

1981
RI - A - 072 -

REMOVAL OF HALOMETHANES
FROM WATER
WITH OZONATION



RHODE ISLAND
WATER RESOURCES CENTER
TECHNICAL REPORT NO. 3

RHODE ISLAND WATER RESOURCES CENTER

PROJECT NO. A-072-RI

TERMINATION REPORT

APRIL, 1981

- 1. TITLE OF PROJECT: REMOVAL OF HALOMETHANES FROM WATER WITH OZONATION
- 2. PROJECT STARTING AND TERMINATION DATES: October 1, 1979 - February 28, 1981
- 3. PRINCIPAL INVESTIGATOR: Pei Men Chang, Ph.D., Professor
Charles E. Olney, Ph.D., Professor

4. NAME OF APPLICANT INSTITUTION: Department of Aquaculture Science and Pathology
Department of Food Science and Technology, Nutrition and Dietetics
College of Resource Development
University of Rhode Island
Kingston, RI 02881

5. ORIGINAL PROJECT OBJECTIVES AND ANY REVISED OBJECTIVES:

The objective of the project was to determine factors influencing the formation and removal of trihalomethane (THM) from water with ozonation.

6. FINDINGS, RESULTS AND CONCLUSIONS:

"The work upon which this publication is based was supported in part by funds provided by the Office of Water Research and Technology, (Project No. A072-RI, U S Department of the Interior, Washington, D.C."

A. Effects of Sparging and Ozone on THM Concentration

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Ozone from a laboratory generator was sparged at rates of 30-60 mg/min into 100 ml water solutions containing 100 ppb concentrations of the halogenated methane, ethane and ethylene compounds. After sparging a 10 ml aliquot was shaken with 5 ml petroleum ether to extract the residual THMs, which were analyzed by electron capture gas chromatography. Peaks were identified by retention time on two columns and quantitated by comparing peak heights with those of standards. Similar samples were treated with oxygen gas to assess the effect of sparging, and the ozone oxidative effect was measured by their differences. Diluted standards and extracts of untreated spiked water were run with each set of treated samples.

Sparging alone caused considerable reduction in THM concentration. When the gas flow rate was at 2 liters per min (Table I) the reduction of carbon tetrachloride (CCl_4), trichloroethylene ($\text{CCl}_2=\text{CHCl}$) and bromoform (CHBr_3) were approximately the same under oxygen or ozone treatment. It was therefore not possible to determine the reduction of THM due to ozone oxidation.

In a second experiment (Table II), eight (8) THM compounds were treated with oxygen or ozone at a gas flow rate of 2 liters per min. There were no differences in THM reduction between the oxygen and ozone treatment at 360 seconds post-treatment. However, at 60 seconds post-treatment dibromochloromethane (CHBr_2Cl), chloroform (CHCl_3), methyl iodide (CH_3I), bromodichloromethane (CHBrCl_2) and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) all showed a reduction, which was due to ozone oxidation. These reductions were 16%, 14%, 17%, 42% and 12% respectively.

Because it was difficult to distinguish the oxidative effect between ozone and oxygen at a gas flow rate of 2 liters per min, the flow rate was reduced to 0.65 liter/min. The voltage for the ozone generator was also increased from 3 KV to 4 KV. Under these conditions, ozone production was approximately 56 mg/min. A comparison of six compounds under these conditions is given in Table III. The percentages of reduction due to one minute of ozone oxidation were 10, 12, 38, 10, 9 and 16% at 0C and 19, 18, 33, 12, 10 and 19% at 25 C for methyl iodide, chloroform, trichloroethylene, bromotrichloromethane, tetrachloroethylene and dibromochloromethane, respectively. The THM which responded to ozone most effectively was trichloroethylene. It was reduced 38% at 0C and 33% at 25 C.

Five of these compounds reported in Table III (at low rate of sparging, 0.65 l/min) were also reported in Table II (at high rate of sparging, 2 l/min). Their comparison showed that volatility losses were slightly reduced at the lower gas flow rate and ozone oxidation was more apparent at 30 seconds after the start of ozonation. At 60 seconds after treatment oxidative values were similar between the two treatments.

B. Reduction of THM Compounds by Residual Ozone in Water

In this study, residual ozone in water was added to the chlorinated hydrocarbons for determining the oxidation ability of ozone. Five compounds, methyl iodide (CH_3I), chloroform (CHCl_3), trichloroethylene ($\text{CCl}_2=\text{CHCl}$), bromotrachloromethane (CBrCl_3), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) were selected for this test. Each compound was made up to 10 ppm in acetone and 0.1 ml of it was added to a test tube, followed by 10 ml of ozonated water. The solution was mixed and held for 3 min at 0 C. The concentration of the residual ozone in the water at pH 7 was 14 mg per liter.

Results in Table IV showed that ozone partially oxidized all five compounds at pH 7. The percent of reduction of each compound due to ozone was $\text{CCl}_2=\text{CHCl}$, 97%; $\text{CCl}_2=\text{CCl}_2$, 45%; CBrCl_3 , 37%; CHCl_3 , 32%; and CH_3I , 31%. It appears that ozone is particularly effective in destroying trichloroethylene.

The significant slower reaction of tetrachloroethylene as compared with trichloroethylene may be explained by the electron withdrawing effect of the extra chlorine atom and an increase in steric hindrance.

C. Effects of Ozone on THM Precursors

Experiments with combinations of chlorination and ozonation on solutions of phenol, toluene, acetone and methanol were conducted.

Phenol: In this study, one ppth of phenol in water solution was used. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C. Chlorination was carried out by adding to the one ppth water solution, 3.1 ppth sodium hypochlorite for 2 hours.

Ozonated phenol solution was divided into 2 aliquots, one of which was chlorinated immediately after ozonation. The results of this study are presented in Table V. Ozonation alone did not reduce the phenol concentration (20%) as much as chlorination alone (29%). Chlorination after ozonation reduced 33% of phenol from water solution, while chlorination after oxygen reduced 30% of the phenol. When ozonation followed chlorination, 43% of phenol was removed as compared to 25% with oxygen. It is evident that chlorination alone, ozonation alone and in combination partially removes phenol, a precursor of THM. The best sequence for the removal of phenol is chlorination followed by ozonation.

Chlorination of phenol-water solution may convert some of the phenol in the water to chlorophenols; at least three new compounds were formed in this study (Table V). Ozone, before or after chlorination, reduced the levels of chlorophenols by 30%.

Chloroform formed during the chlorination of phenol was 402 ppb and the following ozonation reduced 63% of it. In the ozonation-chlorination treatment, the chloroform produced was higher than that produced by chlorine

treatment alone. The amounts were 1236 and 402 ppb, respectively. This was probably due to the formation of small molecular weight fragments during ozonation, which provided more chances for chloroform formation during the subsequent chlorination process (Eisenhauer, J. Water Poll. Contr. Fed. 40, 1987, 1968). If ozonation-chlorination is applied in the field, there should be an additional treatment between ozonation and chlorination to remove the small molecular weight fragments produced by ozonation. That could be accomplished by either filtration or adsorption onto activated charcoal.

Toluene: In this study, the same procedure applied to the phenolic water solution was applied to toluene. The results are presented in Table VI.

When chlorination of toluene-water solution was carried out, no chlorinated toluene was formed as seen with the phenol-water solution. Chlorination alone had little effect on toluene, while ozone and oxygen both reduced the concentration of toluene from water solution. This is probably due to aeration, since toluene is a volatile compound. There was a 67% reduction following both treatments.

Chloroform formed during chlorination of toluene was 712 ppb. This was reduced to 400 ppb when chlorination was followed by ozonation. Comparison with the chlorine-oxygen treatment, where 698 ppb of chloroform was formed, it suggests that the removal of chloroform was at least partially due to oxidation by ozone.

Acetone: The same procedure applied to the phenolic water solution was applied to acetone. The results are presented in Table VII.

Acetone is highly volatile; it is also water soluble. After ozone or oxygen treatment 78-80% of the acetone remained in the water. Chlorination alone seemed to be less effective than ozonation, since 96% of acetone was still detectable in the water solution.

Acetone was a stronger precursor of chloroform than phenol, toluene or methanol. Chloroform formed was so high with acetone that later ozonation did not show any effect on its removal.

Methanol: The same procedure applied to phenol, acetone and toluene was applied to methanol. The results are presented in Table VIII.

Methanol like acetone, is volatile and water soluble. Like acetone, ozone and oxygen treatment did not reduce the concentration of the compound in water. This is due to its water solubility. After ozone and oxygen treatment, there were still 91 and 98% left in the solution, respectively. Chlorination of methanol produced a compound(s) which had shorter retention time than that of methanol. The new product was not identified, nor reduced by subsequent ozone treatment. Chlorination alone produced 783 ppb of chloroform, which was lower than that produced by ozonation followed by chlorination (4500 ppb).

Table IX summarizes the formation of chloroform following chlorination and/or ozonation. Ozonation alone does not produce any chloroform. Chlor -

ination alone or in combination with ozone all produces chloroform. With phenol and methanol, treatment with ozone prior to chlorination increases the amount of chloroform 3 and 6 times respectively over that formed by chlorination alone. With phenol and toluene, ozonation after chlorination reduced chloroform level 63% and 43% respectively.

D. Conclusion

In the Study of the reduction of THM in water by ozonation, it was found that in the application of ozone by sparging, the sparging alone caused considerable reduction of THM.

To better assess the oxidative effect of ozone, residual and dissolved ozone were used in the treatment of THM. Under these conditions, oxidative losses of methyl iodide, chloroform, bromotrichloromethane, tetrachloroethylene and trichloroethylene were 31, 32, 40, 56 and 97%. Ozonation is effective in destroying a number of THM particularly trichloroethylene. Experiments with combinations of chlorination and ozonation on solution of phenol, toluene, acetone and methanol were conducted. Sparging with ozone or oxygen for 3 minutes at 0 C and pH 7 reduced toluene levels, but had little effect on the total concentration of the other three compounds, which are water soluble. With all four compounds treatment with ozone alone does not produce any chloroform, however, treatment with chlorine produced 400-870 ppb of chloroform. With phenol and methanol, treatment with ozone prior to chlorination increased the amount of chloroform 3 and 6 times respectively over that formed by chlorination alone. With phenol and toluene, ozonation after chlorination reduced chloroform level 63% and 43% respectively.

7. A STATEMENT DESCRIBING THE RESEARCH RESULTS IN LANGUAGE A LAYMAN CAN UNDERSTAND

Chloroform and other trihalomethanes are carcinogens and their prevention and/or removal from drinking water is essential to the health of the population.

The formation of chloroform and other THM results from the interaction between chlorine and precursors present in the water. The precursors could be any organic matter in the surface or ground water. Thus the removal of chlorine and/or precursors from water will reduce the THM in the finished water. In addition the removal of any THM already formed in water would be a beneficial step in the treatment of water.

In this study, ozone, an alternative disinfectant, produced no THM from organic matter. Ozone had little effect on the removal of three precursors of THM (phenol, acetone and methanol). However, when precursors such as phenol and toluene were treated with chlorine followed by ozone, the chloroform level (a form of THM) was reduced 63% and 43% respectively from that produced by chlorination alone. In other experiments, ozone was shown to partially reduce other THMs in water.

It appears from these studies that ozonation is a better disinfectant

for drinking water with its ability to reduce and limit THM formation.

8. A STATEMENT DESCRIBING HOW THE RESULTS ARE BEING APPLIED IN THE WATER RESOURCES FIELD

The majority of water plants in the U.S. currently use chlorine as their source of disinfectant. However, since the discovery of THM formation following chlorination was reported, alternative means of disinfecting water are being studied.

This study showed that ozonation, an alternative means of water disinfection, reduces and limits THM formation in water and is therefore a better disinfectant.

9. PUBLICATIONS

"Ozonation of trihalomethanes, pesticides and four common organic compounds in water" by You Lu. Masters Thesis in Food Science and Nutrition, University of Rhode Island, Kingston, 1980.

TABLE I. Reduction of THM^a following sparging with oxygen or ozone gas at 2 l/min flow rate^b

Compound	pH	Sparging Time (sec)	% Reduction		
			Ozone	Oxygen	Ozone Oxidation
CCl ₄	2	20	69	78	-9 ^c
		40	96	96	0
		60	98	98	0
	7	20	69	78	-9
		40	96	94	2
		60	98	98	0
CCl ₂ =CHCl	2	20	63	67	-4
		40	91	92	-2
		60	100	100	0
	7	20	75	67	8
		40	95	92	3
		60	100	100	0
CHBr ₃	2	20	25	12	13
		40	26	33	-7
		120	58	56	2
	7	20	14	10	4
		60	22	28	-6
		120	55	55	0

- a. The concentration of CCl₄, CCl₂=CHCl and CHBr₃ in untreated water solution were 49, 75, and 72 ppb, respectively.
- b. The operation conditions were: Oxygen flow rate = 2 l/min; Generator voltage = 3 KV; Temperature = 25 C.
- c. (-) sign indicates that the reduction of THM compound was greater with oxygen than with ozone.

TABLE II. Reduction of eight THM compounds following sparging with oxygen or ozone gas at 2 liters per min flow rate^a

Compounds ^b	Sparging ^c Time (sec)	% Reduction		
		Ozone	Oxygen	Ozone Oxidation
CHBrCl ₂	30	29	15	14
	60	46	4	42
	120	67	48	19
	360	90	79	11
CHBr ₂ Cl	30	33	38	-5 ^d
	60	70	54	16
	120	100	71	29
	360	100	100	0
CH ₃ I	30	43	28	15
	60	70	53	17
	120	90	76	14
	360	100	99	1
CHCl ₃	30	36	35	1
	60	70	56	14
	120	91	97	-6
	360	100	95	5
CCl ₂ =CCl ₂	30	70	67	3
	60	84	72	12
	120	94	87	7
	360	100	100	0
CH ₂ BrCl	30	66	63	3
	60	87	84	3
	120	96	96	0
	360	100	100	0
CBrCl ₃	30	43	41	2
	60	58	61	-3
	120	81	83	-2
	360	95	97	-2
CH ₃ CCl ₃	30	35	47	8
	60	72	80	-8
	120	91	95	-4
	360	100	100	0

a. The ozone production was approximately 27 mg/min

b. The concentrations of CHBrCl₂, CHBr₂Cl, CH₃I, CHCl₃, CCl₂=CCl₂, CH₂BrCl, CBrCl₃ and CH₃CCl₃ in untreated water were 119, 98, 86, 124, 141, 134, 96 and 87 ppb, respectively.

c. Operation conditions were: Flow rate = 2 l/min; Generator voltage = 3 KV; pH = 7; Temperature = 25^o

d. (-) sign indicates that the reduction of THM compounds was greater with oxygen than with ozone.

TABLE III. Reduction of THM following sparging with oxygen or ozone gas at 0.65 l/min flow rate

Compound ^b	Temp. C	Sparging ^c Time (sec)	% Reduction		
			Ozone ^a	Oxygen	Ozone Oxidation
CCl ₂ =CHCl	0	30	60	27	33
		60	75	37	38
		240	100	72	28
	25	30	89	49	40
		60	97	64	33
		240	100	96	4
CH ₃ I	0	30	37	23	14
		60	47	31	16
		240	74	68	6
	25	30	65	41	24
		60	72	53	19
		240	94	93	1
CHBr ₂ Cl	0	30	28	9	19
		60	32	16	16
		240	52	45	9
	25	30	56	29	27
		60	62	43	19
		240	100	100	0
CHCl ₃	0	30	30	19	11
		60	33	21	12
		240	48	44	4
	25	30	50	33	17
		60	59	41	18
		240	76	78	-2
CBrCl ₃	0	30	39	24	15
		60	46	36	10
		240	78	73	5
	25	30	66	45	21
		60	73	61	12
		240	100	100	0
CCl ₂ =CCl ₂	0	30	52	40	12
		60	61	52	9
		240	87	85	2
	25	30	77	59	18
		60	84	74	10
		240	100	100	0

a. The ozone production was approximately 56 mg/min

b. The concentration of CCl₂=CHCl, CH₃I, CHBr₂Cl, CHCl₃, CBrCl₃ and CCl₂=CCl₂ measured in untreated water solution were 120, 109, 121, 116, 112 and 124 ppb, respectively.

c. Operation conditions were: Flow rate = 0.65 l/min; Generator voltage = 4 KV; pH = 7.

TABLE IV. Reduction of THM following treatment with residual ozone in water (at pH 7 and 0 C).

Compound ^a	% Reduction		
	Ozone ^b	Oxygen	Ozone Oxidation
CCl ₂ =CHCl	100	3	97
CCl ₂ =CCl ₂	45	0	45
CBrCl ₃	37	0	37
CHCl ₃	40	8	32
CH ₃ I	48	17	31

- a. The concentration of CCl₂=CHCl, CCl₂=CCl₂, CBrCl₃, CHCl₃ and CH₃I measured in water solution were 67, 64, 63, 99 and 67 ppb, respectively.
- b. Residual ozone concentration was 14 mg per liter.

TABLE V. Chloroform formation following ozonation^a and/or chlorination^b of Phenol

Compounds	Relative amount (%) in the water solution							
	None	O ₃	O ₂	Cl ₂	O ₃ +Cl ₂	O ₂ +Cl ₂	Cl ₂ +O ₃	Cl ₂ +O ₂
Phenol	100	80	94	71	67	70	57	75
Chlorophenols ^c	0	0	0	100	73	116	70	130
CHCl ₃	0	0	0	100 ^d	307 ^e	45	37 ^f	(-) ^g

- a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.
- b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.
- c. Three new products were formed, which were not identified. They are presumed to be chlorophenols based on retention time.
- d. The actual amount of chloroform formed was 402 ppb.
- e. The actual amount of chloroform formed was 1236 ppb.
- f. The actual amount of chloroform formed was 149 ppb.
- g. Sample lost

TABLE VI. Chloroform formation following ozonation^a and/or chlorination^b of toluene

Compounds	Relative amount (%) in the water solution							
	None	O ₃	O ₂	Cl ₂	O ₃ +Cl ₂	O ₂ +Cl ₂	Cl ₂ +O ₃	Cl ₂ +O ₂
Toluene	100	33	33	90	22	22	19	23
CHCl ₃	0	0	0	100 ^c	70 ^d	58	56 ^e	97 ^f

- a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.
- b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.
- c. The actual amount of chloroform formed was 720 ppb.
- d. The actual amount of chloroform formed was 510 ppb.
- e. The actual amount of chloroform formed was 400 ppb.
- f. The actual amount of chloroform formed was 698 ppb.

TABLE VII. Chloroform formation following ozonation^a and/or chlorination^b of acetone

Compounds	Relative amount (%) in the water solution							
	None	O ₃	O ₂	Cl ₂	O ₃ +Cl ₂	O ₂ +Cl ₂	Cl ₂ +O ₃	Cl ₂ +O ₂
Acetone	100	80	78	96	85	90	91	73
CHCl ₃	0	0	0	100 ^c	100	107	100	100

- a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.
- b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.
- c. The actual amount of chloroform formed was 8680 ppb.

TABLE VIII. Chloroform formation following ozonation^a and/or chlorination^b of methanol

Compounds	Relative amount (%) in the water solution							
	None	O ₃	O ₂	Cl ₂	O ₃ +Cl ₂	O ₂ +Cl ₂	Cl ₂ +O ₃	Cl ₂ +O ₂
Methanol	100	91	98	0	89	99	0	0
New Products	0	0	0	100	0	0	100	97
Chloroform	0	0	0	100 ^c	574 ^d	58	112 ^e	52

- a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.
- b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.
- c. The actual amount of chloroform formed was 783 ppb.
- d. The actual amount of chloroform formed was 4500 ppb.
- e. The actual amount of chloroform formed was 877 ppb.

TABLE IX. Summary: Chloroform formation following ozonation^a and/or chlorination^b of organic compounds

Compounds	Amount of chloroform (ppb) formed			
	O ₃	Cl ₂	O ₃ +Cl ₂	Cl ₂ +O ₃
Phenol	0	402	1236	149
Toluene	0	720	510	400
Acetone	0	8680	8680	8680
Methanol	0	783	4500	877

- a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7
- b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.