indicated by standard o-tolidine reagent. Fifteen minute contact in distilled water.

<u>Test substance</u>	<u>Methyl orange</u>	<u>Neutral red</u>	<u>Dimethylamino azobenzene</u>	<u>Ortho-tolidine</u>
Aniline	no decolor.	no decolor	no decolor.	less than .03 ppm
NH ₄ Cl	55 minutes	35 minutes	40 minutes	.3 ppm
Phenol	50 "	45 "	25 "	.35 ppm
Acetamide	faint color	20 "	25 "	.35 ppm
Ammonia	slight color	35 "	25 "	.3 ppm
CH ₃ NH ₂ ·HCl	60 minutes	35 "	45 "	.25 ppm
Asparagine	faint color	45 "	30 "	.3 ppm.
Bacto-peptone	faint color	25 "	25 "	.3 ppm
Aspartic acid	slight color	25 "	40 "	.25 ppm
Urea	20 minutes	30 "	10 "	.3 ppm
(Control)	20 minutes	20 minutes	25 minutes	.3 ppm

Table #9 Effect of 1 ppm of test substance upon .5 ppm of free chlorine indicated be time required for decolorization of dyes. O-tolidine values show amount of chlorine indicated by standard o-tolidine reagent. Twenty-four hour contact in distilled water.

<u>Test substance</u>	<u>Methyl orange</u>	<u>Neutral red</u>	<u>Dimethylamino azobenzene</u>	<u>Ortho-tolidine</u>
Aniline	no decolor.	faint color	no decolor	less than .03 ppm
NH ₄ Cl	" "	40 minutes	60 minutes	.2 ppm
Phenol	" "	60 "	slight color	.15 ppm
Acetamide	60 minutes	35 "	no decolor.	.2 ppm
Ammonia	slight color	40 "	no decolor.	.3 ppm
CH ₃ NH ₂ ·HCl	no decolor.	slight color	" "	.15 ppm
Asparagine	" "	faint color	faint color	.15 ppm
Bacto-peptone	60 minutes	" "	no decolor.	.15 ppm
Aspartic acid	no decolor.	slight color	60 minutes	.2 ppm
Urea	2 hours	2 hours	60 "	.1 ppm
(Control)	35 minutes	45 minutes	40 minutes	.2 ppm

Table #1 Effect of 1 ppm of test substance upon .5 ppm of free chlorine, indicated by time required for decolorization of dyes. O-tolidine values show amount of chlorine indicated by standard o-tolidine reagent. Fifteen minute contact in tap water.

<u>Test substance</u>	<u>Methyl orange</u>	<u>Neutral rdd</u>	<u>Dimethyl aminoazo.</u>	<u>Ortho-tolidine</u>
Aniline	no decolor.	no decolor.	no decolor.	less than .03 ppm
NH ₄ Cl	3 hours	slight color	slight color	.3 ppm
Phenol	slight color	" "	no decolor.	.25 ppm
Acetamide	40 min.	2 hours	slight color	.3 ppm
Ammonia	40 "	20 min.	faint color	.3 ppm
CH ₃ NH ₂ ·HCl	slight color	slight color	slight color	.15 ppm
Asparagine	" "	" "	" "	.2 ppm
Bacto-peptone	" "	" "	faint color	.25 ppm
Aspartic acid	" "	no decolor.	40 min.	.15 ppm
Urea	3 hours	25 minutes	40 "	.25 ppm
(Control)	30 min.	30 min.	faint color	.3 ppm

Table # 11 Effect of 1 ppm of test substance upon .5 ppm of free chlorine indicated by time required for decolorization of dyes. O-tolidine values show amount of chlorine indicated by standard o-tolidine reagent. Twenty-four hour contact in tap water.

<u>Test substance</u>	<u>Methyl orange</u>	<u>Neutral red</u>	<u>Dimethylamino azobenzene</u>	<u>Ortho- tolidine</u>
Aniline	no decolor.	no decolor.	no decolor.	less than .03 ppm
NH ₄ Cl	" "	" "	" "	.15 ppm
Phenolt	" "	" "	" "	less than .03 ppm
Acetamide	slight color	" "	" "	.2 ppm
Ammonia	no decolor.	" "	" "	.25 ppm
CH ₃ NH ₂ ·HCl	" "	" "	" "	.03 ppm
Asparagine	" "	" "	" "	less than .03 ppm
Bacto-peptone	" "	" "	" "	.05 ppm
Aspartic acid	" "	" "	" "	less than .03 ppm
Urea	slight color	slight color	" "	.1 ppm
(Control)	slight color	slight color	slight color	.25 ppm

Evidences of binding of chlorine by the various nitrogen compounds, as shown by the preceding tables, is somewhat inconclusive. There is indication of some binding in the cases in which the time required for decolorization of the dye in the presence of the nitrogen compound is considerably greater than the time required for decolorization of the dye in the control, containing chlorine alone. The presence of the nitrogen compound has at least slowed down the reaction between chlorine and the dye. The complete binding which Besemann describes, is best shown by the reaction obtained with ammonia in tap water with 24 hour contact (table #11), and in distilled water with 24 hour contact (table #9). Here decolorization of the dye did not occur, yet a sufficient chlorine concentration, as shown by ortho-tolidine, was present to have caused decolorization, had a combination between chlorine and ammonia not taken place. The results indicate, on the whole, slighter differences in oxidizing power between free chlorine and chloroamine than Besemann found. In most cases where the dyes were not decolorized, little or no chlorine was shown by ortho-tolidine, indicating the change of practically all the chlorine into compounds which, unlike chloroamine, do not react with ortho-tolidine. This combination took place usually in the longer contact periods, although in the case of aniline, binding occurred almost at once.

Some of the combinations of the various nitrogen compounds with chlorine, decolorized one dye completely but perhaps affected another only slightly. (See aspartic acid, 15 minute contact in tap water, table #10; bacto-peptone and ammonium chloride, 24 hour contact in distilled water, table #9; asparagine, 15 minute contact in distilled water, table #8; etc.)

Experimental, part II.

The second difference between chlorine and chloroamine, which was studied, is their different oxidizing power toward nitrites. In the method devised by Berliner, it is assumed that the presence of nitrites precludes the co-existence of free chlorine, as such. It should therefore be possible to insure a rapid removal of free chlorine, if not already absent, by the addition of excess nitrite which ^{be} could, subsequently removed by peroxide and the remaining chloroamine determined by ortho-tolidine. A nitrite concentration sufficient to remove free chlorine rapidly might, however, also react with part or all of the chloroamine. The results obtained by this method are summarized in the following tables.

The monochloroamine used was prepared by the following method, recommended by Tiller and Chapin (19):

One hundred cc of a solution containing 0.2 gm of

ammonium sulfate and 40 cc of M/10 borax, is mixed with an equal volume of a solution containing 2 cc of M sodium hydroxide solution and 10 cc of strong chlorine water. The resulting mixture has a pH of 9.0

The available chlorine content of solutions of chloroamine prepared in this way was from 150 to 225 parts per million, depending upon the strength of the chlorine solution used. The available chlorine was titrated iodometrically, and the solution diluted to the desired chlorine content. (This chloroamine solution was similar to free chlorine in its action upon dyes, but when titrated, showed fractions of available chlorine in neutral and acid solution, similar to the results noted by Harold (2).)

A stock solution containing 100 ppm of nitrite nitrogen was prepared from sodium nitrite.

Commercial 3% hydrogen peroxide was used for removal of excess nitrite, the procedure given by Berliner being followed. One-half cc of peroxide was found to oxidize as much as 1.0 ppm of nitrite nitrogen in 5 minutes, so completely that no color was produced with ortho-tolidine.

The chloroamine-chlorine mixture used was prepared by mixing 50 cc of a chloroamine solution containing 1 ppm of available chlorine, with 50 cc of chlorine water containing 1 ppm of free chlorine. The resulting mixture contained,

therefore, 0.5 ppm of free chlorine and 0.5 ppm of chlorine as chloroamine. The chlorine solution referred to in the tables contained 0.5 ppm of free chlorine only. The ortho-tolidine readings represent the chlorine content in ppm. The reactions of the dyes are similar to those previously obtained. All tests were run in distilled water.

Table #12 Effect of 1 ppm of nitrite nitrogen in contact 2 hours.

<u>Reagent</u>	<u>Cl₂ only,</u> <u>with nitrite</u>	<u>NH₂Cl</u> <u>Cl₂,</u> <u>with nitrite</u>	<u>NH₂Cl</u> <u>Cl₂,</u> <u>no nitrite</u>
Ortho-tol.	no chlorine	no chlorine	.5 ppm
Meth. orange	no decolor.	no decolor.	20 min.
Dimethylamino.	" "	" "	30 min.

Table #13. Effect of 1 ppm nitrite nitrogen in contact 15 minutes.

<u>Reagent</u>	<u>Cl₂ only,</u> <u>with nitrite.</u>	<u>NH₂Cl</u> <u>Cl₂,</u> <u>with nitrite.</u>	<u>NH₂Cl</u> <u>Cl₂,</u> <u>no nitrite.</u>
Ortho-tol.	.05 ppm	.07 ppm	.5 ppm
Meth. orange	slight decolor.	no decolor.	15 min.
Dimethylamino.	" "	" "	25 min.

Table #14. Effect of 0.5 ppm nitrite nitrogen in contact 1 hour.

<u>Reagent</u>	<u>Cl only,</u> <u>with nitrite.</u>	<u>NH₂Cl</u> <u>Cl₂</u> <u>with nitrite</u>	<u>NH₂Cl</u> <u>Cl₂</u> <u>no nitrite</u>
Ortho-tol.	.15 ppm	.07 ppm	.5 ppm
Meth. orange	slight decolor.	slight decolor.	30 min.
Dimethylamino.	" "	no decolor.	30 min.

Table # 15. Effect of 0.1 ppm of nitrite nitrogen in contact for 16 hours.*

Reagent	Cl ₂ only, with nitrite.	NH ₂ Cl Cl ₂ , with nitrite.	NH ₂ Cl Cl ₂ , no nitrite.
Ortho-tol.	.05 ppm	.4 ppm	.5 ppm
Meth. orange	no decolor.	30 min.	20 min.
Dimethylamino.	" "	40 min.	25 min.

Table # 16. Effect of 0.1 ppm nitrite nitrogen in contact 24 hours.**

Reagent	Cl ₂ only, with nitrite.	NH ₂ Cl Cl ₂ , with nitrite.	NH ₂ Cl Cl ₂ , no nitrite.
Ortho-tol.	no chlorine	.07 ppm	.5 ppm
Meth. orange	no decolor.	no decolor.	30 min.
Dimethylamino.	" "	" "	30 min.

Table #13 shows that within 15 minutes, a nitrite nitrogen concentration of 1 ppm had reduced the free chlorine from 15 ppm to .05 ppm, but had at the same time, reduced the total chlorine in the NH₂Cl-Cl₂ mixture to almost the same amount. This indicates that when the nitrite concentration is large, both free chlorine and chloroamine are apparently simultaneously destroyed by it. The results shown

*Control, .5 ppm chlorine without nitrite, showed .4 ppm chlorine after 16 hours.

**Control, .5 ppm chlorine without nitrite, showed .3 ppm chlorine after 24 hours.

in table #12, for a contact period of 2 hours, show that in a longer time interval both the free chlorine and the chloroamine were completely destroyed. In table # 14, the results indicate that the chlorine in the chloroamine-chlorine mixture had even been more completely destroyed than that in the solution containing only free chlorine.

The theoretical oxidation ratio between chlorine and nitrite nitrogen can be calculated from the following equation: $\text{NaNO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{NaNO}_3 + 2\text{HCl}$, showing 71 parts of chlorine equivalent to 14 parts of nitrite nitrogen. This is practically a nitrite nitrogen- chlorine ratio of 1:5. Table #15 shows that with a nitrite nitrogen concentration of 0.1 ppm, equivalent to 0.5 ppm chlorine, the tendency was to destroy the chlorine first, while the chloroamine underwent little change. After a longer contact period (table #16), the chlorine in the chloroamine-chlorine mixture had also been almost completely destroyed.

It is therefore evident that in no case has the chloroamine chlorine remained entirely unaffected during the removal of free chlorine by treatment with excess nitrite, and that in the cases in which it is least affected, the time required for the reaction between the chlorine and nitrite is too long for a laboratory control test.

Summary and Conclusions.

1. The difference in the decolorization of methyl orange, dimethylaminoazobenzene, and neutral red, by chlorine alone and chlorine in the presence of ammonia, is neither sufficiently uniform nor sufficiently consistent to serve as a means of differentiation between free chlorine and the chloroamine formed from chlorine and ammonia.
2. Chlorine, in the presence of several of the organic compounds studied, will no longer decolorize the dyes or give a color with ortho-tolidine, indicating a combination between them.
3. When free chlorine and chloroamine exist in the same solution, an excess of nitrite will destroy both, if the concentration of nitrite be great enough and the time of contact long enough. Lower concentrations of nitrite in contact for longer periods will destroy a greater amount of chlorine than of chloroamine, but in no case is the free chlorine destroyed and the chloroamine left entirely unaffected.

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