Circular No. 15 1935

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BY

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AUG. 26th 1818

DEPARTMENT OF REGISTRATION AND EDUCATION

STATE WATER SURVEY DIVISION

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Urbana, Illinois

[Printed by authority of the State of Illinois]

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Reprinted from JOURNAL OF THE AMERICAN WATER WORKS ASSOCIATION
Vol. 26, No. 11, November, 1934

THE DETERMINATION OF FREE CHLORINE

BY D. TARVIN, H. R. TODD, AND A. M. BUSWELL

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A number of reagents have been proposed for determination of free chlorine or chloramine in water. Phelps suggested the use of o-tolidine in acetic acid (1) and Ellms and Hauser devised a method for estimation of chlorine based upon the use of o-tolidine in hydrochloric acid (2). The starch iodide test has been used for some time by certain workers. More recent suggestions are the use of dimethyl-p-phenylenediamine hydrochloride as a reagent for chlorine (3) and methyl orange for the estimation of chlorine in the absence of chloramine.

The chief interfering substances in the accurate determination of chlorine by o-tolidine have been found to be manganese, nitrites and iron (1, 5, 6, 7, 8). At an earlier date Boruff and Buswell showed that there was no interference from nitrites and iron under the conditions necessary for making the o-tolidine test for free chlorine (9). But with the present general use of chloramine instead of chlorine longer reaction time must be allowed for the development of full color. Where this long reaction time is used, nitrites and iron, as well as manganese, interfere in the test. Obviously, the o-tolidine reagent is not entirely satisfactory and attempts have been made to adapt the reagent to the purpose by making corrections or eliminating the cause of interference either mechanically or chemically (4).

In the o-tolidine test, each of the following would exert an effect: concentration of chlorine, oxidation potential of the chlorine or chloramine, pH and HCl concentration, concentrations of manganese and iron and the degree of oxidation of each, concentration of nitrite, concentration of the reagent and reaction time. With these things in mind work has been carried on in an attempt to find a reagent which would eliminate part of the difficulties experienced with o-tolidine. This investigation has been divided into three parts, involving (I) the application of the principle of oxidation-reduction potentials to the problem (II) nitrite interference in the o-tolidine test and (III) the nature of o-tolidine reactions.

I. APPLICATION OF THE PRINCIPLE OF OXIDATION-REDUCTION POTENTIALS TO THE PROBLEM

Conant and Fieser (10) have shown that the reduction potentials of various quinones are functions of their structure. From this it seemed possible that certain reduced compounds which give the quinonoid structure upon oxidation might be investigated and a system selected which would have such potential that it would be oxidized by chlorine or chloramine, but would not be affected by some of the substances interfering in the present o-tolidine test. The oxidation-reduction potentials of various systems involved are given in table 1. E_0 is the "normal potential" at pH = 0 (referred to the system $H^+ \longrightarrow H^0 = 0$) and E is the potential at another definite pH value (11). In each case the oxidized form in the system has been placed on the left and the reduced form on the right so that all E_0 values are positive.

In this connection, it should be noted that Clark, Cohen, and Gibbs (11) determined the potentials of certain organic meriquinone-amine systems to be as follows:

System of	*E_0 (volts)*
o-tolidine	+0.873
benzidine	0.921
p-aminodimethylaniline	0.751

Experimental

As stated above, an attempt was made to apply the principle of variations in oxidation-reduction potentials of various oxidant and indicator systems to the problem of determining free chlorine colorimetrically. For this purpose, there were obtained or synthesized in this laboratory pure reduced quinones or compounds which upon oxidation would give the quinonoid structure and hence, color. Fifty compounds were investigated. Of each compound tested, 0.5 gram was weighed out and dissolved in 400 cc. of distilled water. Substances insoluble in water were treated with sufficient HC1 or NaOH to convert them to the soluble salt form and were then made up to volume with distilled water. Of the solution of the reagent 1 cc. was added to the sample in a 50 cc. Nessler tube in all tests except where other volumes are specified.

The chlorine solution used was made up from bleaching powder, sodium hypochlorite, or as was found better, from chlorine produced in a small generator by reacting $Mn0_2$ and HC1. Chlorine water was added to ammonia free water and allowed to stand until the chlorine demand was satisfied. Where chloramine was desired, the calculated amount of NH_3 was added and the solution allowed to stand 45 minutes. The usual o-tolidine test was then applied to check the chlorine concentration. The compounds used were tested also with chlorinated tap water. The effects of manganese, nitrites, iron, pH and acid concentration were investigated.

Five series of compounds were investigated, these being derivatives of benzene, naphthalene, anthracene, benzidine and miscellaneous compounds. The compounds and results obtained with each series follow.

Derivatives of Benzene

Compounds investigated:

(1) hydroquinone
(2) p-ethoxyphenol
(3) p-aminophenol
(4) o-aminophenol
(5) p-monomethylaminophenol
(6) o-monomethylaminophenol sulfate
(7) p-dimethylaminophenol hydrochloride
(8) p-dimethylaminophenol sulfate
(9) o-dimethylaminophenol
(10) m-dimethylaminophenol
(11) aniline
(12) dimethylaniline
(13) m-nitrodimethylaniline
(14) p-phenylenediamine
(15) p-aminodimethylaniline sulfate
(16) o-toluidine
(17) 2,4-diaminotoluene sulfate;
(18) 2,4-diaminoanisole
(19) o-aminobenzenesulfonic acid
(20) 3,5-dihydroxy-4-nitrotoluene
(21) p-aminoacetophenone
(22) w-diethylamino-3,4-dihydroxyacetophenone
(23) phenylurea

The results obtained with the compounds of the benzene series showed them to be considerably inferior to o-tolidine as a chlorine reagent. They were not sensitive enough in acid solution, were too easily oxidized in alkaline solution by air, and some were oxidized by iron.

Compounds numbers 6, 7, 8, 15, and. 18 gave better results than the others listed in the above series. Of these number 15, i.e., p-aminodimethylaniline or dimethyl-p-phenylenediamine has been used in the form of the hydrochloride by some workers (3). In this laboratory ferric iron was found to oxidize the compound as indicated in the foregoing table of oxidation-reduction potentials.

Derivatives of Naphthalene

(24) l-naphthylamine-3,6,8-trisulfonic acid
(25) 2-naphthylamine-6,8-disulfonie acid (amino G acid)
(26) 2-naphthylamine-5,7-disulfonic acid (amino J acid)
(27) 2-amino-8-naphthol-6-sulfonic acid
(28) l-amino-8-naphthol-3,6-disulfonic acid (H acid)
(29) 2-amino-3,6-disulfonic acid (amido R acid)
(30) aminoquinoline (not strictly a derivative of naphthalene)

In general, the production of color by the action of chlorine with derivatives of naphthalene was somewhat better than that produced with derivatives of benzene. The compounds studied were more stable in solution and were more resistant to oxidation by dissolved oxygen than the derivatives of benzene. The presence of amino and hydroxyl groups in the 1,8 or 2,8 position seemed to be necessary for production of a satisfactory color and the presence of the sulfonic acid group appeared to. intensify the color. The chief objections to use of these compounds as chlorine reagents were that (1) manganese interfered, (2) nitrite interfered, and (3) color was fugitive in some cases.

Best results in the above series were obtained with two compounds: (27) 2-amino-8-naphthol-6-sulfonic acid produced a good yellow color in acid solution with chlorinated tap water and a deep red color when the chlorine concentration was increased. Both oxidized manganese and nitrite produced color with the compound in acid solution. The alkaline solution of the compound darkened on standing for 72 hours. (28) H acid or 1-amind-8-naphthol-3,6-disulfonic acid produced in tap water a greenish yellow color in acid and reddish brown color in alkaline solution. Color faded after a short time. Manganese and nitrite both produced color with the compound in acid solution.

Derivatives of Anthracene

Compounds investigated:

(31) alpha-aminoanthraquinone
(32) anthraquinone and diphenylanthranol
(33) 2,4-diphenylhydroquinone

In general, compounds of this type are very insoluble in water and give only feeble colors with chlorine as would be expected. They were therefore eliminated from further consideration.

Derivatives of Benzidine

Compounds investigated:

(34) benzidine
(35) 3,3'-dimethylbenzidine (o-tolidine)
(36) 3,3'-diethylbenzidine
(37) 3,3'-dichlorobenzidine
(38) 3,3'-benzidinedisulfonic acid
(39) 3-benzidinemonosulfonic acid
(40) 2,2'-benzidinedisulfonic acid
(41). 2,2'-dinitrobenzidine
(42) 3,3'-dimethyl-5,5'-dinitrobenzidine
(43) diphenylbenzidine

Five of the above compounds (numbers 36, 37, 40, 41, and 43) were not available: and were therefore synthesized and purified in this laboratory.

Conant.and Fieser have shown that substitution of alkyl, phenylene, or hydroxyl groups lowers the reduction potential of quinohe and that halogen, carboxyl, and sulfonic acid groups raise the reduction potential (10). Therefore an attempt was made to improve upon the o-tolidine reagent by substitution of various groups in the benzidine nucleus. By this means it was thought possible to increase sensitivity to chlorine while eliminating interference from other substances. The detailed results obtained with the various compounds follow:

(34) Benzidine. This compound is not as sensitive to chlorine as o-tolidine. Manganese interfers considerably, giving a permanent yellow color.

(35) 3,3'-dimethylbenzidine (o-tolidine). Some.of the limitations of this compound have been mentioned. - Nitrite interference is discussed later in this paper.

(36) 3,3'-diethylbenzidine. Replacement of :the methyligroups of o-tolidine by ethyl gives a compound which is very similar in its action to o-tolidine in all respects.

(37) 3,3'-dichlorobenzidine. This compound gave color with chlorine varying from green to blue;. The-color was not permanent but faded after a few minutes. A modification of the standard procedure to addition of 1 drop instead of 1 cc. of reagent gave a color lasting for 20 minutes.

With oxidized manganese the compound gave a fleeting blue color which changed to green when HCl was added. As little as 0.04 p.p.m. of nitrite-nitrogen produced a yellow color which deepened to orange with increasing nitrite concentration. The compound gave no color with 2.0 p.p.m. ferric iron in 45 minutes.

(38) 3,3'-benzidinedisulfonic acid. This compound reacted in a very similar manner to (37) with chlorine and chloramine. When more HCl was added the color changed to yellow and then faded out entirely.

With manganese a green color was produced which lasted 10 minutes, but faded rapidly to pink when excess HCl was added. The compound is apparently more sensitive to nitrite than o-tolidine. As little as 0.03 p.p.m. of nitrite-nitrogen was found to give a yellow color which deepened to orange with increasing nitrite concentration. Ferric iron (2.0 p.p.m.) produced no color in 45 minutes.

(39) 3-benzidinemonosulfonic acid.. Elimination of one of the sulfonic acid groups from the. disulfonic acid was found to be of little benefit. The results obtained were similar to those with the disulfonic acid, but the colors produced were of a more dusky hue and lacked the brilliance and intensity obtained with the disulfonic acid.

(40) 2,2'-benzidinedisulfonic acid. It was thought that shifting the sulfonic acid groups to a different position in the molecule might change the potential sufficiently to correct the difficulties with the 3,3' compound. The results were disappointing. Only a pale yellow was produced with strong chlorine solution.

(41) 2,2'-dinitrobenzidine.. The solution of this compound was of such intense yellow color that 1 cc. gave considerable color to 50 cc. of distilled water and the color was only slightly deepened by chlorine. The chlorine color apparently was not deepened by action of oxidized manganese.

(42) 3,3'-dimethyl 5,5'-dinitrobenzidine. Substitution of two hydrogens on o-tolidine by nitro groups was found to give a reagent the solution of which was highly colored. A deep yellow color was produced in chlorinated tap water, but the color of the reagent interfered with the color produced by action of chlorine.

(43) Diphenylbenzidine. It was thought that substitution of one hydrogen of each amino group by a phenyl might give a satisfactory reagent. The resulting compound was too insoluble for practical work.

A comparison with the results obtained with the other four series shows the benzidine series to be the best of those investigated. Throughout the benzidine series color is produced in acid, but not in alkaline solution. Ortho-tolidine was found superior as a chlorine reagent to the other compounds studied. Compounds with which there was no interference from manganese and nitrite produced only fleeting or temporary colors with chlorine and chloramine.

Miscellaneous

(44) tetramethyldiaminodiphenylmethane
(45) p,p'-diacetyldiaminodipheny]methane
(46) 3,3', 4,4'-tetraminodiphenylmethane
(47) p-aminobenzophenone
(48) p,p'-diaminodiphenyl ether
(49) diphenylamine
(50) methyl red

The above list (excluding methyl red) was investigated to determine the effect of introducing various groups between two phenyl groups. The only compound found sensitive enough to have value as a chlorine reagent was (46) 3,3', 4,4'-tetraminodiphenylmethane. However, both manganese and nitrite produce color with this compound in acid solution so it was eliminated from further consideration. All other compounds above produced only faint colors with chlorine. From this it appears that introduction of a group between two phenyl groups diminishes both the solubility of the compound and the intensity of color produced with chlorine.

Methyl red was not found satisfactory as it was decolorized by chlorine solution, but not by chloramine.

Table 2 summarizes the results obtained by the action of various substances upon compounds studied.

Discussion

As noted above, o-tolidine was found to be the best reagent for the determination of chlorine of the compounds investigated. Compounds giving satisfactory color with chlorine in alkaline solution were oxidized by air and those giving satisfactory color with chlorine in acid solution were oxidized by manganese and in some cases by iron. The correlation between oxidation potentials and interference due to manganese and iron should be considered. The oxidation potentials of tri and tetravalent manganese are high enough in acid solution to cause oxidation of o-tolidine. Ferric iron also produces some color on long standing in acid solution with o-tolidine. In alkaline solution both manganese and iron precipitate. However, the E_0 value for hypochlorite is high in alkaline solution (table 1). This implies that a compound to be relatively free from interference by manganese and iron must be used in alkaline solution. No such compound was found in this investigation because those compounds which produced satisfactory colors with chlorine in alkaline solution were oxidized by air.

The starch-iodide test has been used in alkaline or slightly acid solution with some success for determination of chlorine in the presence of manganese by Scott (3) and Hinman (17). The explanation for this apparently lies in the low oxidation-reduction potential of +0.53 volt for the iodine-iodide system as compared with the higher potentials in alkaline solution of the hypochlorite and chloramine systems.

TABLE 1

Oxidation-reduction potentials

SYSTEM	E_0 (VOLTS)	E (VOLTS)				AUTHORITY REFERENCE NUMBER
		pH 5.3	pH 6.0	pH 8.0	pH 11.6	
$HClO-Cl^-$	1.500	1.27	1.22	1.13	0.88	(12, 13)
			1.12	0.96		(14)
Chloramine			0.87	0.67		(14)
$Mn^{++++}-Mn^{++}$	1.577					(15)
$Mn^{+++}-Mn^{++}$	1.511					(15)
$NO_2^- - NO$	0.980					(16)
$NO_3^- - NO_2^-$	0.950					(16)
$Fe^{+++} - Fe^{++}$	0.750					(12)

II. NITRITES IN THE O-TOLIDINE TEST

Various workers have reported nitrite interference in the o-tolidine test (4, 7, 8). The presence of nitrite has been attributed to the oxidation of ammonia by bacteria or chlorine (7, 8). Iron pipe is reported to catalyze the latter reaction (7). The dangers from nitrite, as shown below, are (a) that color may be produced with o-tolidine thereby giving high results in the test for free chlorine, and *(b)* that chlorine or chloramine may be reduced by nitrite. Scott has summarized the differences between the colors produced by action of o-tolidine with nitrite and o-tolidine with chlorine and has suggested a correction of 0.08 p.p.m. apparent chlorine reading for each 1.0 p.p.m. of nitrite nitrogen (4).

TABLE 2

*Effect of various substances on compounds investigated**

COMPOUND NUMBER	COLOR WITH						AIR OXIDATION		COMMENT
	Chlorine			Manganese 0.4 p.p.m. Acid	Nitrite 0.5 p.p.m. Acid	Iron 2.0 p.p.m. Acid			
	Acid	Neut.	Alk.				Acid	Alk.	
1	−		+			+		+	
2			Faint						Not sensitive enough
3	+	+	++					+	
4	+		++			+		+	
5	+		+			−		+	
6	+	+	+++			−		+	
7–8	−	+	++			−		+	
9	+		+			−		+	
10	−		Very faint						Not sensitive enough
11			Faint						Not sensitive enough
12	+	+	+						Not sensitive enough
13	−		+						Not sensitive enough
14	+	++				+	Slow		
15	+	++	+			+		+	
16	Faint	Faint	Faint						Not sensitive enough
17	Very faint		Very faint						Not sensitive enough
18	++		+						
19	−		Very faint						Not sensitive enough
20–21	−		−						
22			Very faint						Not sensitive enough
23–24	−		−						
25–26	Very faint								Not sensitive enough
27	++		Faint	+	+			Slow	
28	++		+	+	+				Color fades
29	Faint	Faint	Faint						Not sensitive enough
30–33	−		−						Very insoluble
34	++		−	+					
35	++		−	+	+	+			
36	++		−	+					
37	++ (F)		−	+ (F)	++	−			
38	++ (F)		−	+ (F)	++	−			
39	++		−	+ (F)	+				
40	−	Faint	−						Not sensitive enough
41–42	+		−						Reagent highly colored
43	Very faint		−						Very insoluble
44	Faint		−						Not sensitive enough
45									Very insoluble
46	++		−	+	++				
47	−		−						Very insoluble
48	Faint		Faint						Not sensitive enough
49	Very faint		Very faint						Not sensitive enough
50	Decolorized								

* Intensity of color is indicated by number of + marks.
(F), color fades.

Experimental

Work carried on in.this laboratory showed that as little as 0.05 p.p.m. of nitrite nitrogen would produce detectable color with o-tolidine on standing for 7 minutes, which color increased on standing and in 60 minutes matched the 0.02 chlorine standard. Where 0.20 p.p.m. nitrite nitrogen was used, detectable color was produced in 3 minutes, false chlorine reading of 0.03 p.p.m. in 15 minutes and 0.05 p.p.m. in 60 minutes. The addition of excess HCl was found (1) to cause fading of the nitrite o-tolidine color when added after the color had developed and (2) to inhibit formation of the nitrite o-tolidine color when added previous to addition of o-tolidine. Quantitative data to show the effect of acid concentration and pH on nitrite o-tolidine color are given in table 3. Nessler tubes (50 cc.) were used.

TABLE 3

NITRITE NITROGEN USED	HCl (1:10) ADDED	TOTAL HCl	APPARENT CHLORINE (30 MIN.)	pH
Effect of addition of acid to o-tolidine nitrite color				
p.p.m.	*cc.*	*cc.*	*p.p.m.*	
1.0		0.5 (O. T.)	0.07	2.0
	0.5	1.0	0.04	
	1.0	1.5	0.03	
	2.0	2.5	0.03	
Effect of addition of acid to nitrite (0.5 cc o-tolidine then added)				
1.0	0.5	1.0	0.02	1.75
	1.0	1.5	0.02	

The results indicate that addition of excess acid is most effective previous to addition of o-tolidine and that pH values below 2.0 diminish nitrite o-tolidine color.

In contrast to the production of nitrite o-tolidine color (which is generally supposed to cause high results in the o-tolidine test) it was found that the intensity of o-tolidine-chlorine or chloramine color was decreased when nitrite was added after the color had developed. This led to an investigation of the relations existing between chlorine, chloramine, nitrite and o-tolidine in solution.

Confirming Hulbert (8) it was found experimentally that chlorine and nitrite cannot exist long in solution at the same time. Theoretically, this is indicated by the oxidation-reduction potentials of the systems involved (table 1). Quantitative data showing the relations existing between chlorine, chloramine, and nitrite in acid and neutral solution were obtained as follows:

In 50 cc. Nessler tubes were placed amounts of standard sodium nitrite solution such that the final concentrations would range from 0.03 to 0.24 p.p.m. nitrite nitrogen. Chlorine solution was then added so that the chlorine concentration would be 0.30 p.p.m. To each of one set of tubes was added 1.0 cc. of 1:10 HC1 (same strength acid as used for standard o-tolidine reagent) to the second set was added 0.5 cc. HC1 and to the third no HC1. The mixtures were allowed to stand for 5 minutes and remaining nitrite then determined by Standard Methods procedure (18). Results are given in table 4-A.

The above procedure was repeated except that 0.30 p.p.m. monochloramine was used and the mixtures allowed to stand in the dark for 30 minutes before determining final nitrite. Results are given in table 4-B.

A comparison of average nitrite nitrogen oxidized by the two compounds shows the following:

Average nitrite nitrogen oxidized

	1 cc. HC1	0.5 cc. HCl	No HCl
	p.p.m.	*p.p.m.*	*p.p.m.*
By 0.30 p.p.m. chlorine (5 minutes)...........	0.074	0.071	0.077
By 0.30 p.p.m. chloramine (30 minutes)........	0.066	0.072	0.034

Theoretically, 0.30 p.p.m. of chlorine or equivalent chloramine should oxidize 0.060 p.p.m. of nitrite nitrogen to nitrate. The table above shows that in acid solution both chlorine and chloramine oxidize nitrite quantitatively. In neutral or basic solution, chloramine oxidizes a part of the nitrite. Therefore, chloramine and nitrite can exist simultaneously in solution, so long as the solution is not acid. This raises the question as to what happens in the o-tolidine test when acid o-tolidine reagent is added to water containing both chloramine and nitrite. If part or all of the nitrite is oxidized upon acidification and therefore does not react with o-tolidine, a blanket correction for nitrite of 0.08 × nitrite nitrogen = apparent chlorine (4) would not be feasible.

In order to investigate the possibility of reduction of chloramine by nitrite when acid o-tolidine solution is added, the data shown in table 5 were obtained. Readings were made at the end of 30 minutes.

The above data show that concentrations up to 0.75 p.p.m. nitrite nitrogen cause high readings for chloramine. Concentrations greater than 0.75 p.p.m. nitrite nitrogen cause the readings to diminish so that with increasing nitrite concentration apparent chlorine reading becomes too low. These facts indicate that high concentrations of nitrite do reduce chloramine in the o-tolidine test. If a subtraction of 0.08 p.p.m. of false color for each 1 p.p.m. nitrite nitrogen be made it is seen that the calculated value obtained for chloramine actually

TABLE 4-A

Oxidation of nitrite by 0.30 p.p.m. chlorine (5 minutes)

INITIAL NITRITE	NITRITE N OXIDIZED		
	1 cc. HCl	0.5 cc. HCl	No HCl
p.p.m.	p.p.m.	*p.p.m.*	*p.p.m.*
0.03			
0.06			
0.09	0.085	0.075	0.056
0.12	0.070	0.072	0.075
0.15	0.072	0.080	0.075
0.18	0.085	0.065	0.090
0.24	0.060	0.065	0.090
Average..........	0.074	0.071	0.077

TABLE 4-B

Oxidation of nitrite by 0.30 p.p.m. chloramine (30 minutes)

INITIAL NITRITE	NITRITE N OXIDIZED		
	1 cc. HCl	0.5 cc. HCl	No HCl
p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
0.03			0.020
0.06			0.035
0.09	0.060	0.075	0.042
0.12	0.060	0.072	0.040
0.15	0.075	0.075	0.035
0.18	0.070	0.070	0.030
0.24	0.066	0.070	0.035
Average...........	0.066	0.072	0.034

becomes negative where nitrite nitrogen is very high. In other words, low nitrites tend to cause high o-tolidine readings for chloramine and high nitrites tend to cause low o-tolidine readings for chloramine.

As shown above, a correction factor for nitrite is unsatisfactory, but increasing the HCl concentration in the o-tolidine test diminishes nitrite interference. Therefore o-tolidine solution was made up as specified in Standard Methods of Water Analysis (18) except that 0.5 gram o-tolidine and 150 cc. concentrated acid were used. The volume of reagent added to the sample tested was twice the volume specified by Standard Methods (i.e., 2.0 cc. of reagent per 100 cc. sample instead of 1 cc. of reagent per 100 cc. sample). In this way the acid concentration in the sample tested was three times, and the o-tolidine concentration the same as, that used in the Standard Methods test. The result was that nitrite interference was greatly diminished, but the readings obtained averaged 25 per cent lower than the true chloramine values. This indicates that high acid concentration not only inhibits production of o-tolidine-nitrite color, but also favors reduction of chloramine by nitrite so that low chloramine readings are obtained. However, such values are more nearly correct than those obtained by the use of a correction factor for nitrite where the latter is high. In addition, the modified reagent provides sufficient acid to react with high alkalinity and 15 minutes

TABLE 5

Effect of nitrite upon determination of chloramine

NO_2-N	READINGS FOR NH_2Cl			
	0.30 p.p.m.	0.18 p.p.m.	0.10 p.p.m.	0.04 p.p.m.
p.p.m.				
0.00	0.30	0.18	0.10	0.04
0.10	0.30	0.18	0.10	0.04
0.30	0.30	0.23	0.12	0.05
0.50	0.35	0.23	0.13	0.06
0.75	0.38	0.30	0.18	0.10
1.00	0.33	0.27	0.17	0.08
1.50	0.20	0.08	0.09	0.06
2.00	0.20	0.08	0.06	0.06
3.00	0.10	0.04	0.04	0.04
5.00	0.06	0.04	0.04	0.04

is sufficient for development of full color with chloramine. Interference due to ferric iron is diminished by use of the modified reagent.

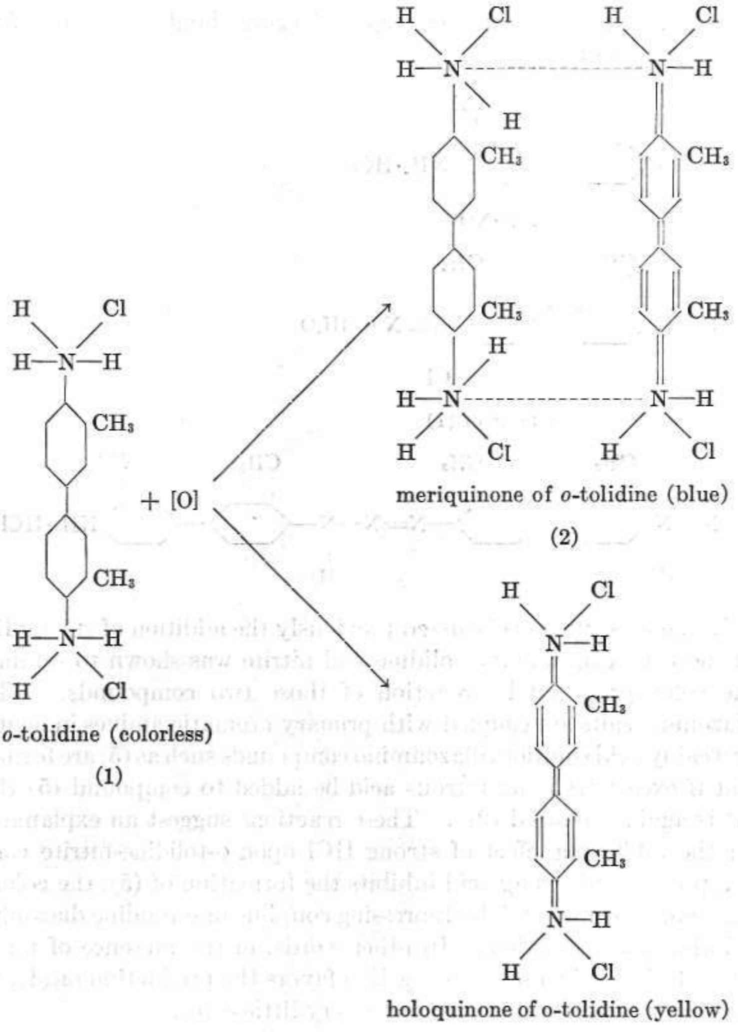
From the above it is apparent that the use of o-tolidine made up in higher acid concentration than specified by Standard Methods of Water Analysis (18), also suggested by Scott (4), is preferable to the use of a correction factor for nitrites.

III. NATURE OF ORTHO-TOLIDINE REACTIONS

The above considerations warrant some discussion of the reactions of o-tolidine. Willstatter and Kalb first showed that mild oxidation of benzidine produced a green substance and that upon oxidation with silver oxide or lead peroxide a deep yellow quinonoid substance was formed (19, 20). This compound contained two less hydrogen atoms than benzidine and was p,p'-diiminodiphenyl. Such fully oxidized products of diamines were termed holoquinones. In addition to the holoquinones, Willstatter and Piccard -isolated colored, crystalline, partial oxidation products of diamines which were called meriquinones (21). For example, Wurster's red is the meriquinone produced by partial oxidation of p-aminodimethylaniline. The structure of meriquinones was shown to be analogous to that of quinhydrone, but meriquinones are not necessarily composed of equimolecular parts of oxidant and reductant.

Clark, Cohen, and Gibbs applied the above considerations to the o-tolidine test and by means of potentiometric and spectrophotometric studies explained the varying color reactions shown by o-tolidine (11). The reactions involved are shown on page 1659. From these reactions it became evident that the variations in color experienced in the o-tolidine test were due to the superimposing of different degrees of oxidation upon the effects of variable pH. The use of strong hydrochloric instead of acetic acid favors the development of (3) instead of (2) with resultant greater stability. Likewise, the concentration of o-tolidine present is important since low concentration favors the formation of the completely oxidized form or holoquinone.

The reaction of nitrite with o-tolidine, while not explained previously, may be of different nature than the above. The color produced by the action of nitrite on o-tolidine is of different hue and slower in development than that produced with chlorine. If standard o-tolidine reagent be added to an acid solution of sodium nitrite

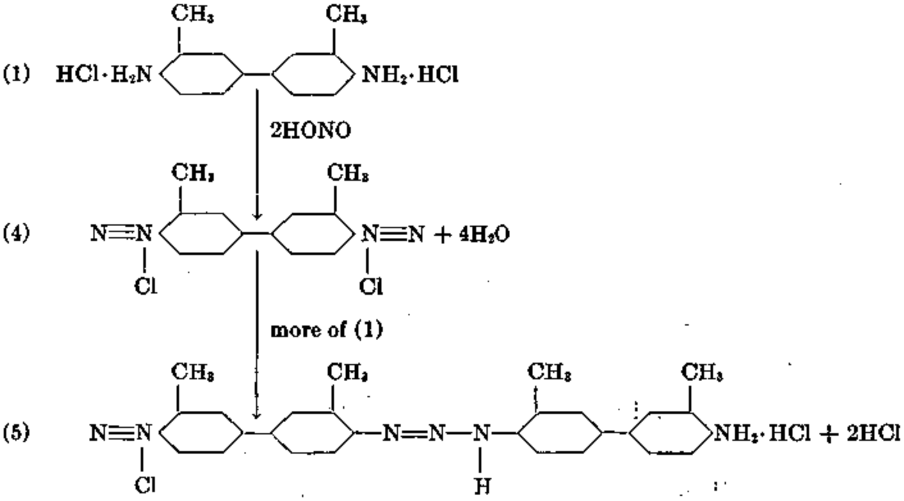


o-tolidine (colorless)
(1)

meriquinone of *o*-tolidine (blue)
(2)

holoquinone of o-tolidine (yellow)
(3)

and standard alpha-naphthylamine solution added to the mixture, a red color develops slowly which acquires great intensity in 30 to 60 minutes. This color reaction indicates diazotization of o-tolidine with nitrous acid, followed by coupling with alpha-naphthylamine. In the standard o-tolidine test for chlorine there is no alpha-naphthylamine present, of course, but the tendency of diazonium salts to couple with aromatic amines may well bring about a reaction of the following type:



In the experiments discussed previously the addition of strong HCl to the tube containing o-tolidine and nitrite was shown to diminish the color produced by reaction of those two compounds. When diazonium salts are coupled with primary aromatic amines in neutral or weakly acid solution, diazoamino compounds such as (5) are formed. But if excess HCl and nitrous acid be added to compound (5) then (4) is again produced (21). These reactions suggest an explanation for the inhibiting effect of strong HCl upon o-tolidine-nitrite color, i.e., presence of strong acid inhibits the formation of (5), the colored diazoamino compound, by repressing coupling of o-tolidine diazonium chloride with o-tolidine. In other words, in the presence of nitrite and o-tolidine the use of strong HCl favors the production of (4), the diazonium salt, which should have very little color.

SUMMARY

1. A study has been made of the possibility of elimination of interference in the color test for free chlorine, by applying the principle of oxidation-reduction potentials to various oxidant and indicator systems. Fifty compounds were investigated and a study was made of the relation of structure and position of groups in substituted benzidine derivatives to the action of the compound as an indicator in the

test for free chlorine. The most satisfactory chlorine indicators of the compounds studied were p-aminodimethylaniline, 2,4-diaminoanisole, l-amino-8-naphthol-3, 6-disulfonic acid, 2-amino-8-naphthol-6-sulfonic acid, benzidine, 3-benzidinemonosulfonic acid, 3,3'-dichlorobenzidine, 3,3'-benzidinedisulfonic acid, 3,3'-diethylbenzidine, o-tolidine, and 3,3',4,4'-tetraminodiphenylmethane. Of these compounds o-tolidine was the most satisfactory, but was not ideal.

The above work has served to emphasize the large number of variables involved in the test for free chlorine. The difficulty with selection of a better indicator than o-tolidine for determination of free chlorine was that the oxidation potential of manganese was high enough to cause interference in acid solution. Ferric iron and nitrite also interfered to some extent. In alkaline solution the compounds investigated either did not produce color with chlorine or, as in the case of some benzene derivatives, they were so easily oxidized that they were affected by dissolved oxygen.

2. The relations existing between chlorine, chloramine and nitrite in solution have been investigated. It was shown that chlorine and nitrite cannot exist long together in distilled water, either with or without addition of acid. In contrast, it was shown that chloramine and nitrite can exist simultaneously in neutral, but not in acid solution. The presence of nitrite in the standard o-tolidine test for chloramine gives high or. low results depending upon the concentration of nitrite. Greater than 0.75 p.p.m. nitrite-nitrogen was found to reduce chloramine when the acid o-tolidine was added and allowed to stand for 30 minutes. A modification of the standard o-tolidine reagent which involved increasing the HCl concentration was found to diminish nitrite interference in the test for chloramine. With the increased acid concentration' low. readings were obtained for chloramine due to reduction of chloramine by nitrite. The modified o-tolidine test was found to be more satisfactory than the use of a correction factor for nitrite.

3. The various color reactions of o-tolidine have been discussed and experimental evidence obtained for the formation of a diazonium salt from o-tolidine and nitrite. It is indicated that the diazonium salt couples with more o-tolidine to give a yellow diazoamino compound. The presence of strong HCl is shown to diminish intensity of the o-tolidine-nitrite color by favoring the production of o-tolidine diazonium chloride instead of the more highly colored diazoamino compound.

CONCLUSIONS

Previous investigations (4, 23, 24) and the results in the present paper indicate that a more strongly acid solution than that specified by Standard Methods of Water Analysis (18) is advisable for the determination of free chlorine. For the modified reagent 0.5 gram of o-tolidine and 150 cc. of concentrated HCl are made up to 1000 cc. with distilled water by a similar procedure to that described in Standard Methods of Water Analysis. Addition of 2.0 cc. of the modified reagent to 100 cc. of sample has the following apparent advantages: (1) maximum color with chloramine develops in 15 minutes; (2) color due to nitrite is avoided and (3) interference due to iron is minimized: Whether the acid concentration in the test should be made three times that in the present Standard Methods test, as specified above, or four times, as specified by Scott (25), depends upon the alkalinity of the sample.

The above reagent does not avoid interference due to manganese.

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