RESEARCHES OF CHLORINE REACTIONS WITH SOME ORGANIC COMPOUNDS IN PRESENCE OF AMMONIA IN WATER SOLUTIONS

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Abstract
The formation of trichloramine in water solutions in absence and presence of methyl-ethyl-ketone and of phenyl-methyl-ketone at pH=6,7,8, and its decay versus time were searched in this paper. From ultraviolet spectra analysis it was determined, that trichloramine concentrations in samples with ketonic compounds are samaller than those of blank samples, e.g., in the presence of phenyl-methyl-ketone (20 mg/L) were smaller with 15% for chlorine:ammonia ratio 12:1 by weight, and with 17.3% for ratio 14:1, at pH=6. NCl_3 formation takes place in first minutes after reagent mixing and its decay may be described by the first order kinetic law, with values of constant rates between $0.18 \cdot 10^{-2}$ - $0.43 \cdot 10^{-2}$ min^{-1} for blank samples; $0.24 \cdot 10^{-2}$ - $0.56 \cdot 10^{-2}$ min^{-1} for samples with phenyl-methyl-ketone; and $0.14 \cdot 10^{-2}$ - $0.44 \cdot 10^{-2}$ min^{-1} for those containing methyl-ethyl-ketone. Half reaction times of NCl_3 decay, for mass ratio chlorine:ammonia 12:1 are 288 minutes in case of blank sample, 247 minutes for sample with phenyl-methyl-ketone (5.0 mg/L) and 249 minutes for sample with methyl-ethyl-ketone (5.0 mg/L), at pH=7. The obtained results may be used by utilities, for determination of useful chlorine:ammonia ratio taking into account organic content of raw water, and trichloramine measurement by ultraviolet absorption for on-line monitoring of water treatment by breakpoint chlorination.

Introduction

The harmful action of disinfection by-products (DBP) formed during water treatment onto human health involved numerous researches for improving chlorination process. In some cases, after an utility operation review, unexpesive improvements of water treatment may be developed: exchange of points for chlorine introduction in water; a monitoring progam for plant operation; optimization of processes like coagulation and softening for advanced removal of naturally organic matter (NOM) from waters (1,2,3).

In order to realize both disinfection and oxidation in water treatment for drinking purposes, besides chlorine other reagents are used: chloramines, chlorine dioxide, ozone. Chloramination is used especially in North America, and few European countries like England, Spain (4,5,6).

Recent reports on chloramination applied to water treatment reveals on possible reactions between a mixture of chlorine, ammonia and some organic compounds in surface waters. Formation and decay of trichloramine in water solutions, both in absence and in presence of methyl-ethyl-ketone and phenyl-methyl-ketone was analysed in this paper.

Materials and Methods

In order to study trichloramine formation, water solutions containing chlorine and ammonia in mass ratios of 12:1 and 14:1 (mg:mg) were prepared for pH = 4, 6, 7, 8 by using of phosphate buffers. Trichloramine formation and decay versus reaction time was followed both by analysis of its concentrations with ultraviolet spectrophotometry and N, N - diethyl-p-phenylendiamine with ferrous ammonia sulphate (DPD-FAS) method (7). These samples were considered as blanks.

In another set of experiments, formation and decay of NCl_3 was investigated in presence of two concentrations of phenyl-methyl-ketone (5.0 mg/L; 20 mg/L) and methyl-ethyl-ketone (5.0 mg/L; 20 mg/L), at pH = 6,7,8. UV absorption spectra of prepared solutions were recorded by use of an Jasco-530 instrument, 1999. In water solutions, trichloramine reveals an absorption maxima for 220 nm.
When chlorine and ammonia are introduced in the same solution, for 6:1; 8:1; 10:1; 12:1; 14:1, mass ratios (mg:mg), pH drops in range 3.8-4.1, and trichloramine formation takes place in 60-120 minutes. By determination of absorption maxima at 220 nm, and corresponding NCl_3 concentrations with DPD-FAS method, a linear correlation was established:

$$Y = 0.044X + 0.0699, \text{ with } r^2 = 0.982 \quad (1)$$

Where: Y = absorption; X = concentration.
In order to establish ketones effect on nitrogen chloride decay, kinetic of the process was analysed. The results obtained showed the decay process follows a first order kinetic, and rate constants were computed with the relation:

$$k_1 = \frac{1}{t} \ln \frac{C_o}{C} \quad (2)$$

Where: k_1 = rate constant; t = reaction time; C_0 = initial concentration; C = concentration for time "t". Also, half times ($t_{1/2}$) corresponding to first order reactions were computed by use of equation:

$$t_{1/2} = \frac{1}{k_1} \ln 2 \quad (3)$$

Results and Disscussion
Formation of trichloramine in water solutions depends on chlorine:ammonia ratio, pH, contact time of reagents and the presence or absence of some reactive organic species.
Absorption curves in ultraviolet spectra, for solutions of chlorine with ammonia in ratios 6:1; 8:1; 10:1; 12:1; 14:1 (mg:mg) revealed that the trichloramine formation in water solutions at pH = 4 is ready in about 60-120 minutes after reagents mixing. At this pH, the decreasing of absorption maxima of trichloramine at 220 nm, takes place slowly against time.
In fig. 1 there are presented curves describing NCl_3 formation at pH = 6: blank sample (1); blank sample with 5.0 mg/L methyl-ethyl-ketone (2); blank sample and 5.0 mg/L phenyl-methyl-ketone (3), for chlorine:ammonia mass ratio 12:1 (mg:mg), and 5 minutes after reagents mixing. From these spectra, it is obvious that by introduction of ketones in chlorine-ammonia solutions, formation of NCl_3 decreases in the following order: (3) < (2) < (1); the corresponding quantities determined after 5 minutes of reagent mixing are: 4.9 mg/L (3); 5.6 mg/L (2); 6.0 mg/L (1). In fig. 2 are presented spectra for the same solutions, but 3 hours after reagents mixing. The values of absorption decreased for all samples and the order of absorptions at 220 nm is the same: (3) < (2) < (1). The increasing of ketone concentrations to 20 mg/L, led to decreasing of nitrogen chloride formed in its presence: 4.7 (3) mg/L; 5.0 mg/L (2); 6.0 mg/L (1), 3 hours after reagents mixing. Similar results were obtained for chlorine:ammonia ratio 14:1.
The quantities of NCl_3 formed decreased with pH increasing. Thus, at pH=8 concentration of blank sample is 4.1 mg/L; 4.0 mg/L for sample with methyl-ethyl-ketone, and 3.9 mg/L for sample with phenyl-methyl-ketone, five minutes after reagents mixing.
For all samples taken into consideration, trichloramine concentrations formed in presence of phenyl-methyl-ketone where smaller than those recorded in absence of this ketone; the concentrations were smaller for 20.0 mg/L aromatic ketone with 15.0 %, for chlorine:ammonia ratio 12:1%, and 17.3 % for ratio 14:1, at pH = 6, 5 minutes after mixing; in case of methyl-ethyl-ketone presence, trichloramine concentrations decreased with 9.3-14.6 % at pH=6. When pH is increased, the decresing of NCl_3 concentrations took place, with 2.9 - 9.3% at pH = 7 and 2.4 – 3.5 % at pH = 8, comparatively with those of blank samples.

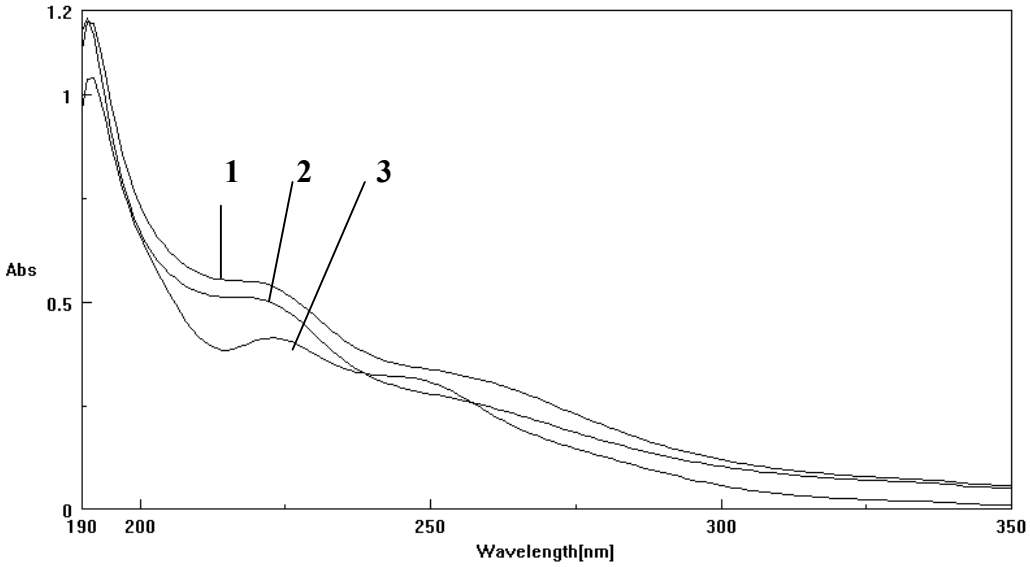

Fig.1 Ultraviolet absorption spectra for trichloramine solutions: chlorine:ammonia = 12:1 (mg:mg); pH = 6; time = 5 minute after reagents mixing; (1) blank sample; (2) blank sample + 5.0 mg/L methyl-ethyl-ketone; (3) blank sample + 5.0 mg/L phenyl-methyl-ketone.

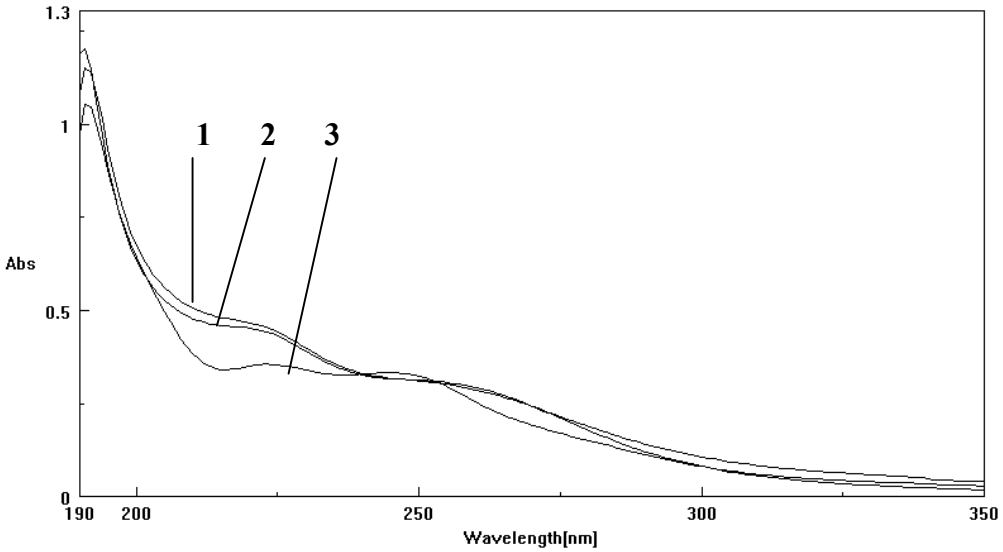

Fig. 2 Ultraviolet absorption spectra for trichloramine solutions: chlorine:ammonia = 12:1 (mg:mg); pH = 6; time = 3 hours after reagents mixing; (1) blank sample; (2) blank sample + 5.0 mg/L methyl-ethyl-ketone; (3) blank sample + 5.0 mg/L phenyl-methyl-ketone.

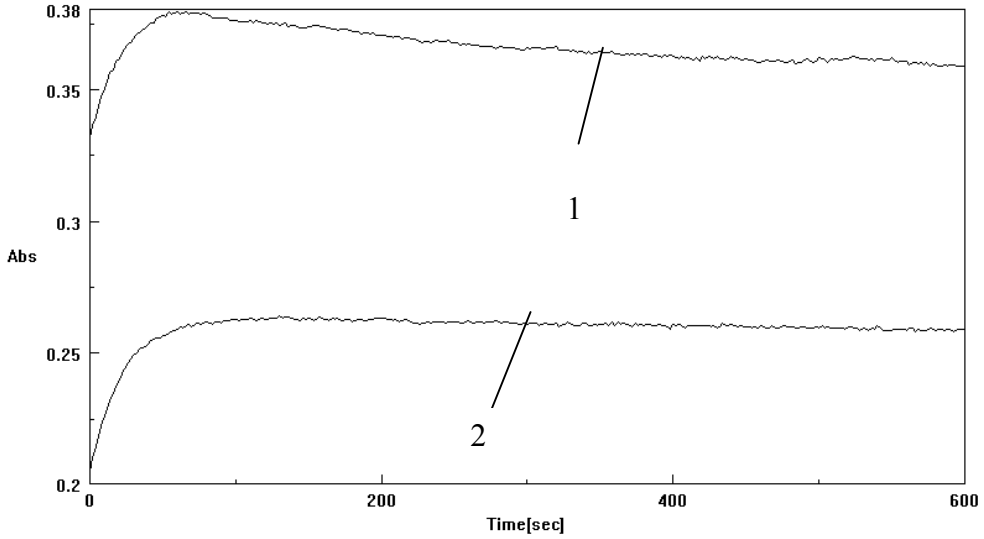

Fig. 3 Dependence of absorbance (220 nm) against reaction time for trichloramine solutions: chlorine: ammonia = 12 : 1 (mg:mg); pH = 6; (1) blank sample; (2) blank sample + 5.0 mg/L phenyl-methyl-ketone.

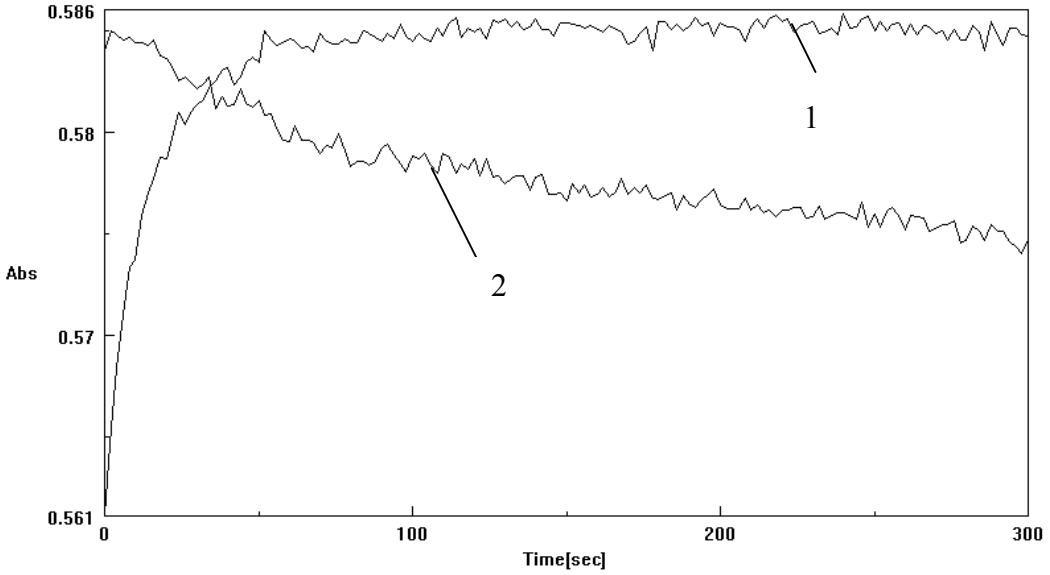

Fig. 4 Dependence of absorbance (220 nm) against reaction time for trichloramine solutions: chlorine: ammonia = 14 : 1 (mg:mg); pH = 8; (1) blank sample; (2) blank sample + 20.0 mg/L phenyl-methyl-ketone.

The dependence of absorbance corresponding trichloramine formation (220 nm) against reaction time recorded immediately after reagents mixing, is presented in fig. 3 and 4. At pH = 6, and chlorine:ammonia ratio 12:1, it is abvious that absorptions corresponding to blank sample are greater (0.38 cm^{-1}, curve 1) then those of sample with 5.0 mg/L phenyl-methyl-ketone (0.26 cm^{-1}, curve 2), at 50-100 seconds after reagents mixing, fig. 3. The same trend is determined at pH=8, fig. 4. Although the value of absorption is almost the same (0.583 cm^{-1}) for the two curves in the first 30 seconds, then that corresponding to blank sample (0.585 cm^{-1}, curve 1) remains constant and that with phenyl-methyl-ketone decreased continuously (0.575 cm^{-1}, curve 2), even from the beginning of the process.

Conclusions

Presence of phenyl-methyl-ketone and methyl-ethyl-ketone in solutions of trichloramine, prepared by mixing of chlorine and ammonia solutions in mass ratios 12:1 and 14:1, at pH=6,7,8, revealed trichloramine decreasing concentrations with 3.5-22.2% and 2.4-14.6% respectively, comparatively with blank samples. NCl_3 formation at pH=6,7,8 is a very rapid reaction, that takes place in about 50-200 seconds, after reagents mixing.

Decay of trichloramine may be described by first order kinetic law, with values of constant rates between $0.18 \cdot 10^{-2}$ - $0.43 \cdot 10^{-2}$ min^{-1}, for blank samples; $0.24 \cdot 10^{-2}$ - $0.56 \cdot 10^{-2}$ min^{-1}, for samples with phenyl-methyl-ketone; and $0.14 \cdot 10^{-2}$ - $0.44 \cdot 10^{-2}$ min^{-1}, for samples containing methyl-ethyl-ketone.

Half times corresponding to NCl_3 decay for mass ratio chlorine:ammonia 12:1 are 288 minutes for blank sample, 247 minutes for sample with phenyl-methyl-ketone (5.0 mg/L) and 249 minutes for that with methyl-ethyl-ketone (5.0 mg/L), at pH=7. By pH increasing, the values of half times also increases, for all studied systems.

Practical implications consist of development of an spectrophotometric method for trichloramine monitoring during breakpoint treatment, and improved of NCl_3 analysis by taken into consideration of interferences due to organic species from waters.

References

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