

Trichloramine Formation and Decay during Breakpoint Process

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Abstract Trichloramine formation and decay in water samples containing chlorine:ammonia mass ratios 10:1 and 12:1 (mg/L:mg/L) at pH=6.0 and 7.0, in the absence and the presence of ketonic compounds, was searched in this paper. From ultraviolet spectra analysis it was determined that trichloramine formation took place in the first seconds after reagents mixing and concentrations from samples containing ketonic compounds were smaller than those from blank samples. NCl_3 decay may be described by the first order kinetics law, with constant rates between $6.3\text{-}8.1 \times 10^{-3} \text{ min}^{-1}$ for blank samples, $6.9\text{-}8.9 \times 10^{-3} \text{ min}^{-1}$ in case of samples containing methyl ethyl ketone and $7.8\text{-}9.5 \times 10^{-3} \text{ min}^{-1}$ for those with methyl phenyl ketone. The results revealed that even in conditions of breakpoint process, free chlorine was consumed in some extent in reactions with organic compounds.

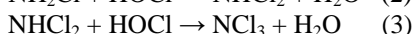
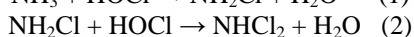
Keywords: trichloramine, breakpoint, ketonic compounds, rate constant

1. Introduction

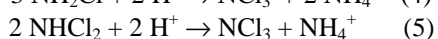
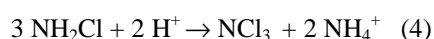
The harmful action of the disinfection by-products (DBP) formed during water treatment on human health involved numerous researches, for improving of chlorination process. In some cases after a utility operation review, improvements of water treatment may be developed: a monitoring program for plant operation, exchange of the points for chlorine introduction in water, optimization of the processes like coagulation and softening for advanced removal of naturally organic matter (NOM) from waters [1-6].

In order to realize both disinfection and oxidation during water treatment for drinking purposes, besides chlorine other reagents are used: chloramines, chlorine dioxide, ozone. Chloramination is used especially for the treatment of surface waters in North America and few european countries like England, Spain, Finland. It is also used for the treatment of ground waters that contains ammonia.

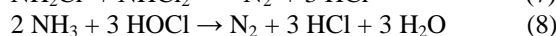
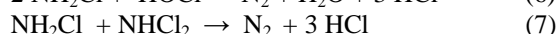
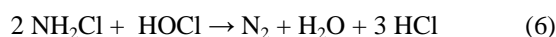
Chloramines formation depends on chlorine:ammonia mass ratio, pH, contact time, mixing conditions, presence or absence of some reactive organic species [7-10]. By mixing of chlorine with ammonia solutions, the formation of mono-, di- and trichloramine take place:



Trichloramine is also formed by slow disproportionation of mono- and dichloramine:



For chlorine:ammonia mass ratios higher than 7.6:1 (mg/L:mg/L) breakpoint process takes place, that consists of chloramines and ammonia oxidation:



In case of ratios $\geq 10:1$ there is a decrease of combined chlorine accompanied by the increase of trichloramine and free chlorine [11,12]. Depending on the reaction conditions, breakpoint process is finished in 4-6 hours after reagents mixing. Then, in treated water there are small concentrations of di-, trichloramine and free chlorine.

The influence of methyl ethyl ketone and methyl phenyl ketone on trichloramine formation and decay in water samples for chlorine:ammonia mass ratios 10: and 12:1 (mg/L:mg/L), was studied in this paper.

2. Experimental

In order to study trichloramine formation and decay, water samples containing chlorine and ammonia in mass ratios (R) 10:1 and 12:1 (mg/L:mg/L) were prepared at pH = 6.0 and 7.0, using buffer consisting of monopotassium phosphate and sodium hydroxide, 0.1N each other. Trichloramine presence in water samples was determined using its absorption maxima from 220 nm and for quantitative analysis, N,N-diethyl-p-phenylenediamine with ferrous ammonia sulphate (DPD-FAS) method was used [13].

In another series of experiments, formation and decay of NCl_3 was investigated in presence of two concentrations of methyl ethyl ketone (mek) and methyl phenyl ketone (mpk) (5.0 mg/L, 20 mg/L), for the same chlorine:ammonia mass ratios and pHs. UV absorption spectra of prepared

solutions were recorded versus time using an UV-Vis instrument Jasco-530, 1999.

In order to establish ketones effect on trichloramine decay, kinetics of the process was analysed. The results obtained showed the decay process follows a first order kinetics, both for blank samples containing NCl_3 only and for those with ketones; the rate constants were computed with the relation:

$$k_1 = \frac{1}{t} \ln \frac{C_0}{C} \quad (9)$$

where: k_1 = rate constant, min^{-1} ; t = reaction time; C_0 = initial concentration, mg/L ; C = concentration at time "t", mg/L . Also, half times ($t_{1/2}$) corresponding to the first order reactions were computed using the relation:

$$t_{1/2} = \frac{1}{k_1} \ln 2 \quad (10)$$

3. Results and Discussion

Formation of trichloramine was recorded in the first minutes after reagents mixing. UV absorption measured at 220 nm against time for the sample containing chlorine:ammonia mass ratio 10:1 ($\text{mg/L}:\text{mg/L}$) at $\text{pH} = 6.0$ was more intense than of the sample containing in addition methyl phenyl ketone (figure 1). Similar evolution of uv spectra was determined for the samples containing mass ratio 12:1 ($\text{mg/L}:\text{mg/L}$) (figure 2).

Maximum concentrations of trichloramine were formed in the absence of ketones (blank samples), 1.9 mg/L at $\text{pH} = 6.0$ and 0.84 mg/L for $\text{pH} = 7$ at one hour after reagents mixing. For the mass ratio 10:1 ($\text{mg/L}:\text{mg/L}$) at $\text{pH} = 6.0$, trichloramine amount decreased with 12.1 % in the presence of 5.0 mg/L methyl ethyl ketone and with 28.5 % in that of 5.0 mg/L methyl phenyl ketone, figure 3a. At higher ketone concentrations, 20 mg/L , the formation of NCl_3 decreased with 23.1 % and 42.8 %, respectively, figure 3b.

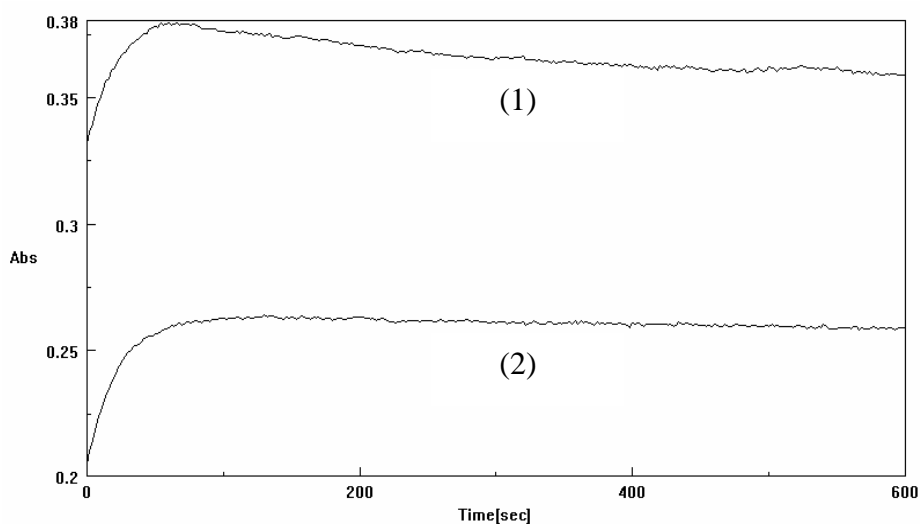


Figure 1. Absorbance measured at 220 nm vs. time, for samples containing $R = 10:1$ ($\text{mg/L}:\text{mg/L}$), $\text{pH} = 6$; NCl_3 (1), $\text{NCl}_3 + 5.0$ mg/L methyl phenyl ketone (2)

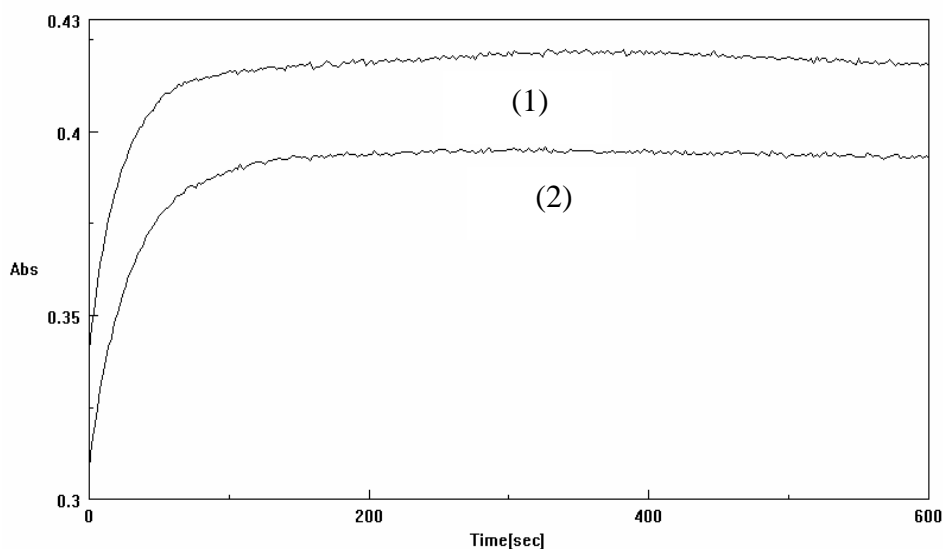


Figure 2. Absorbance measured at 220 nm vs. time, for samples containing $R = 12:1$ ($\text{mg/L}:\text{mg/L}$), $\text{pH} = 6$; NCl_3 (1), $\text{NCl}_3 + 5.0$ mg/L methyl phenyl ketone (2)

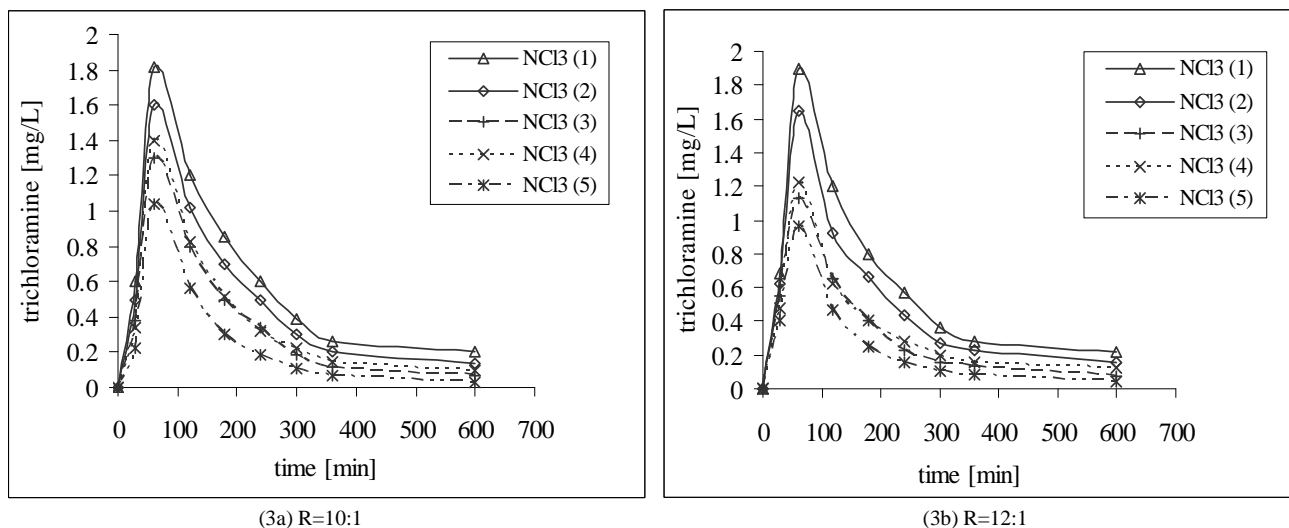


Figure 3. Trichloramine evolution vs. time at pH = 6.0, R = 10:1 (a), 12:1 (b);
 NCl₃ (1), NCl₃ + 5.0 mg/L mek (2), NCl₃ + 5.0 mg/L mpk (3),
 NCl₃ + 20.0 mg/L mek (4), NCl₃ + 20.0 mg/L mpk (5)

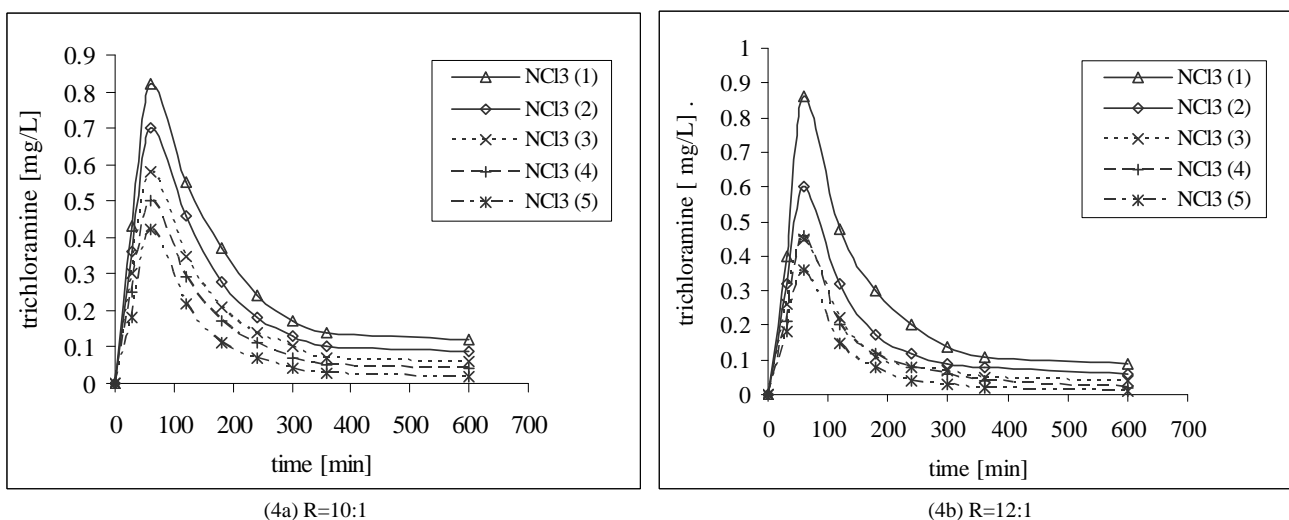
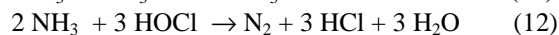
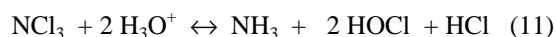


Figure 4. Trichloramine evolution vs. time at pH = 7.0, R = 10:1 (a), 12:1 (b);
 NCl₃ (1), NCl₃ + 5.0 mg/L mek (2), NCl₃ + 5.0 mg/L mpk (3),
 NCl₃ + 20.0 mg/L mek (4), NCl₃ + 20.0 mg/L mpk (5)

The results obtained at pH = 7 were closed to those recorded at pH = 6.0: 14.6 - 29.2 % in case of 5.0 mg/L ketones and 39.0 - 48.7 % for 20 mg/L, figure 4a. Similar results were determined for R = 12:1 (mg/L:mg/L), figure 4b. From these data it was obvious that the decreasing of trichloramine formation in the presence of ketones was due to the reactions of chlorine with these organic compounds. Residual chlorine concentrations determined in case of blank samples ranged between 1.4 - 3.3 mg/L, after 10 hours. When methyl ethyl ketone was present in samples, residual chlorine was 0.3 - 0.8 mg/L and in case of methyl phenyl ketone, 0.15 - 0.40 mg/L after the same time. Residual concentrations of NCl₃ ranged between 0.02 - 0.22 mg/L.

For trichloramine decomposition the hydrolysis reaction was proposed, with the formation of ammonia, hypochlorous and hydrochloric acid; in the next step, ammonia oxidation takes place:



The rate constants for trichloramine decay versus time are presented in table 1. At pH = 6.0 and R = 10:1 (mg/L:mg/L), the rate constants determined for samples containing 5.0 mg/L methyl ethyl ketone, $6.9 \times 10^{-3} \text{ min}^{-1}$ and 5.0 mg/L methyl phenyl ketone, $7.8 \times 10^{-3} \text{ min}^{-1}$, were somewhat higher comparatively with that determined in their absence, $6.3 \times 10^{-3} \text{ min}^{-1}$. Similar results were obtained for the samples containing 20 mg/L ketones. The small increasing of the rate constants for NCl₃ decomposition in the presence of ketones is due to the consumption increasing of hypochlorous acid resulted from hydrolysis: it may react both with ketones and ammonia, in concurrent reactions. For the mass ratio Cl₂:NH₃ = 12:1 (mg/L:mg/L), similar increasing of the rate constants took place.

TABLE 1. Rate constants ($k_1 \times 10^{-3}$) and half times ($t_{1/2}$) for NCl_3 decay in blank samples and those containing mek and mpk: a - 5 mg/L ketone; b - 20 mg/L ketone; pH = 6.0 (1), pH = 7.0 (2)

reagents	$\text{Cl}_2 : \text{NH}_3 = 10:1$ [mg/L:mg/L]				$\text{Cl}_2 : \text{NH}_3 = 12:1$ [mg/L:mg/L]			
	k_1 [min^{-1}]		$t_{1/2}$ [min]		k_1 [min^{-1}]		$t_{1/2}$ [min]	
	a	b	a	b	a	b	a	b
$\text{Cl}_2 + \text{NH}_3$ (1)	6.3	6.3	110	110	6.9	6.9	100	100
$\text{Cl}_2 + \text{NH}_3 + \text{mek}$ (1)	6.9	8	100	86	7.7	8.7	90	79
$\text{Cl}_2 + \text{NH}_3 + \text{mpk}$ (1)	7.8	9.6	88	72	8.4	10.1	82	68
$\text{Cl}_2 + \text{NH}_3$ (2)	6.4	6.4	108	108	8.1	8.1	85	85
$\text{Cl}_2 + \text{NH}_3 + \text{mek}$ (2)	7.1	8.3	97	83	8.9	10.1	78	68
$\text{Cl}_2 + \text{NH}_3 + \text{mpk}$ (2)	7.8	10	88	69	9.5	11.7	73	59

The increasing of the rate constants values were more important for samples containing methyl phenyl ketone than for those containing methyl ethyl ketone, both at pH 6.0 and 7.0. Also, the half times for trichloramine decomposition were dependent on pH values.

These results are in agreement with the data presented on the consumption of chlorine by methyl phenyl ketone, 0.5:1.0 mol:mol at pH = 7.0 [14]. Also, as it was reported previously the concentration of volatile organic chlorine formed in samples containing chlorine and ammonia in mass ratios 10:1 - 12:1 (mg/L:mg/L) and 7.2 mg/L methyl ethyl ketone, ranged in 0.10 - 0.15 mg/L [15]. Thus, even for chlorine ammonia mass ratios corresponding to the breakpoint process, the reactions between chlorine and organic compounds with the formation of by-products, take place.

4. Conclusions

Formation and decomposition of trichloramine was depended on chlorine:ammonia mass ratio, pH, time and presence or absence of organic compounds. Maximum concentrations of trichloramine were formed in the absence of ketones, 1.9 mg/L (pH = 6.0) and 0.84 mg/L (pH = 7), one hour after reagents mixing. Trichloramine concentrations formed in the presence of 5.0 - 20 mg/L ketones decreased with 12.1 - 29.2 % in case of methyl ethyl ketone, and 28.5 - 48.7 % in that of methyl phenyl ketone, for mass ratios 10:1 and 12:1 (mg/L:mg/L).

Decomposition of NCl_3 took place by hydrolysis to ammonia, hypochlorous acid and hydrochloric acid. Then, ammonia was oxidized by hypochlorous acid. The rate constants for trichloramine decomposition increased with chlorine:ammonia mass ratio and pH, and ranged between $6.3-8.1 \times 10^{-3} \text{ min}^{-1}$. The presence of ketones increased somewhat the rate constants comparatively with those determined in their absence: $6.9-8.9 \times 10^{-3} \text{ min}^{-1}$, for

samples containing methyl ethyl-ketone and $7.8-9.5 \times 10^{-3} \text{ min}^{-1}$ for methyl phenyl ketone. Both kinetics data and the analysis of residual chlorine showed that in conditions of breakpoint process, chlorine was involved in some extent in reactions with organic compounds.

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