"THM-R"

Reducing Trihalomethanes in Drinking Water

INTRODUCTION:

A two and a half-year study by DABCO Chemical, Inc., York, Pa. has developed an economical, effective chemical compound to reduce trihalomethanes in drinking water.

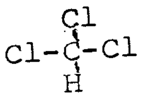
These extensive tests were conducted using many different water sources varying in alkalinity, hardness, pH, and total organic carbon (TOC).

BACKGROUND:

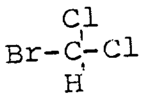
THM's are organic compounds consisting of one carbon atom, one hydrogen atom, and three halogen atoms. The only significant halogens responsible for the formation of trihalomethanes in water are chlorine, bromine, and iodine. Iodine is rare and won't even be discussed further. The problem is that the U.S. Environmental Protection Agency (USEPA) considers chloroform (the trihalomethane containing three chlorine atoms) to be carcinogenic in rats and mice and therefore, possibly in humans. U.S. EPA also considers the other trihalomethanes as potential carcinogens by association.

Trihalomethanes aren't usually found in raw waters; but if they are, it is usually in low concentrations. They are formed by the reaction of free chlorine (or bromine or iodine instead of chlorine as a disinfectant) with certain organic compounds in the water, mainly humic and fulvic acids. These organic compounds are produced by decaying vegetation; such as leaves, twigs, and weeds. These organic compounds which combine with the free chlorine are called "trihalomethane precursors" or simply "precursors." The precursors alone usually aren't harmful but can cause a bad taste or odor in the drinking water. This is because the organic precursors can act as nutrients for microbiological growth.

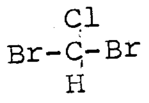
On November 29, 1979, the U.S. Environmental Protection Agency amended the Interim Primary Drinking Water Regulations of the Safe Drinking Water Act so as to constitute a maximum contaminant level (MCL) of trihalomethanes. The MCL is presently set at .10 mg/l or 100 ug/l of total trihalomethanes. The 0.10 mg/l concentration is approximately 0.10 parts per million (ppm) while 100 ug/l is approximately 100 parts per billion. In this study, the calculations for the concentrations will be in ug/l (micro-grams per liter, or parts per billion). The maximum contamination levels (MCL) were set for total trihalomethanes (TTHM's). The TTHM is found by adding the concentrations of the four most prevalent trihalomethanes found in drinking water. They are all formed by similar techniques all might have toxic effects, and all four can be prevented by the same methods. The four common trihalomethanes are trichloromethane, or more commonly chloroform, bromodichloromethane, dibromochloromethane and tribromomethane, or more commonly bromoform.


$\mathrm{Cl{-}\overset{Cl}{\underset{H}{C}}{-}Cl}$

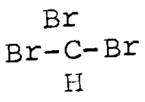
chloroform


$\mathrm{Br{-}\overset{Cl}{\underset{H}{C}}{-}Cl}$

bromodichloromethane


$\mathrm{Br{-}\overset{Cl}{\underset{H}{C}}{-}Br}$

dibromochloromethane


$\mathrm{Br{-}\overset{Br}{\underset{H}{C}}{-}Br}$

bromoform

Numerous studies, including this one, show that the concentration of trihalomethanes is significantly increased upon the treatment of a chlorine to the water. Any free chlorine residual, no matter what the source is, can form trihalomethanes when reacting with precursors.

Also see final ruling February 28, 1983, in the Federal Register.

PURPOSE OF TESTING:

The extensive research and testing by DABCO Chemical, Inc. was done to develop an improved coagulation and clarification step to reduce THM's without sacrificing bacteriological safety or present disinfecting techniques with the use of "THM-R".

Up to 46% reduction in THM formation can be achieved using pre-chlorination with no changes to the existing treatment. (see Figure No. 1). With pre-chlorination THM-R has the ability to settle out a high percentage of chloroform produced plus any precursors that have not reacted to form trihalomethanes.

Up to 92% reduction in THM formation can be achieved by post chlorinating only (see Figure 2). 100% reduction can be achieved by the use of THM-R plus GAC plus post-chlorination only.

It is much easier to remove the precursors than it is to remove the chloroform, once the reaction has taken place.

On all the samples tested, the percent reductions were amazingly consistent. The reduction of 46% with pre-chlorination and 92% with post chlorination seemed independent of chloroform levels ranging from a low of 30 ug/l to a high of 256 ug/l.

A Hewlett-Packard 5830A Gas Chromatograph was used to determine the concentrations of THM's in all tests. The liquid/liquid extraction method (501.2) was used as prepared by the U.S. EPA Laboratory, dated November 6, 1979.

All tests were run with the temperature at 20 degrees Celsius, a pH of 7.0 - 7.8 and a free chlorine residual of 1 mg/l with two hours contact time.

Factors Influencing Trihalomethane Formation

1. The form and amount of chlorine
2. pH
3. TOC (Total Organic Carbon)
4. Time
5. Temperature

1. The lower the pH of raw water the more effective the chlorine (HOCl). This free chlorine is more reactive to the nitrogen in the water to form chloramines. Chloramines form faster than trihalomethanes, although both reactions take place as nitrogen compounds and carbon compounds of organic matter are present.

If pre-chlorination is reduced without sacrificing taste and odor or bacteriological efficiency, the amount of THM formation will drastically be reduced.

2. The pH of the water is a factor as THM's are formed to a greater degree at higher pH's.

3. TOC (Total Organic Carbon). The higher the TOC the more precursors are in the raw water. Extensive precursors work has been done by A. A. Stevens[11] in this regard. Knowing the TOC in the raw water plus the chlorine level and considering the pH and reaction time of the chlorine, one may predict with some degree of accuracy the total trihalomehtane potential. (TTHMP) (See Chart No. 1.) This Chart was developed using the constant developed by A. A. Stevens and using (AMW) average molecular weight of (1500). This Chart may vary somewhat due to the ratio of humic acid to fulvic acid changing the average molecular weight. Humic acid tends to produce more trihalomethanes than the fulvic acid.

4. Time is an important factor as the longer the chlorine has to react with the precursors the more trihalomethanes are formed. This is evidenced by higher THM's at the far ends of distribution systems. THM-R has the ability to remove these

unreacted precursors thereby reducing THM formation by up to 46% even with no changes in pre-chlorination.

5. As the temperature of the raw water rises, the amount of decaying organic matter and algae growth increase the fulvic and humic acids concentrations. Therefore, higher THM's are produced in the warmer months of the year.

SUMMARY AND CONCLUSIONS

The use of "THM-R" to improve the coagulation and clarification step in existing treatment plants will reduce total trihalomethanes (TTHM) well below EPA requirements of 100 ug/l on a moving average.

Up to 46% reduction in THM formation can be achieved using present pre-chlorination practices.

The point of chlorination was determined to be very important in minimizing the formation of THM's. Water companies experiencing high THM's should move their point of chlorination to follow coagulation/sedimentation. With this post chlorination and the use of THM-R up to 92% THM, formation reduction can be achieved.

When pre-chlorination is removed, an alternate disinfectant may be used to alleviate any possible taste and odor problems. In every case, the use of THM-R reduced the TTHM. See Figures No. 3 and 4 for potassium permanganate and hydrogen peroxide data.

There was a 30% reduction of TTHM in using GAC versus PAC which seems to bear out previous EPA studies. The use of THM-R in conjunction with hydrogen peroxide reduced the TTHM from 72.90 ug/l to 32.26 ug/l than if hydrogen peroxide were used alone.

Results show that ozone, potassium permanganate and hydrogen peroxide used as alternatives to chlorine for pre-treatment were greatly improved using THM-R.

In all waters tested the percentage reduction of THM formation seemed to be unrelated to the initial concentration of the THM precursors.

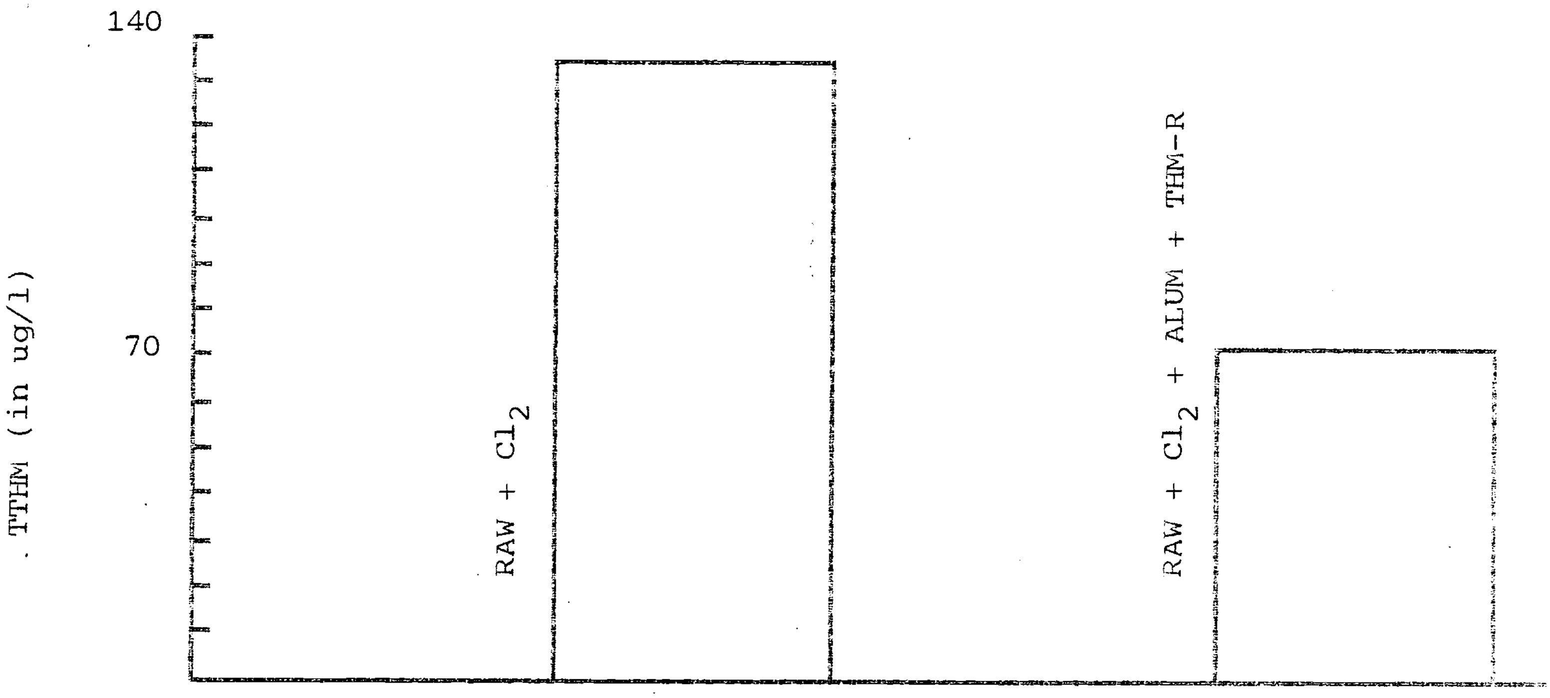


Figure 1

Showing 46% Reduction using THM-R on Prechlorinated Water

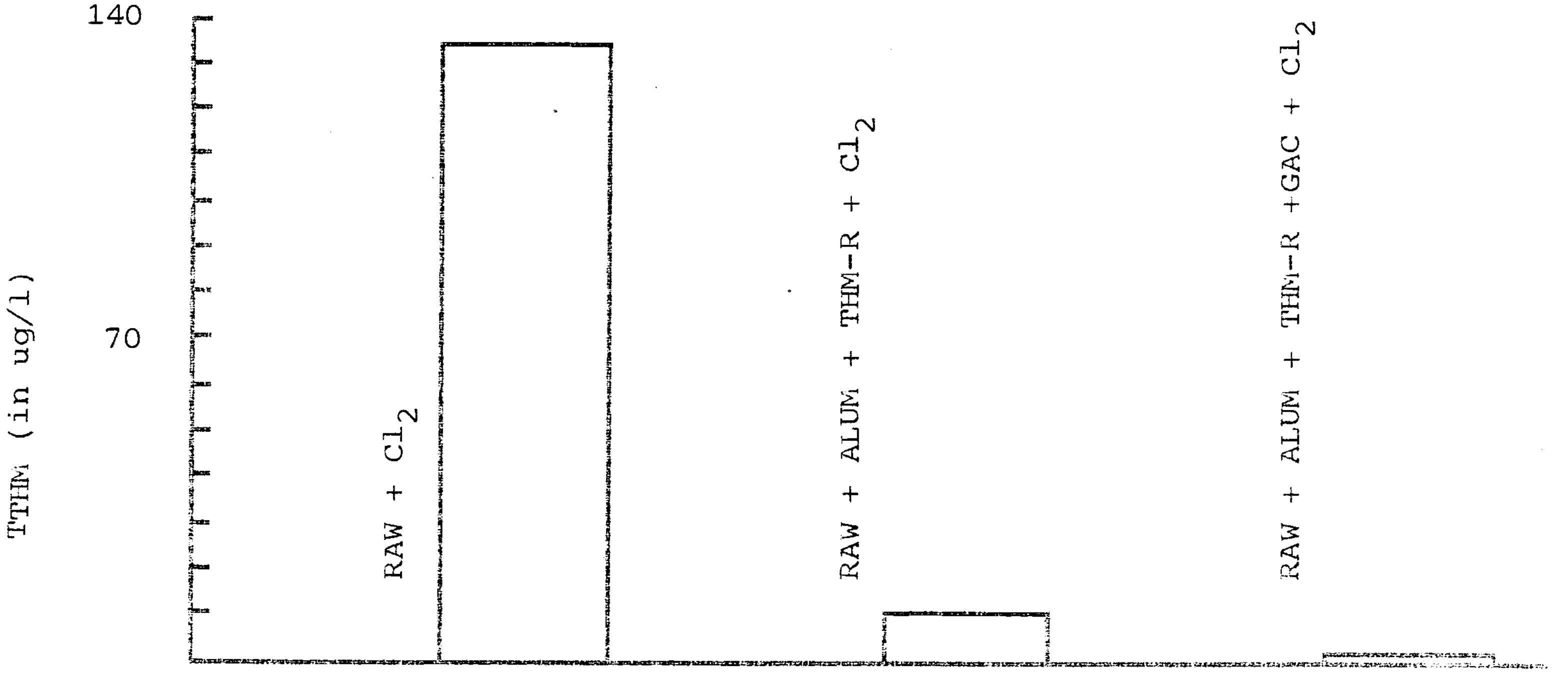


Figure 2
Showing up to 92% Reduction
Changing Point of Chlorination

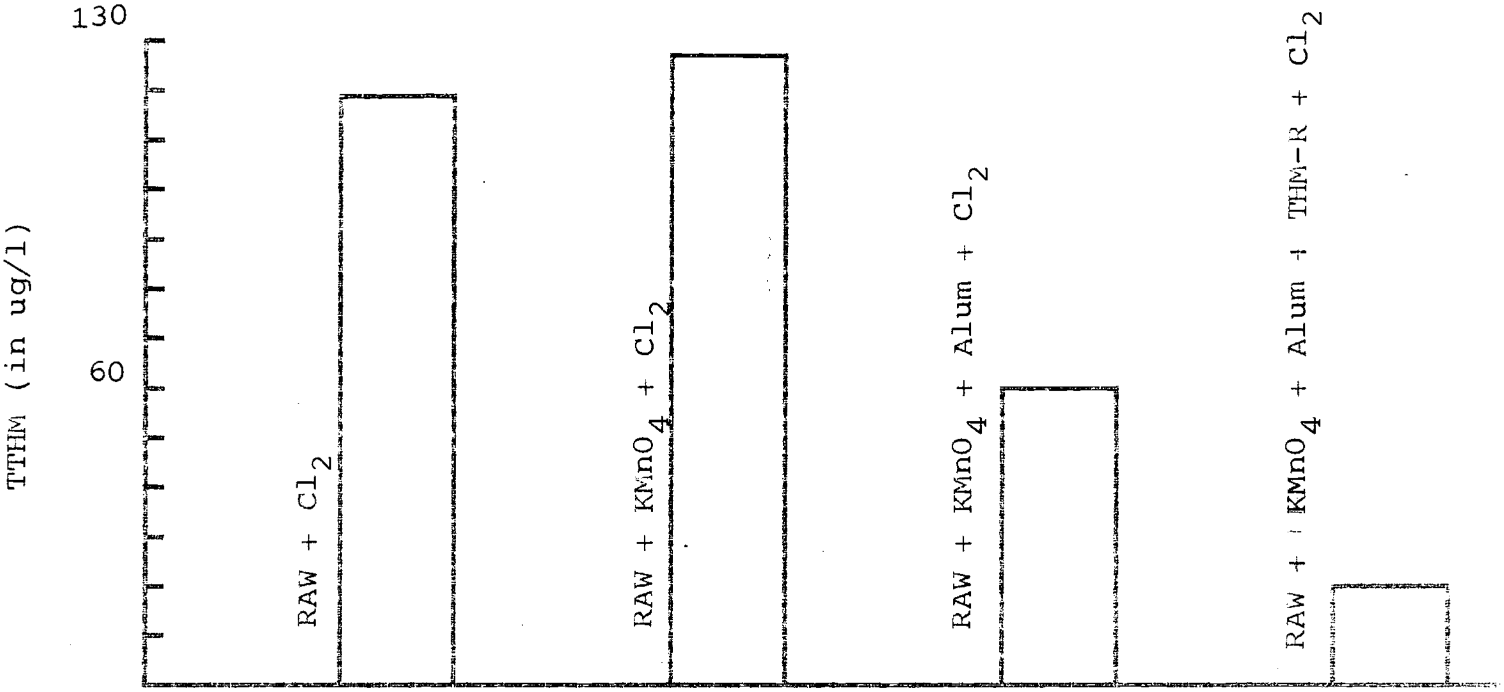


Figure 3

Reduction using "THM-R" in Conjunction with Potassium Permanganate

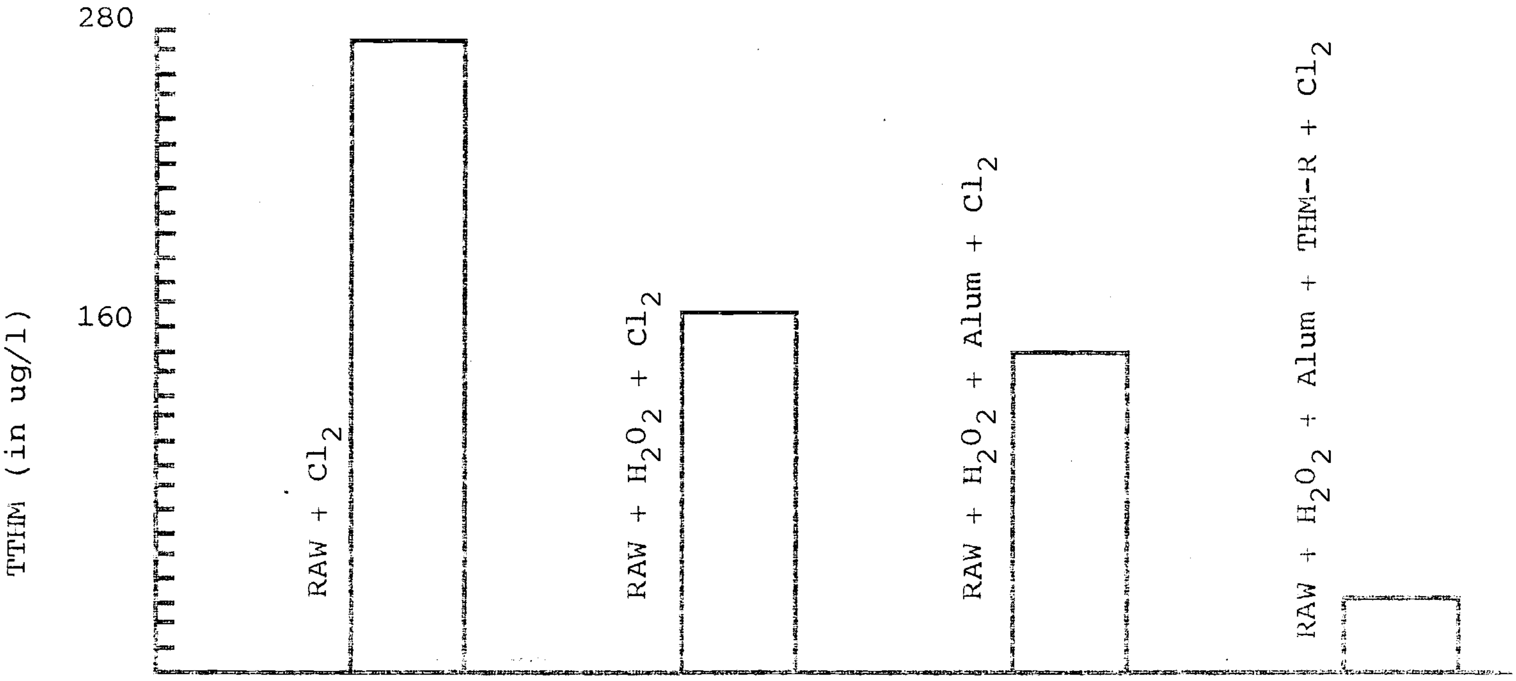


Figure 4

Reduction using "THM-R" in Conjunction with Hydrogen Peroxide

CHART 1

THIS SHOWS THEORETICAL VALUES FOR TTHM's WITH VARYING [TOC] AND [HOCl]
THE VALUES ARE THE [TTHM] IN ppb OR ug/l

[TOC]	[HOCl] in ppm									
in ppm	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6
0	0	0	0	0	0	0	0	0	0	0
1	2	4	8	13	21	31	44	60	80	104
2	3	8	15	26	41	62	88	121	161	209
3	5	12	23	39	62	93	132	181	241	313
4	7	15	30	52	83	124	176	242	322	418
5	8	19	38	65	104	155	220	302	402	522
6	10	23	45	78	124	186	264	363	483	627
7	11	27	53	91	145	217	309	423	563	731
8	13	31	60	104	166	248	353	484	644	836
9	15	35	68	118	187	279	397	544	724	940
10	16	39	76	131	207	310	441	605	805	1045
11	18	43	83	144	228	341	485	665	885	1149
12	20	46	91	157	249	372	529	726	966	1254
13	21	50	98	170	270	402	573	786	1046	1358
14	23	54	106	183	290	433	617	847	1127	1463
15	24	58	113	196	311	464	661	907	1207	1567
16	26	62	121	209	332	495	705	967	1288	1672
17	28	66	128	222	353	526	749	1028	1368	1776
18	29	70	136	235	373	557	793	1088	1449	1881
19	31	74	144	248	394	588	838	1149	1529	1985
20	33	77	151	261	415	619	882	1209	1610	2090
21	34	81	159	274	436	650	926	1270	1690	2194
22	36	85	166	287	456	681	970	1330	1771	2299
23	38	89	174	300	477	712	1014	1391	1851	2403
24	39	93	181	313	498	743	1058	1451	1932	2508
25	41	97	189	327	519	774	1102	1512	2012	2612
26	42	101	197	340	539	805	1146	1572	2093	2717
27	44	104	204	353	560	836	1190	1633	2173	2821
28	46	108	212	366	581	867	1234	1693	2254	2926
29	47	112	219	379	601	898	1278	1754	2334	3030
30	49	116	227	392	622	929	1322	1814	2415	3135
31	51	120	234	405	643	960	1367	1875	2495	3239
32	52	124	242	418	664	991	1411	1935	2575	3344
33	54	128	249	431	684	1022	1455	1995	2656	3448
34	56	132	257	444	705	1053	1499	2056	2736	3553
35	57	135	265	457	726	1084	1543	2116	2817	3657
36	59	139	272	470	747	1115	1587	2177	2897	3762
37	60	143	280	483	767	1146	1631	2237	2978	3866
38	62	147	287	496	788	1176	1675	2298	3058	3971
39	64	151	295	509	809	1207	1719	2358	3139	4075
40	65	155	302	522	830	1238	1763	2419	3219	4180

NOTE: pH =7.0, TIME=200 minutes, STP(STANDARD TEMP. AND PRESSURE),
RATE CONSTANT=1E+10 for the Kinetic Model