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Comparative Measurements of Combined Residual Chlorine around the Break Point

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Recent development of analytical method for the combined residual chlorine enables us to identify individual content of mono-, di-, and tri-chloramine together with that of free available residual chlorine in ppm order. Applying both amperometric titration method and Palin method, comparative measurements of these chloramines gave us some insight into the mechanisms of the break point where residual chlorine decreases remarkably despite of the increasing addition of chlorine to the treating water in which ammoniacal nitrogen or albuminoid nitrogen is contained in a few ppm. Basic study of the break point became necessary to carry out faultless operation of a full automatic controlled chlorination plant by the break point chlorination process by making residual chlorine recorders and Venturi-tubes as the transmitters of control signals. The system maintains constant amount of free residual chlorine at the effluent irrespective of the amount of ammoniacal nitrogen and the amount of water to be treated by the plant should change at random. Suggestions are given to the mechanisms of the break point and the reaction mechanisms are discussed for the appearance and disappearance of chloramines from the measured results.

Few reports have been found, which are dealing with the break point when ammoniacal nitrogen or albuminoid nitrogen containing water is chlorinated.[1-4] Studies carried out in the past are mostly concerned with the measurements of total residual chlorine, however, and few attempts have been done to determine the content of individual chloramines.[5-11]

Recent development of analytical chemistry made in quantitative analysis of these chloramines together with the measurement of free available residual chlorine in ppm order, for instance, amperometric titration method and Palin method[4] opened us a substantial way to get insight into the mechanisms for the formation and decomposition of these chloramines around the break point.

Generally speaking, amperometric titration method is suitable for the determination of mono-, di-chloramine, and free available residual chlorine in absence of tri-chloramine by an accuracy of plus minus 0.01 ppm, while Palin method is suitable for all kinds of chloramines and free chlorine, but the accuracy of the measurements is lower than the former. The author presents in this paper his measured results of individual amount of chloramines and free chlorine by using these two methods for the same samples to get relative accuracy of the results. Appearance and disappearance of chloramines before and after the break point is ascertained and on the basis of the measured results, the reaction mechanisms are discussed to make some approach to the reasons of the break point.

The experiments are carried out on the samples of chlorine demand zero water, to which ammoniacal nitrogen is added as ammonium chloride to make the solutions containing between 0.1 and 1.5 ppm of ammoniacal nitrogen, and the amount of chlorine added to this solution varied in the range of 0.2 to 20 ppm. The retention time is maintained always in two hours and pH is controlled at 7.0 throughout the experiments. Evident break points are indicated in each case as they are shown in table and figures.

Experimental

Samples and Reagents. *Concentrated Chlorine Solution.* Chlorine gas was absorbed in distilled water having zero chlorine demand and prepared 1737—2837 ppm chlorine solution whose total residual chlorine

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TABLE 1

Chlorine added	Method of analysis		NH$_3$-N, ppm				
			0.1	0.5	1.0	1.5	Temp., °C
0.20	A. T.	Free	0	0	0	0	13.5
		Mono	0.20	0.20	0.18	0.16	
		Di	0.01	0	0.01	0.02	
		Total	0.21	0.20	0.19	0.18	
	Palin	Free	0	0	0	0	13.5
		Mono	0.20	0.10	0.15	0.15	
		Di	0	0.05	0	0	
		Tri	0	0	0	0	
		Total	0.20	0.15	0.15	0.15	
0.50	A. T.	Free	0	0	0	0	7.2
		Mono	0.425 “o”	0.41	0.43	0.44	
		Di	0.045	0.06	0.03	0.025	
		Total	0.47	0.47	0.46	0.465	
	Palin	Free	0	0	0	0	9.6
		Mono	0.42 “o”	0.40	0.44	0.40	
		Di	0.04	0.05	0.04	0.05	
		Tri	0.05	0	0	0	
		Total	0.51	0.45	0.48	0.45	
0.80	A. T.	Free	0.025	0.025	0.00	0.00	9.6
		Mono	0.195	0.585	0.78	0.64	
		Di	0.16 “x”	0.04	0.05	0.07	
		Total	0.38	0.65	0.83	0.71	
	Palin	Free	0.02	0	0	0	9.6
		Mono	0.17	0.66	0.60	0.68	
		Di	0.18 “x”	0.05	0.10	0.06	
		Tri	0	0	0.09	0.13	
		Total	0.37	0.71	0.79	0.87	
1.0	A. T.	Free	0.10	0	0	0.005	9.5
		Mono	0.12	0.81	0.82	0.815	
		Di	0.07	0.04	0.02	0.08	
		Total	(0.29)	0.85	0.84	0.80	
	Palin	Free	0.14	0.01	0.00	0.00	9.5
		Mono	0.09	0.81	0.81	0.83	
		Di	0.10	0.06	0.08	0.12	
		Tri	0	0.02	0.10	0.06	
		Total	(0.33)	0.89	0.99	1.01	
1.5	A. T.	Free	0.40	0	0	0	2.5
		Mono	0.0	1.43	1.22	1.18	
		Di	0.11	0.05	0.12	0.135	
		Total	0.51	1.48	1.34	1.315	
	Palin	Free	0.35	0	0	0	2.5
		Mono	0	1.22	1.15	1.36	
		Di	0	0.13	0.17	0.05	
		Tri	0.20	0.19	0.13	0.26	
		Total	0.55	1.54	1.45	1.67	
2.0	A. T.	Free	0.81	0.09	0.00	0.03	9.5
		Mono	0.13	1.74	1.37	1.43	
		Di	0.08	0.02	0.31	0.20	
		Total	1.02	1.85	1.68	1.66	
	Palin	Free	0.73	0.04	0.00	0.00	9.5
		Mono	0.12	1.60	1.30	1.39	
		Di	0.05	0.04	0.35	0.21	
		Tri	0.10	0.06	0.24	0.12	
		Total	1.00	1.74	1.89	1.72	
3.0	A. T.	Free	1.74	0.00	0.01	0.00	3.5
		Mono	0.08	2.06 “o”	2.31	2.32	
		Di	0.29	0.59	0.34	0.18	
		Total	2.11	2.65	2.66	2.50	
	Palin	Free	1.75	0.00	0.00	0.00	3.5
		Mono	0.10	2.00 “o”	2.25	2.30	
		Di	0.05	0.65	0.28	0.26	
		Tri	0.24	0.64	0.98	0.48	
		Total	2.14	3.29	3.51	3.04	

TABLE 1 (Continued)

Chlorine added	Method of analysis		NH_3-N, ppm				
			0.1	0.5	1.0	1.5	Temp., °C
4.0	A. T.	Free	2.74	0.00	0.05	0.04	7.5
		Mono	0.10	0.75	2.57	2.46	
		Di	0.28	1.13 "x"	0.34	0.52	
		Total	3.12	1.88	2.96	3.02	
	Palin	Free	1.92	0.01	0.01	0.05	7.5
		Mono	0.11	0.67	2.52	2.29	
		Di	0.10	1.25 "x"	0.37	0.57	
		Tri	0.28	0.08	0.16	0.16	
		Total	2.41	2.01	3.06	3.07	
5.0	A. T.	Free	3.95	0.43	0.01	0.08	12
		Mono	0.23	0.12	3.69 "o"	3.42	
		Di	0.20	0.07	0.64 "x"	0.50	
		Total	4.38	(0.62)	4.34	4.00	
	Palin	Free	3.76	0.32	0.00	0.10	12
		Mono	0.04	0.16	3.76 "o"	3.33	
		Di	0.08	0.04	0.75 "x"	0.70	
		Tri	0.00	0.16	0.66	0.56	
		Total	3.88	(0.68)	5.17	4.69	
8.0	A. T.	Free	7.45	3.15	0.02	0.18	12
		Mono	0.03	0.07	0.29	5.81 "o"	
		Di	0.40	0.66	0.50	1.32	
		Total	7.88	3.88	(0.81)	7.31	
	Palin	Free	7.05	3.01	0.00	0.10	12
		Mono	0.00	0.09	0.29	5.30 "o"	
		Di	0.00	0.12	0.50	1.40	
		Tri	0.40	0.78	0.00	0.30	
		Total	7.45	4.00	(0.79)	7.10	
10.0	A. T.	Free	8.02	5.10	1.11	0.08	16
		Mono	0.02	0.08	0.01	3.34	
		Di	0.06	0.30	0.24	2.16	
		Total	8.10	5.48	1.36	5.58	
	Palin	Free	8.74	4.61	1.02	0.13	16
		Mono	0.00	0.05	0.03	3.86	
		Di	0.02	0.11	0.10	2.30	
		Tri	0.30	0.90	0.30	0.82	
		Total	9.06	5.67	1.45	7.11	
12.0	A. T.	Free	10.24	6.62	2.57	0.01	12
		Mono	0.26	0.03	0.03	1.30	
		Di	0.28	0.65	0.70	2.70 "x"	
		Total	10.78	7.30	3.30	4.01	
	Palin	Free	9.13	5.91	2.07	0.00	12
		Mono	0.00	0.00	0.01	1.21	
		Di	0.00	0.30	0.20	3.03 "x"	
		Tri	0.60	2.00	1.22	0.10	
		Total	9.73	8.21	3.50	4.34	
15.0	A. T.	Free	13.20	10.42	5.43	2.18	11
		Mono	0.07	0.03	0.02	0.04	
		Di	0.43	0.31	0.86	0.46	
		Total	13.70	10.76	6.31	(2.68)	
	Palin	Free	13.51	9.97	4.04	2.00	11
		Mono	0.00	0.00	0.00	0.00	
		Di	0.00	0.00	0.09	0.08	
		Tri	0.78	2.46	3.92	0.64	
		Total	14.29	12.43	8.05	(2.72)	
20.0	A. T.	Free	17.80	14.09	10.78	5.58	14
		Mono	0.02	0.03	0.13	0.30	
		Di	0.50	1.03	1.40	1.15	
		Total	18.32	15.15	12.31	7.03	
	Palin	Free	18.33	13.97	10.88	4.55	14
		Mono	0.00	0.00	0.00	0.02	
		Di	0.00	0.00	0.00	0.26	
		Tri	1.24	2.56	2.94	2.68	
		Total	19.57	16.53	13.82	7.51	

was determined by the titration method with 0.1 N thiosulfate solution and excess addition of potassium iodide. Each concentration of these mother solutions were checked before mixing them to 1 *l* of distilled water to make desired concentration of residual chlorine solution ranging between 0.2 to 20 ppm by total residual chlorine. Final concentration of diluted solution was calibrated before each experiments with amperometric titration method having an accuracy of plus minus 0.01 ppm throughout the whole range.

Distilled Water. Usual method4) to get zero chlorine demand water was used. No residual chlorine nor ammonia was confirmed in the distilled water.

Buffer Solution for pH 7.0. Nitrogen content of potassium dibasic phosphate and of sodium monobasic phosphate was tested to be less than 0.01 ppm. Standard solution of pH 7.0 was prepared in accordance with normal process4) as it is written in chemical text books. In order to keep the sample solution containing both ammoniacal nitrogen and residual chlorine at pH 7.0 even at their highest content, namely, the added amounts of chlorine and ammoniacal nitrogen equivalent to 20 ppm and 1.5 ppm respectively, the amount of buffer solution was estimated to be 3.84 m*l* per liter of this solution. For the safety's sake, however, every experiments were carried out by the addition of 5.0 m*l* buffer solution to each 1 *l* of sample solution irrespective of the amount of chlorine and ammoniacal nitrogen contained. pH value of thus prepared solutions underwent another check from time to time before entering the experiments by colorimetric method.

Sample Water Containing Ammoniacal Nitrogen. 0.3819 gram of chemically pure ammonium chloride was dissolved in one liter of distilled water. This solution corresponds to 100 ppm of ammoniacal nitrogen.

Process of Experiments. To each one liter of distilled water containing 0.1, 0.5, 1.0, and 1.5 ppm of ammoniacal nitrogen, 5 m*l* of buffer solution were added to make its pH 7.0 and checked by the colorimetric method. Calculated amount of mother chlorine solution was added and mixed thoroughfully in a dark brown glass bottles to get 0.2, 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 8.0, 10.0, 12.0, 15.0, and 20.0 ppm of chlorine and was kept in a dark and cool room until 2 hr retention time would come. Taking out this sample at the time, immediate analysis of mono-, di-chloramine and free available residual chlorine-(HOCl) by amperometric titration method, and at the same time, another analysis of mono-, di-, and tri-chloramine, and free chlorine by Palin method were carried out for the same sample at room temperature.

In Palin method, pH of the sample was once adjusted to 3.6 by the addition of sulfuric acid for the measurement of dichloramine, and then, pH was changed to 6.8 by the addition of sodium bicarbonate solution. In all other cases, pH of the sample solution was strictly kept at 7.0. Measured and calculated results of the experiments were given in Table 1 and Figs. 1 to 4 Numbers given in bracket show the total residual chlorine at the break point and markings "o" and "x" indicate the maximum points of monochloramine and dichloramine respectively in the table.

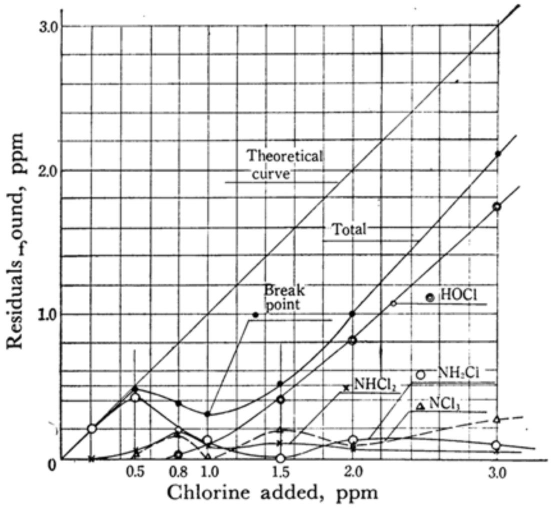


Fig. 1
Retention time: 2 hr
pH: 7.0
Ammoniacal nitrogen: 0.1 ppm

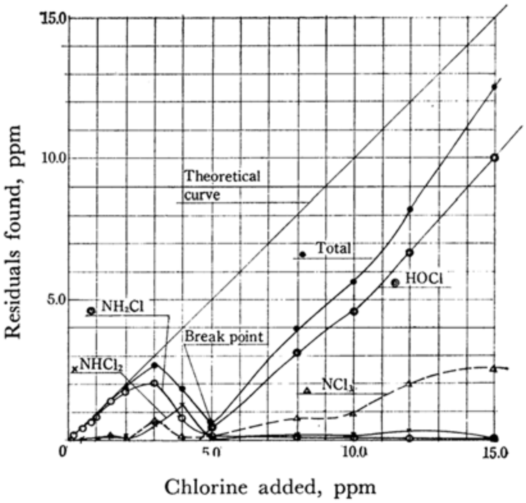


Fig. 2
Retention time: 2 hr
pH: 7.0
Ammoniacal nitrogen: 0.5 ppm

Results and Discussions

Increasing addition of chlorine to the sample, monochloramine increases almost proportionally to some extent as it is indicated in Fig. 1: for instance, as far as the amount of chlorine added becomes 0.5 ppm. It is an evidence that the formation of monochloramine predominates in the initial stage of reaction due to higher velocity than the reactions to make higher chloramines. Then, it arrives to a maximum point where the ratio of ammoniacal nitrogen *versus* chlorine becomes 1 : 5 in ppm or 1 : 1 in mole ratio. Such maximum points are indicated in Fig. 1 at 0.5 ppm, Fig. 2 at 3.0 ppm, Fig. 3 at 5.0 ppm, and Fig. 4 at 8.0 ppm by the amount of chlorine added to the samples. The fact that the curves of total residual chlorine calculated from the sum of measured residuals

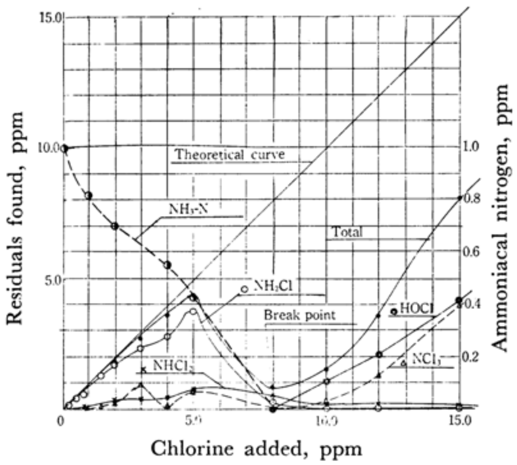


Fig. 3

Retention time: 2 hr
pH: 7.0
Ammoniacal nitrogen: 1.0 ppm

of mono-, di-chloramine, and free chlorine is gradually deviating from the theoretical line, will show some slow decomposition of chloramines is already in progress, for instance in Fig. 4, the curve of monochloramine is lower than the curve of total residual chlorine as far as monochloramine will become maximum by the addition of 8.0 ppm of chlorine. Rapid decreasing curve of monochlorramine after passing through its peak can be explained chiefly by the formation of dichloramine by further oxidation of monochloramine by increasing concentration of free chlorine. Thus the formation of dichloramine becomes remarkable at this stage and it arrives its maximum point following that of monochloramine but before the break point. Maximum point of dichloramine is tabulated as follows:

NH_3-N in ppm	Amount of chlorine added at the max. point of $NHCl_2$ ppm	Dichloramine ($NHCl_2$) found by	
		Amp. titrator ppm	Palin method ppm
0.1	0.8	1.6	1.9
0.5	4.0	1.13	1.25
1.0	5.0	0.65	0.75
1.5	12.0	2.70	3.03

Free chlorine, however, existed in negligible amount at this stage.

By these observations, following reaction may represent the mechanism of the reaction.

$$NH_3 + HOCl = NH_2Cl + H_2O \qquad (1)$$

Decomposition and further oxydation of monochloramine can be explained by,

$$2\ NH_3 + 3\ Cl_2 = N_2 + 6\ HCl \qquad (2)$$

$$2\ NH_2Cl + Cl_2 = N_2 + 4\ HCl \qquad (3)$$

$$2\ NH_2Cl + 2\ HOCl = N_2O + 4\ HCl + H_2O \qquad (4)$$

Since the amount of ammoniacal nitrogen remaining in the solution at the peak of monochloramine curve is already very small, the reaction (2) may be less probable than others. Rapid disappearance of monochloramine after its maximum point may suggest that the reaction,

$$NH_2Cl + HOCl = NHCl_2 + H_2O \qquad (5)$$

is predominant. Another conceivable reaction especially before monochloramine becomes maximum may be,

$$NH_3 + 2\ HOCl = NHCl_2 + 2\ H_2O, \qquad (6)$$

but it may be a side reaction taking place simultaneously with reaction (1). The fact that the ratio of co-existing molecules of mono- to those of dichloramine before monochloramine becomes its maximum is approximately in the range of 5 : 1 to 10 : 1, and that the calculated percentages of chlorine reacted in the reactions (1) and (6) show 80 percent and 20 percent respectively, may suggest that the main reaction in this period would be reaction (1) accompanying 20 percent of reaction (6). The reason why the reaction (5) is not remarkable in this stage is only due to the difference between the reaction velocity of reaction (1) and that of (6).

Dichloramine. Dichloramine becomes maximum in content when the ratio of ammoniacal nitrogen *versus* chlorine becomes 1 : 8 in ppm or 1 : 1.58 in mole ratio. For instance, Fig. 4 shows that the maximum of dichloramine 3.0 ppm when 12.0 ppm of chlorine is added. However, the remaining amount of ammonia at this point is so small that the predominant reaction in this stage should be reaction (5) instead of reaction (6). The chlorine balance for reactions (5) and (6) shows approximately 70 percent and less than 30 percent respectively.

Break Point. The break point appears exclusively after the peak of dichloramine curve where the amount of chlorine residuals, such as, mono-, di-chloramine, and free chlorine become very small. From this reason so-called "Break Point" is given to the point of smallest total residuals at the stage of higher application of chlorine in the treating water. Remarkable characteristics at this point are that the ratio of ammoniacal nitrogen *versus* chlorine again shows a very simple ratio of 1 : 10 in ppm or 1 : 2 in mole ratio as often mentioned before. Major part of existing residuals at this point is consisted of free chlorine which becomes evident just before the break point and it increases very rapidly to compose most of the residuals after the break point. Monochloramine and dichloramine can remain in very low concentration at this point and also after this point. The

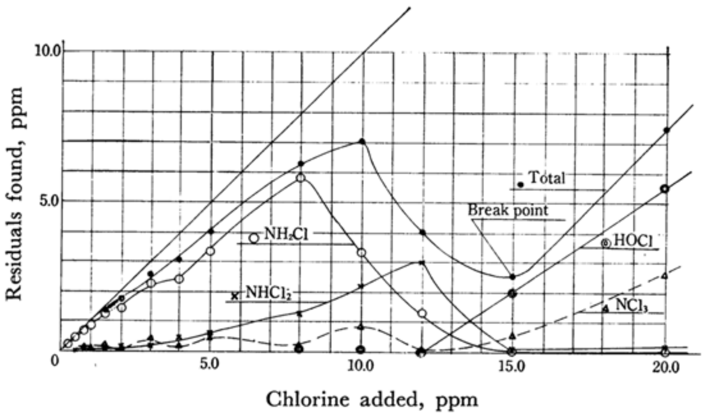


Fig. 5
Retention time: 2 hr
pH: 7.0
Ammoniacal nitrogen: 1.5 ppm

analytical results obtained by amperometric titration method around this point shows higher values of mono-, and di-chloramine than those measured by Palin method, because co-existing trichloramine at this stage would be identified as if it were mono-, di-chloramine, or free chlorine.4) This matter will cause some trouble to keep the free residual chlorine within the range of admissible value in the practical chlorination of raw water in many water treating plants. In most cases, the amount of ammoniacal nitrogen or albuminoid nitrogen changes with a definit time schedule in a day, or sometimes at random, so the control of residual chlorine in the effluent water should be made with a signal given by the amperometric recorder with adequate consideration for the above-mentioned matters. The recorded change of ammoniacal nitrogen in Inagawa Water Purification Plant near Osaka shows almost 0.1 to 1.5 ppm. In this plant, a full automatic controlled chlorination system is operated by the signals both from the amperometric recorders and from the differentials of Venturi-tube composed of so-called cascade system for the controlling of chlorinators to treat both raw water and filtered water. If the control point of amperometric recorder is set at too high residual of free chlorine, trichloramine will play a trick by indicating too high free chlorine, though the real concontent of free chlorine (HOCl) is far less, and this will result too low application of chlorine by the chlorinator and thus disordered recording and unstable chlorination will be made at the effluent. Much easier control of chlorination can be made by taking low concentration of free chlorine just before the break point for the control signal from the amperometric residual chlorine recorder which has almost similar characteristic in measuring residuals with the amperometric titrator. This choice is better for the wide range of ammoniacal nitrogen content and for economical aspect by using less chlorine. So-called super-chlorination is made successfully within a range of deviation for free residual chlorine at the effluent by plus minus 0.05 ppm when the bulk residuals (HOCL) is 1.13 ppm. The results of experiments discussed in this paper produce a part of basic knowledge to help this control of chlorination. The experimental data shows that both amperometric titration method and Palin method will give comparatively similar results before the break point, as it is shown in the table, however, the existence of trichloramine even before the break point may cause considerable difference between the results by these two methods. For instance, the difference of total residual chlorine is remarkable in case of ammoniacal nitrogen of 1.0 ppm and of added chlorine of 5.0 ppm. In this case, the amperometric titrator indicates total residuals of 4.34 ppm, while Palin method indicates 5.17 ppm. This difference is chiefly caused by trichloramine of 0.6 ppm. Such difference increases with the increase of added chlorine as it is shown in Table 1. Amperometric titration method is only available when trichloramine is absent or in smaller amount. Palin method is reliable for the differential determination of individual chloramines and free chlorine, but this method requires some experience in order to get reproducible results.

Total residual chlorine at the break point changes in accordance with the increasing content of ammoniacal nitrogen as shown in the following table,

NH_3-N in ppm	Amount of of Cl_2 added at break ppm	Total residuals found at break ppm	HOCl found at break ppm
0.1	1.0	0.31±0.02	0.13±0.01
0.5	5.0	0.65±0.03	0.37±0.05
1.0	9.5	0.81±0.02	0.60±0.03
1.5	15.0	2.70±0.02	2.09±0.09

The amount of mono- and di-chloramine at and after the break point are negligible by the measurements of Palin method, and substantial residuals are composed of free chlorine and smaller amonnt of trichloramine (Figs. 1—4). Total residual chlorine after the break point increases rapidly by increasing addition of chlorine and the curve is almost parallel with the gradient of the theoretical curve. The major fraction of residuals in this area is composed of free chlorine. The fact that the mole ratio of ammoniacal nitrogen versus added chlorine at the break point is 1 : 2 suggests following reaction,

$$NH_3 + 2\ HOCl = NHCl_2 + 2\ H_2O \qquad (6)$$

seemingly probable.

However, this reaction takes place in smaller extent than the reaction (5) as it was discussed in foregoing paragraph.

Trichloramine. Trichloramine can co-exist with mono-, di-chloramine and with free chlorine in higher concentration even before the break point, but the amount of trichloramine in this stage is not large enough to give substantial differences between the analytical results made by both methods. Trichloramine appears remarkably after the break point and it arrives its maximum content when ammoniacal nitrogen *versus* added chlorine is 1 : 15 in ppm or 1 : 3 in mole ratio (Figs. 1, 2, 3).

This will make us suspect whether the reaction might be,

$$NH_3 + 3\ HOCl = NCl_3 + 3\ H_2O \qquad (7)$$

however, the author is in opinion that this is not the case, because ammoniacal nitrogen will never remain in appreciable amount around the break point: on the contrary, ammonia is tending to zero at the break point (Fig. 3).

Several reports[1,5)] for the re-appearance of ammonia after the break point are doubtful because they might have measured trichloramine or nitrogen instead of ammonia itself due to the difference of analytical methods. The author would like to suggest that the formation of trichloramine is mostly made by the oxidation of cichloramine, and that dichloramine remains in meta-stable state at'and after the break point due to its more stable configuration of molecule which is conceivable from the Octet theory.

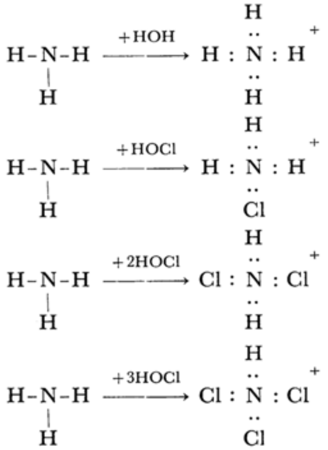
So, the reaction

$$NHCl_2 + HOCl = NCl_3 + H_2O \qquad (8)$$

may be predominant, and the reaction

$$NH_2Cl + 2\ HOCl = NCl_3 + 2\ H_2O \qquad (9)$$

or the reaction (7), or the reaction coming from the interaction of mono-, di-chloramine in presence of free chlorine seems to be less probable, because calculated balance of chlorine around the break point never satisfy these reactions. The Octet theory seems to give us some suggestions to the stability of dichloramine molecule analogously to the formation of stable ammonium ion by dissolving ammonia into water.



$$\mathrm{H{-}\underset{\mid\atop H}{N}{-}H} \xrightarrow{+\mathrm{HOH}} \mathrm{H : \overset{H}{\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}} : H}^{+}$$

$$\mathrm{H{-}\underset{\mid\atop H}{N}{-}H} \xrightarrow{+\mathrm{HOCl}} \mathrm{H : \overset{H}{\underset{Cl}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}} : H}^{+}$$

$$\mathrm{H{-}\underset{\mid\atop H}{N}{-}H} \xrightarrow{+2\mathrm{HOCl}} \mathrm{Cl : \overset{H}{\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}} : Cl}^{+}$$

$$\mathrm{H{-}\underset{\mid\atop H}{N}{-}H} \xrightarrow{+3\mathrm{HOCl}} \mathrm{Cl : \overset{H}{\underset{Cl}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}} : Cl}^{+}$$

In case of monochloramine and trichloramine, they have a single axis of symmetry, while dichloramine has binary axis of symmetry which makes us suspect its larger stability in presence of oxidizing agent HOCl at the break point, otherwise, no plausible explanation can be made for the formation of trichloramine at the stage where no ammonia is identified.

But a fact remains still unsolved why trichloramine alone can exist in stable state at higher chlorine concentration after the break point and why this molecule is less germicidal than other chloramines as it is often reported in biological text books.

Ammoniacal Nitrogen. Ammoniacal nitrogen decreases rapidly by the formation of monochloramine at the first stage of reaction (1). Calculated amount of reacted ammonia for this formation and for the formation of dichloramine in balance, and thus derived residual ammonia may decrease almost straight curve down to the break point. The co-existed residual ammonia at the maximum point of monochloramine is approximately 45 percent of initial concentration. This result is different from that of previous report by Griffins.[5)] Re-appearance of ammonia after the break point is very doubtful because ammonia residual at the break point is practically zero.

Total Residual Chlorine. Total residual chlorine calculated from the sum of mono-, di-, trichloramine, and free available chlorine is slightly less than the amount given by the theoretical curve as far as monochloramine becomes maximum in content. This deviation from the theoretical curve, however, abruptly becomes remarkable after this peak and it becomes so much as to make so-called the break point where mole ratio of ammoniacal nitrogen versus added chlorine is 1 : 2. This deviation at the break point is attributable to the decomposition of chloramines and meta-stable state of dichloramine. Following equations have been suggested by many investigators for the decomposition of ammoniacal nitrogen and chloramines:

$$2\ NH_3 + 3\ Cl_2 = N_2 + 6\ HCl \qquad (2)$$

$$2\ NH_2Cl + Cl_2 = N_2 + 4\ HCl \qquad (3)$$

$$2\ NH_2Cl + 2\ HOCl = N_2O + 4\ HCl + H_2O \qquad (4)$$

$$2\ NHCl_2 + H_2O = N_2O + 4\ HCl \qquad (10)$$

$$2\ NH_2Cl + HOCl = N_2 + 3\ HCl + H_2O \qquad (11)$$

$$NH_2Cl + NHCl_2 = N_2 + 3\ HCl \qquad (12)$$

$$2\ NCl_3 + 3\ H_2O = N_2O_3 + 6\ HCl \qquad (13)$$

$$NH_2Cl + NHCl_2 + HOCl = N_2O + 4\ HCl \qquad (14)$$

The author is now making efforts to identify the main reactions in each stage of the decompositions written in this paper. The results will be reported in the near future.

Conclusions

1) Monochloramine becomes maximum amount when the ratio of NH_3–N : Cl_2 arrives 1 : 1 in mole ratio, then, it undergoes further oxidation by HOCl to form dichloramine as the main reaction and monochloramine decreases rapidly to negligible amount at and after the break point.

2) Dichloramine becomes its maximum content when the ratio of NH_3–N : Cl_2 is 1 : 1.58 in mole ratio 80 percent of its formation is attributable to the oxidation of monochloramine by Eq. (5) and 20 percent to the direct oxidation of ammonia by Eq. (6). Dichloramine decreases rapidly towards the break point. It can stay in a meta-stable state at this point due to its stable configuration of molecule and it will further undergo another oxidation at higher concentration of free chlorine to make trichloramine.

3) Mono- and di-chloramine is not identified in appreciable amount at the break point by both amperometric titration and Palin methods. Free available residual chlorine exists only in smaller amount at this point, too, thus the total residual chlorine is very low to make so-called break point.

4) Free available residual chlorine appears just before the break point and increases almost parallelly with the theoretical curve irrespective of the presence of the break point, where NH_3–N : Cl_2 is 1 : 2 in mol. ratio. Total residual chlorine at the break point is chiefly consisted of free chlorine at low concentration and the amount is varying in accordance with the amount of ammoniacal nitrogen contained in the original sample.

5) Formation of trichloramine after the break point can be explained only by the oxydation of dichloramine and direct oxidation of ammonia or monochloramine to make trichloramine is less conceivable.

6) Trichloramine arrives its maximum in content when NH_3–N : Cl_2 is nearly 1 : 3 in mole ratio and the slow decomposition is taking place at very high concentration of chlorine.

7) Mechanisms of decomposition for these chloramines are not yet clear and some efforts are now being made to explain the reactions by further chemical analysis. Decomposition of monochloramine after its maximum in content is explained partly by the formation of dichloramine, but still remains some doubts for the decomposition into nitrogen and nitrous oxide. Decomposition of dichloramine into nitrogen or else leaves many questions to be checked in future, because its complete decomposition will make us difficult to find out the reasons for the formation of trichloramine after the break point.

Meta-stable state of dichloramine molecule by the Octet theory is suggested.

8) Ammoniacal nitrogen decreases adversely proportional to the increasing addition of chlorine, and it disappears completely at the break point. No ammonia is detectable after the break point, too.

9) Results of these studies were practically applied to a large water purification plant in Inagawa near Osaka and the break point chlorination has been made successfully within a deviation of plus minus 0.05 ppm HOCl in the effluent when the amounts of ammoniacal nitrogen and albuminoid nitrogen in water to be treated varied in the range of 0.1 to 1.5 ppm by fairly regular time schedule every day.