Trihalomethanes Can Cause RO/DI System Problems

by

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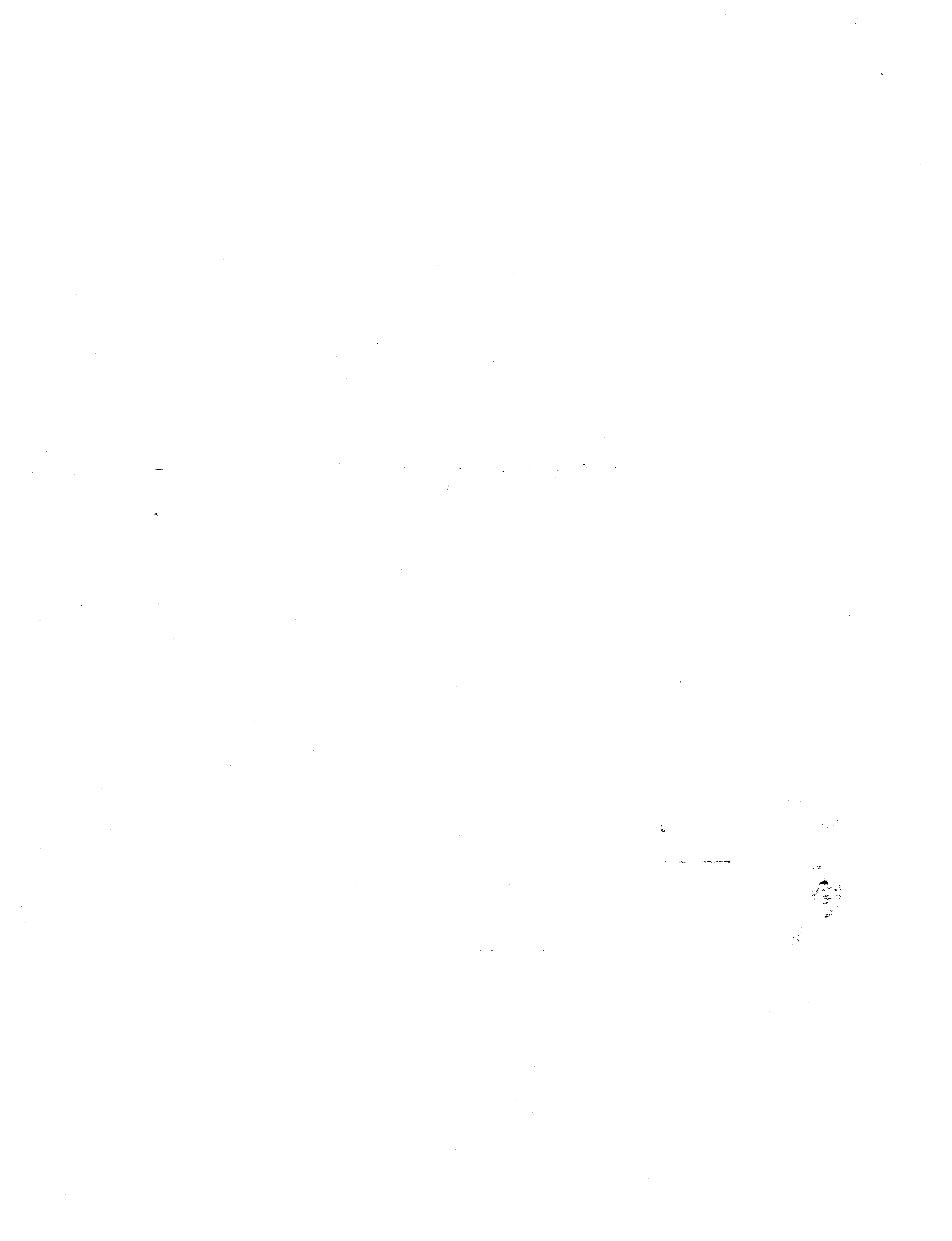

TRIHALOMETHANES CAN CAUSE RO/DI SYSTEM PROBLEMS

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Trihalomethanes (THMs), a group of organic compounds formed during chlorination of water supplies for disinfection, were found to be a source of resistivity drop at final filter of RO/DI Systems. Bromide-containing THMs are readily broken down by the biocidal UV lamps to yield bromide ion in concentrations which can drop the resistivity below specifications. THMs are removed by some ion exchange resins. Measurement of them by on-line TOC analyzers causes an over statement of the amount of TOC in the water, resulting in costly and misdirected trouble-shooting of systems.

INTRODUCTION

A frustrating problem in the production of high purity water has been the loss of water quality, evidenced by a drop in resistivity as the water passes through the biocidal UV lamps. Resistivities of 18.2 at the polishers may drop to 17.5 or lower yet, sometimes to the point where production is shut down. It is generally accepted that organics are the cause of this problem, in fact, several TOC analyzers are based on UV oxidation of organics to ionized species.

As an analytical laboratory, we were frequently asked to help resolve this problem and had attempted various measurements such as TOC analysis of water passing into and out of the UV, and ion chromatography to detect the specific ions formed. Ordinarily, the TOC levels did not change within experimental detection limits. However, we frequently found that bromide ion showed up in the lower resistivity water. This finding sent us on a search for the source of the bromide -- for a neutral organic molecule which was fairly easily decomposed in the UV.

This puzzle was solved with the detection of bromide-containing THMs. These compounds are present in some supply waters that have been disinfected with chlorine. The finding of THMs led to attempts by one facility to improve their RO/DI System to eliminate them. Our studies showed that THMs are removed to some degree by system components, but that they may foul resins.

Source of Trihalomethanes

THMs are formed during free chlorination of drinking water. Aqueous chlorine reacts with natural aquatic humic substances (humic and fulvic acids): (1)

```
                     humic
Free Chlorine + substances -----> THMs + Other Products
                  (+ bromide)
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Bromide ion itself does not participate in this organic substitution reaction but is oxidized by aqueous chlorine to a reactive species, resulting in the pure and mixed halogen THMs as below:

$CHCl_3$	Trichloromethane (chloroform)
$CHBrCl_2$	Bromodichloromethane
$CHBr_2Cl$	Dibromochloromethane
$CHBr_3$	Tribromomethane (bromoform)

The proportions of these four THMs varies, and is dependent upon the concentration of bromide in the water and the length of time for reaction to occur. The prevalence of certain THMs may be greater in some areas where water supplies are low. In the San Francisco Bay Area, intrusion of sea water into depleted water supplies results in increased proportions of the dibromo-and tribromomethanes as well as an increase in total THMs.

A maximum contaminant level of 100 ppb of total THMs in drinking water has been established by the EPA for health reasons. When the 100 ppb level is approached, other disinfectants such as chloramines are substituted for chlorine.

Figure 1 shows the monthly variations of total THMs levels from June 1986 through June 1987 for two water districts.

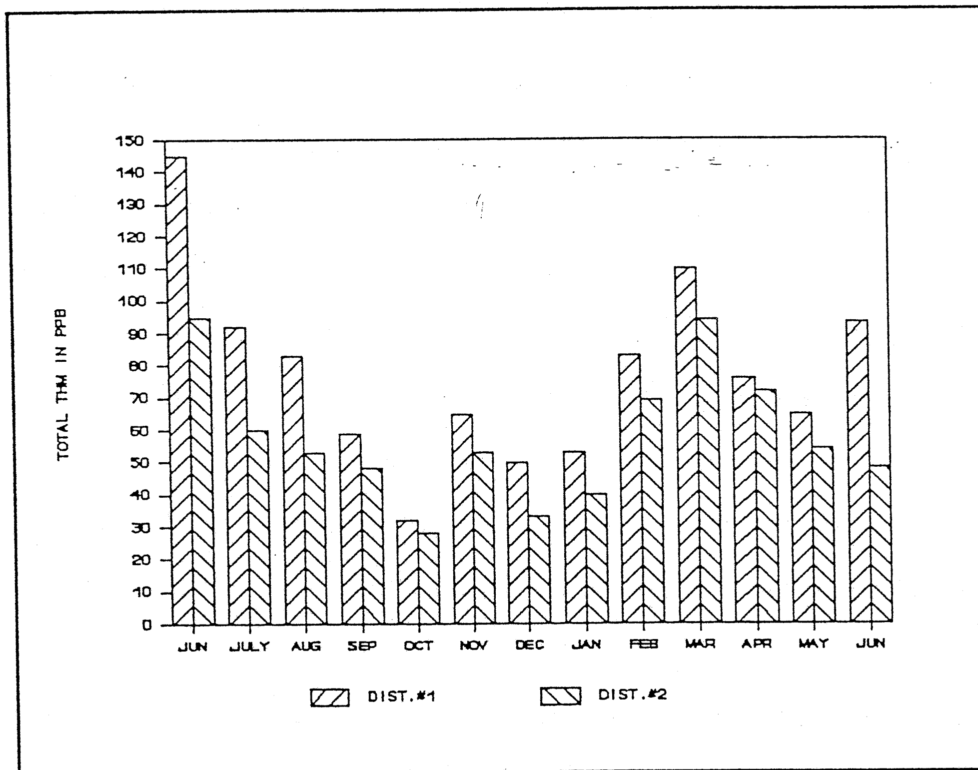


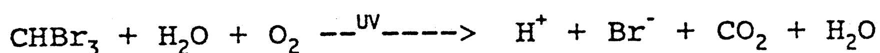
FIGURE 1
TOTAL TRIHALOMETHANE LEVELS IN TWO WATER DISTRICTS IN BAY AREA FROM JUNE 1986 THROUGH JUNE 1987.

PROBLEMS DUE TO THE PRESENCE OF THMs IN RO/DI SYSTEMS IN TWO SEMICONDUCTOR FACILITIES

Case A

In October, 1987, a semiconductor company was having a resistivity drop across the UV lamp from 18.2 megohm to 17 megohm. This facility has two independent DI water systems and the symptoms occurred simultaneously in both systems. It was suspected that the feed water was at fault. Only ionic substances, such as inorganic ions, organic acids and bases and carbon dioxide can cause a change in resistivity. Therefore ion chromatography was used to identify the contaminants. In both systems, approximately 1 ppb of bromide ion was found at post UV but was not detected at pre UV. All other ions remained unchanged. Based on this finding, we reasoned that the incoming water contained "neutral" (non-ionic) organic material that was not removed by any system components. When this organic passes through the UV, it is decomposed to an ionic species. This causes the resistivity drop. In order to identify the organic the technique of gas chromatography (purgeable organics-EPA Methods 601 and 602) was used to analyze the water. It was found that the supply water, as well as RO product water, contained tremendous amounts of THMs. The concentration of these compounds decreased across the UV (UV located at post polishers prior to final filter) while the bromide ion concentration increased. The

amount of bromide could account for the resistivity drop; it could be a product of UV oxidation of the brominated THMs.



$$CHBr_3 + H_2O + O_2 \xrightarrow{UV} H^+ + Br^- + CO_2 + H_2O$$

The levels of THMs in the supply water, pre UV and post UV, are shown in Table I. The bromide concentration was below 0.05 ppb at pre UV and increased to 1.5 ppb at post UV while the level of the brominated THMs decreased across the UV. Although the total level in the city water exceeded EPA specifications, the consequences are irrelevent to the contents of this paper, and will not to be discussed here.

TABLE I

CONCENTRATIONS (ppb) OF THMs AND BROMIDE ION IN WATER AT CASE A FACILITY

	THMs				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	Br^-
SUPPLY	40	13	44	100	-
CITY WATER					
PRE UV	1.3	2.0	3.8	1.0	<0.05
POST UV	1.3	1.9	2.3	0.8	1.5

(- NOT MONITORED)

High intensity 186 nm UV lamps were installed at post RO. They were intended to decompose the THMs upstream of the mixed beds, so the ions formed during this process would be removed.

Table II shows the effect of the 186 nm UV on the post RO water

and the effect of the normal UV on the post polish water for Systems 1 and 2. Notice that the extent of decomposition in the UV increases with increasing bromination of the THMs for both types of UV. For example, in the post RO water of System 1, $CHBrCl_2$ is reduced by only 15% (5.9 to 5.0 ppb), while $CHBr_3$ is reduced by 67% (30 to 10 ppb).

TABLE II

CONCENTRATIONS (ppb) OF THMs AND BROMIDE ION IN WATER AT CASE A FACILITY WITH 186 nm UV LAMP INSTALLED

	THMs				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	Br^-
SYSTEM 1					
POST RO					
PRE UV	1.0	5.9	20	30	-
POST UV	1.0	5.0	11	10	-
POST POLISH					
PRE UV	1.6	2.0	2.8	1.0	<0.05
POST UV	1.6	1.0	2.1	0.5	1.1
SYSTEM 2					
POST RO					
PRE UV	0.1	1.7	12	38	-
POST UV	0.2	1.6	9.5	24	-
POST POLISH					
PRE UV	0.6	0.5	1.3	1.5	<0.05
POST UV	0.6	0.5	1.1	1.1	0.9

(- NOT MONITORED)

Until the determination of the cause of the resistivity drops and the solution to this THMs intrusion problem, this company was buying water from a vendor in order to maintain a supply of the 18 megohm water to their process.

Case B

In March, 1988, another semiconductor company also was having a resistivity drop from 18 megohm to 17 megohm across the UV sterilizer. This company has frequently had this problem in the past. Ion chromatography was used to detect ionic species. Bromide ions were always found at post UV with UV on, but none were detected pre UV or post UV with the UV off.

During this resistivity drop period, the water was monitored for a period of eight weeks with a weekly analysis of THMs, ionic concentrations and TOC. (This company monitors their DI water routinely for TOC, bacteria, particles, residue and silica.)

Again, significant amounts of THMs were in the supply water and were making it through the RO/DI system in high enough concentrations to affect resistivity. Also, the bromide concentration in the process water at 0.9 ppb (on the average) far exceeded the "alert" level (2) for bromide of 0.3 ppb.

Data presented in Table III are typical results obtained from the eight week study. The resistivity drop again can be explained by the formation of bromide ion during oxidation of the brominated THMs by UV light. The TOC readings by their on-line instrument ranged from 35-40 ppb and on occasions as high as 80 ppb over a 24 hour period. At the same time, less than 20 ppb TOC was measured by the laboratory instrument. Normally, the two instruments were in good agreement.

TABLE III

CONCENTRATIONS (ppb) OF THMs AND BROMIDE ION IN WATER AT CASE B FACILITY

	THMs				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	Br^-
CITY WATER	8.8	21	33	12	-
POST RO	8.9	22	33	12	-
PRE UV	6.4	7.0	12	2.5	<0.05
POST UV	6.4	6.6	9.9	1.6	0.9

(- NOT MONITORED)

The cases above indicated that THMs caused more than only resistivity drop problems.

EFFECTS OF THMs ON ION EXCHANGE RESINS

The levels of THMs were reduced by system components other than the UV's, notably the ion exchange resins. The post RO water passes through 2 sites of ion exchange resins (both make-up and polish) before entering the post polish UV. Referring to Tables

II and III, it is seen that there is a significant drop in brominated THMs between the post RO water and the post polish water.

Two experiments were conducted to determine how the THMs were removed.

<u>Test of Reduction by System Components</u>

Water samples throughout Case B's system were taken for THMs analyses. Figure 2 is a schematic of this system showing the results for the 4 THMs at each site.

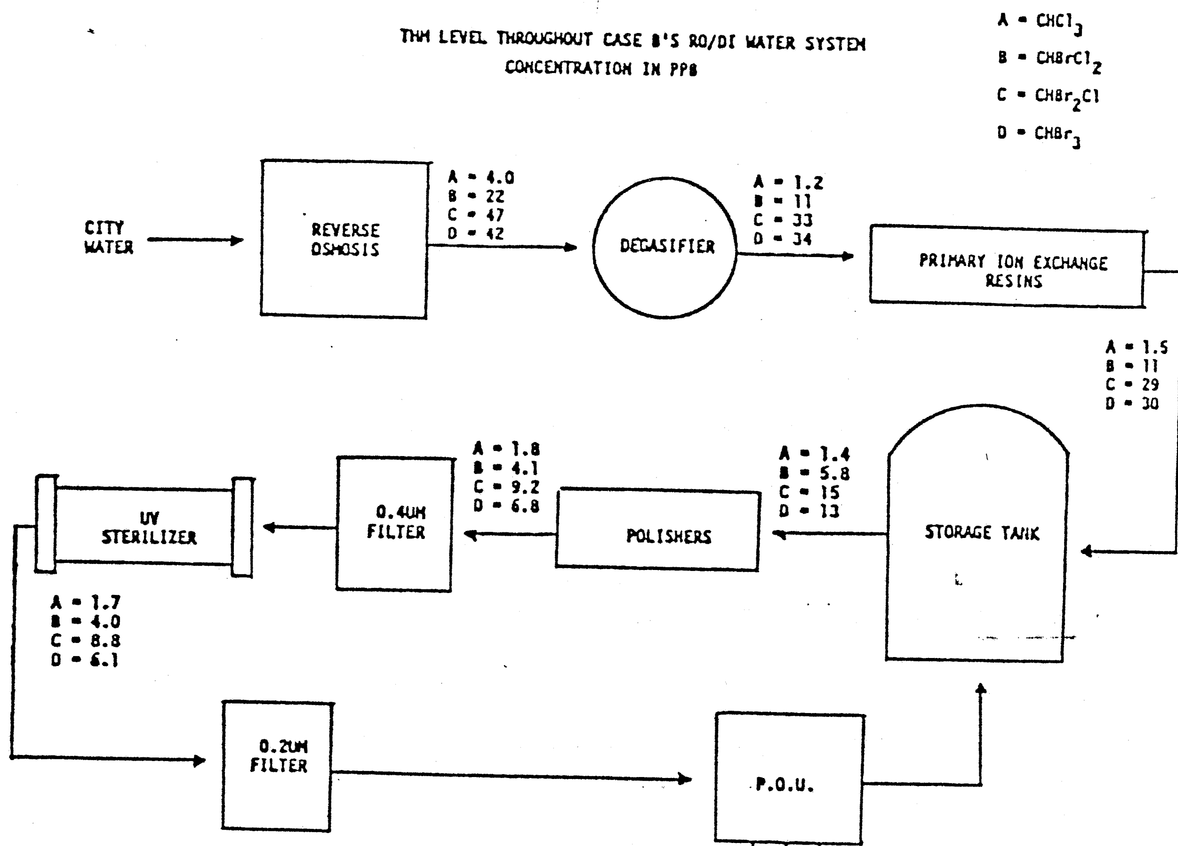


FIGURE 2. SCHEMETIC OF CASE B's RO/DI WATER SYSTEM AND THE CONCENTRATIONS FOR THE FOUR THMS AT EACH SITE.

As shown in Figure 2, the RO unit did not remove any THMs. In the degassifier, 70% of $CHCl_3$, 50% of $CHBrCl_2$, 30% of $CHBr_2Cl$ and only 19% of $CHBr_3$ were removed. These relative removal rates are explainable based on relative volatilities of these THMs.

Only small amounts were taken out by the make-up ion exchange resins, while a more significant reduction occurred at the storage tank.

It should be mentioned that in these tests the constancy of the feed water concentrations of THMs was not monitored, so some of the changes may be due to actual differences in feed water levels. This is especially true for the storage tank, because of the "buffering" effect of the large volume of water, and because some of the water had recirculated through the polishing loop. The polishing resins reduced the brominated THMs even further.

Laboratory Challenge of Resins With THMs

A laboratory experiment was conducted to determine how THMs react with resins. Two types each of the strong cation and strong anion resins most commonly used by semiconductor facilities were selected. Table IV lists the types and activated forms of the selected resins:

TABLE IV

RESINS USED IN CHALLENGE TEST

RESIN TYPE	FUNCTION	FORM
Macroporous	Strong Cation	Hydronium
Gel	Strong Cation	Hydronium
Macroporous	Strong Anion	Chloride
Gel	Strong Anion	Chloride
Macroporous	Strong Anion	Hydroxide
Gel	Strong Anion	Hydroxide

A mixture of THMs of known concentration, similar to the levels normally found in city water, was pumped through the resin columns at a flow rate of 16 liters of water per hour per liter of resin (2 gpm/ft^3.) The standard operating conditions recommended by most resin manufacturers are 1-5 gpm/ft^3. The THMs solution was prepared in 18+ megohm DI water containing <0.5 ppb of ionic concentrations and other trace elements, <20 ppb of TOC and <3 ppb of SiO_2.

The macroporous cation resins in hydronium form removed some THMs at 5 bed volumns (20 minutes after sample loading). The removal efficiency is higher with increasing bromination of the THMs: 50% for $CHBr_3$, 35% for $CHBr_2Cl$, 15% for $CHBrCl_2$ and <10% of $CHCl_3$. However, the removal efficiency decreased to <15% for all THMs at 64 bed volumes (4 hours after sample loading). (See figure 3.) The decrement may have occurred sooner than the 64th bed volume where the second sample point was taken. However, the average

service time for make-up resins is about 2-3 days and for polishing resins up to 3-4 weeks, therefore, the data obtained is sufficient to indicate these resins remove only small amouts of the THMs.

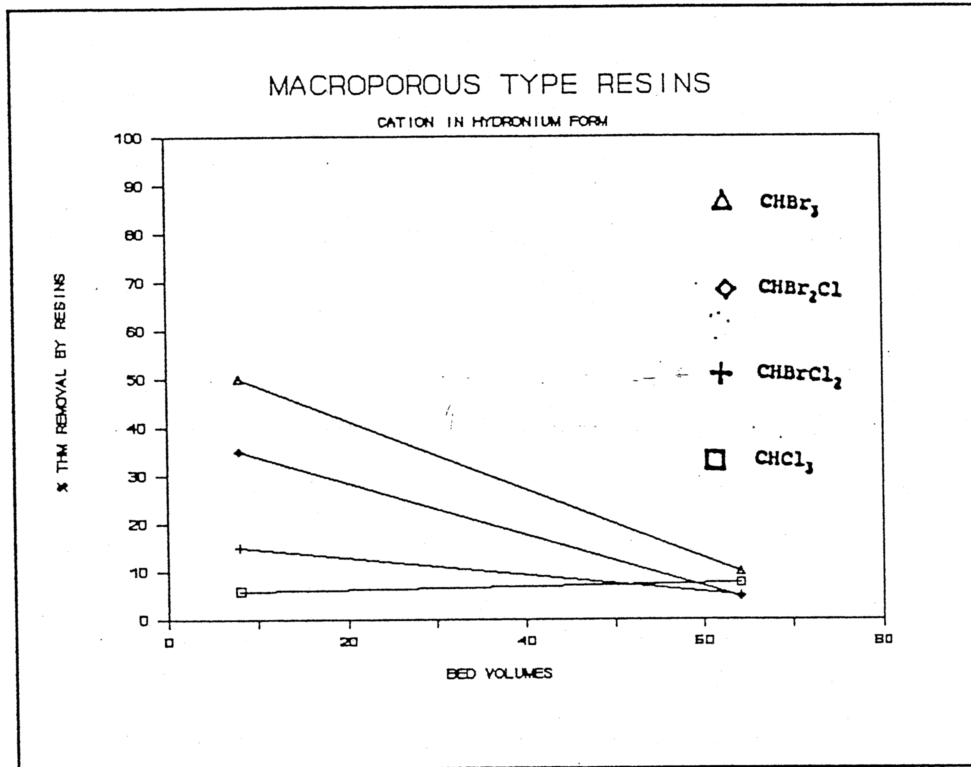


FIGURE 3
MACROPOROUS TYPE CATION RESINS IN HYDRONIUM FORM; PERCENT THMS REMOVAL VS. NUMBER OF BED VOLUMES.

The gel type cation resins in hydronium form showed a similar removal trend except the overall percent removal was only half as much as the macroporous type. (See Figure 4.)

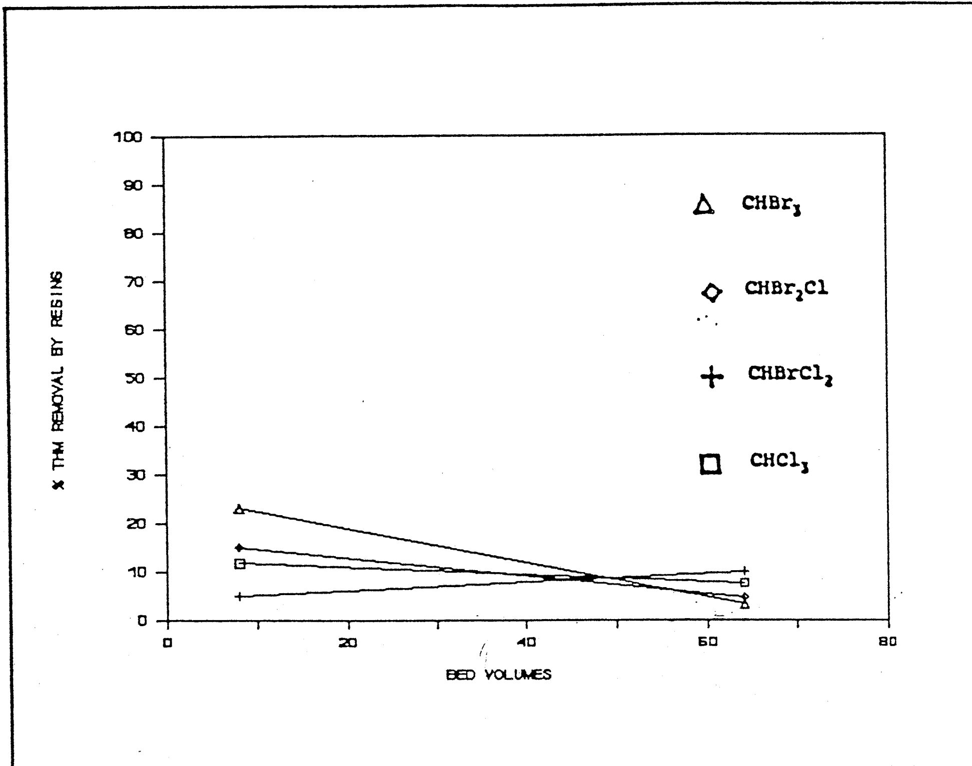


FIGURE 4
GEL TYPE CATION RESINS IN HYDRONIUM FORM; PERCENT THM REMOVAL VS. NUMBER OF BED VOLUMES.

Both the macroporous and gel types anion resins in chloride form also showed a removal trend of all three brominated THMs similar to the above cation resins but at a higher percentage removal. (See Figures 5 and 6.)

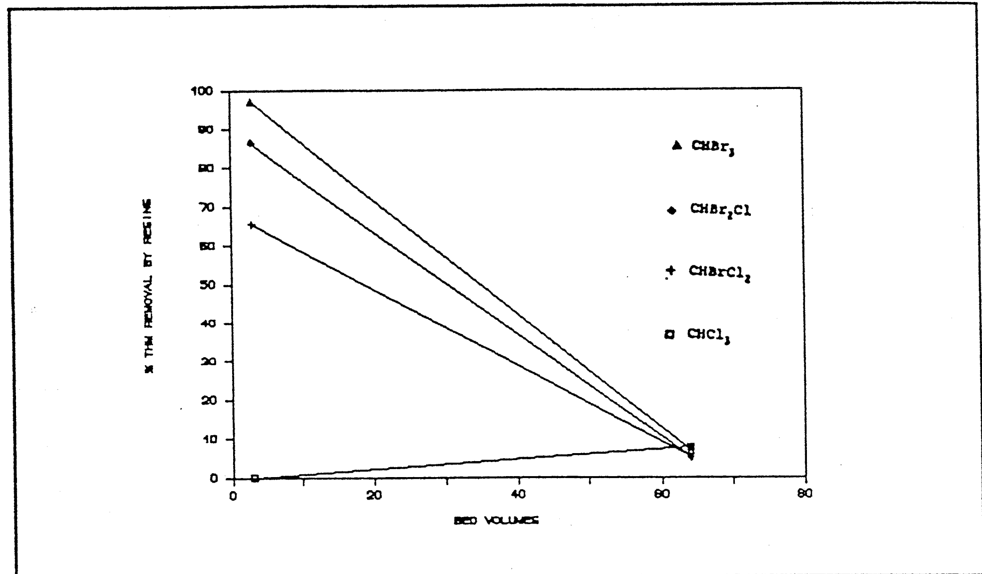


FIGURE 5
MACROPOROUS TYPE ANION RESINS IN CHLORIDE FORM; PERCENT THM REMOVAL VS. NUMBER OF BED VOLUMES.

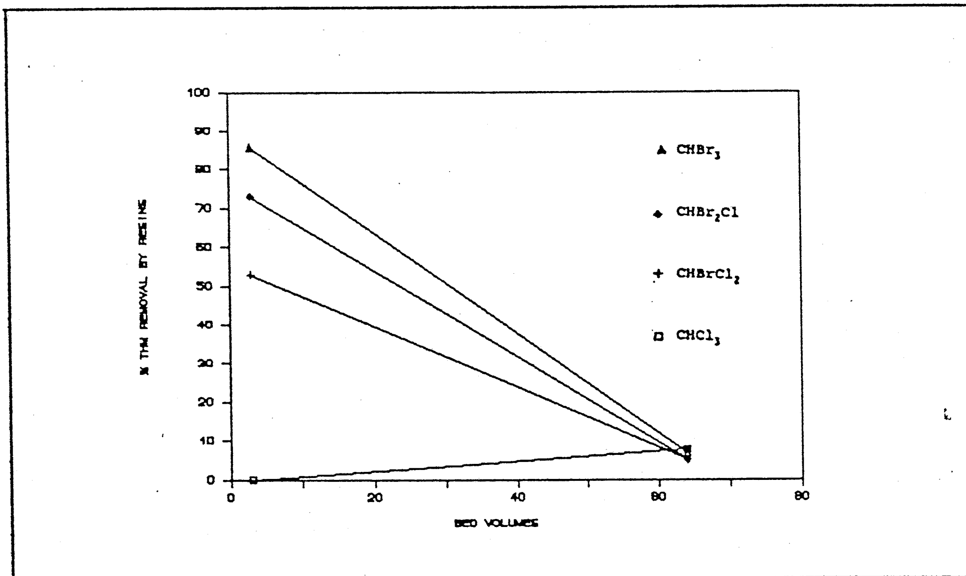


FIGURE 6
GEL TYPE ANION RESINS IN CHLORIDE FORM; PERCENT THM REMOVAL VS. NUMBER OF BED VOLUMES.

Again, the macroporous has higher percent removal than the gel type resins. Note that the percent removal for $CHCl_3$ in all four cases is almost zero. The apparent increasing percent removal shown in these figures are artifacts within experimental error of +/-5%.

Figures 7 and 8 are results for hydroxide forms of the macropoprous and gel type anion resins. The macroporous type shows almost 100% removal even after 700 bed volumes (44 hours of sample loading) for the three brominated THMs and less than 50% for $CHCl_3$. The gel type showed similar removal trends. Again, the gel type resins have lower removal efficiency than the macroporous type.

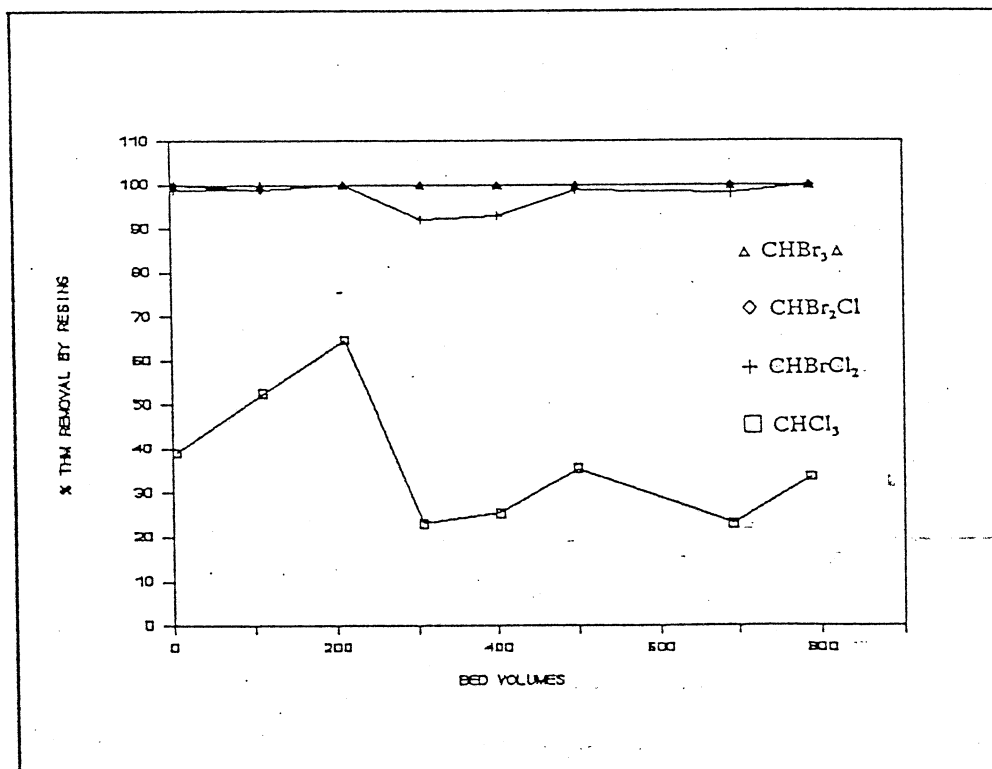


FIGURE 7
MACROPOROUS TYPE ANION RESINS IN HYDROXIDE FORM;
PERCENT THM REMOVAL VS. NUMBER OF BED VOLUMES.

	Concentration of THMs (ppb)	
	Before reacting with NaOH	After reacting with NaOH
$CHCl_3$	22	7.4
$CHBrCl_2$	33	ND*
$CHBr_2Cl$	30	ND*
$CHBr_3$	39	ND*

* = Not Detected

One hundred percent of the brominated THMs disappeared, but $CHCl_3$ did not react completely. The results supported the observations seen with the resin experiments above.

The reason that the brominated THMs are more reactive than chloroform is due to the differences in bond dissociation energy shown below: (3)

Bond Type	Bond Energy (Kcal/Mole)
C --- Cl	79
C --- Br	66

When hydroxide reacts with THMs, the possible products are alcohols, formic acid, carbon monoxide, and other organic products (4, 5). These products may then absorb onto the resins or exchange with the active sites on the resins. It is not known whether the THMS along with the reacted products can be removed by regeneration. No data is available at this time.

One important phenomenon observed in the laboratory was that the resins were clumped together and stuck to the glass column walls after they had been exposed to the THMs. The order of severity is as follows:

Macroporous type in hydroxide form > gel type in hydroxide form > macroporous type in chloride form > gel type in chloride form.

The cation exchange resins, macroporous or gel types, did not show any visible sticking or clumping. The order of severity seen is in direct relation to the percent removal of the THMs. It is obvious that the THMs react with hydroxide but the fact that some THMs were being removed by both the cation resins in hydronium form and the anion resins in chloride form suggest the possibility that the THMs might be absorbed onto the resins. In ion exchange resin analysis, the clumping of resins and resins sticking to the glass walls are indications of hydrophobic substances present on the resins.

EFFECTS OF THMs ON TOC ANALYSIS

The intrusion of THMs in Case B system caused not only the resistivity problem but also the misinterpretation of a problem when the on-line TOC analyzer gave a much higher value than the lab instrument did. The differences in TOC readings can be attributed to the type of organics being oxidized. The on-line analyzers will be sensitive to the hydrogen and bromide ion formed during oxidation, whereas the lab analyzers respond to CO_2 only.

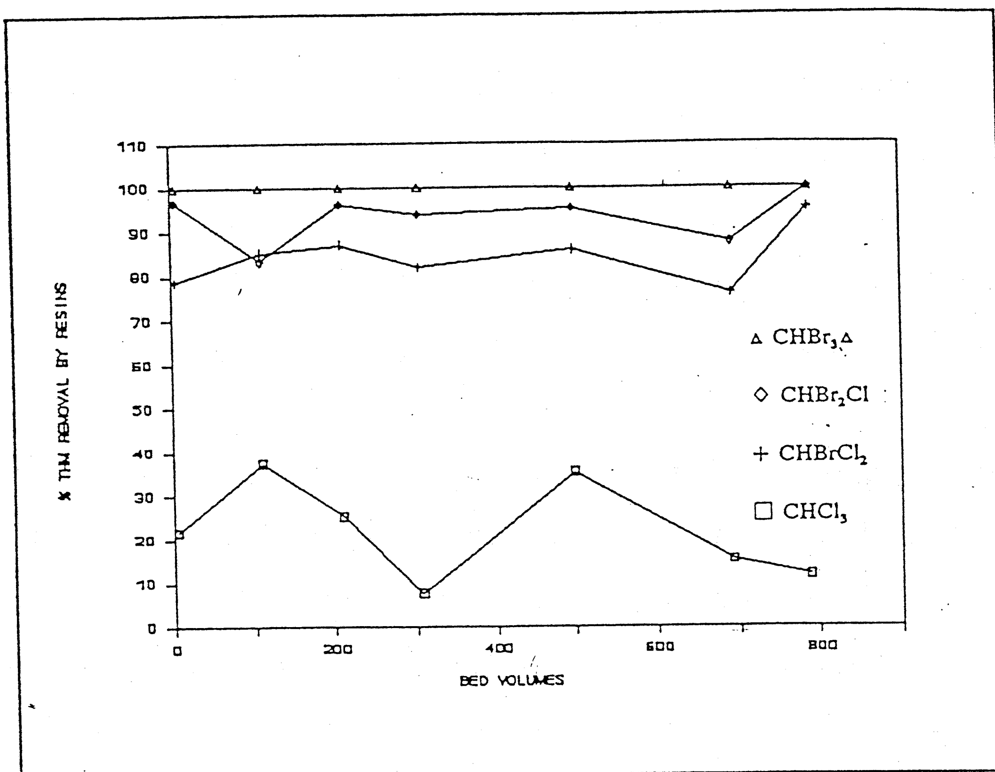


FIGURE 8
GEL TYPE ANION RESINS IN HYDROXIDE FORM; PERCENT THM REMOVAL VS. NUMBER OF BED VOLUMES.

The overall results indicated that most of the THMs are being removed by reactions between the hydroxide and THMs rather than by absorption of THMs onto the resins. This hypothesis is supported by an experiment where a mixture of a known concentration of THMs was reacted with 0.2N sodium hydroxide. Results were as follows:

A lab experiment was conducted to confirm this belief. The TOC analyzers involved were:

1. On-line analyzer using UV oxidation technique with a conductivity detector.
2. Lab analyzer using heat/persulfate oxidation technique with an IR detector. This analyzer is capable of measuring purgeable organics (POC) separately from total oxidizable carbon (TOC).

Both TOC analyzers were used to analyze a 250 ppb methanol standard. The TOC values obtained from both analyzers were comparable to the theoretical calculated carbon values when 250 ppb methanol is oxidized. The theoretical calculated TOC value for 250 ppb methanol is 94 ppb. The TOC value obtained from the on-line TOC analyzer was 77 ppb (DI water blank has been subtracted) and the TOC value obtained from the lab analyzer was 100 ppb (DI water blank has been subtracted). Both TOC analyzers agreed with each other and to the theoretical calculated TOC value within the sensitivities of the analyzers (6).

Table V shows the TOC values obtained from the two analyzers when 75 ppb (quantitatively determined by Gas Chromatography) of bromoform was measured. The lab analyzer in this case gave a more correct carbon value (7) whereas the on-line instrument produced an erroneous high TOC value.

The carbon values presented in Table V under Lab Analyzer are listed as POC and TOC because bromoform can be purged out of water then oxidized to CO_2 and HBr. This is a technique to differentiate purgeable organics from organics not purged out of water, thus enabling identification of the types of organics. However, since bromoform is the only organic present in this case, TOC and POC mean the same thing assuming that bromoform is completly purged from the sample during analysis. The theoretical carbon values are calculated according to the elemental composition. For example, when 1 ppb of $CHBr_3$ is completely oxidized, 0.95 ppb of the 1 ppb organic compound is bromide and only 0.05 ppb is carbon.

Neither instrument can give the "correct" response to halogenated organics, the on-line analyzer because it does not remove oxidation products that highly bias the response, and the lab instrument because it actually does respond only to organic carbon.

TABLE V

TOC MEASUREMENTS OBTAINED FROM BROMOFORM ($CHBr_3$)

FROM BOTH THE ON-LINE AND LAB ANALYZERS

	Conc. ppb	Theoretical Calc. TOC ppb	On-line Analyzer TOC ppb	Lab Analyzer TOC ppb	Lab Analyzer POC ppb
$CHBr_3$	75	3.6	365	39	3.5
DI Water Blank			28	18	<1

Analysis of the influent and effluent from the on-line analyzers by Ion Chromatography showed tremendous increases of bromide ion. (See Table VI.)

TABLE VI

ION CHROMATOGRAPHIC ANALYSIS OF BROMIDE

IN THE INFLUENT AND EFFLUENT WATER

FROM ON-LINE TOC ANALYZER

Calc. Conc. Br^- ppb	Influent Br^- ppb	Effluent Br^- ppb
71	0.2	23

Figure 9 is a plot of the specific resistivity of water with various ionic contaminants. The hydrogen and bromide ions formed from the oxidation of bromoform are enough to cause a large change in resistivity which is then misinterpreted as TOC by the on-line analyzer.

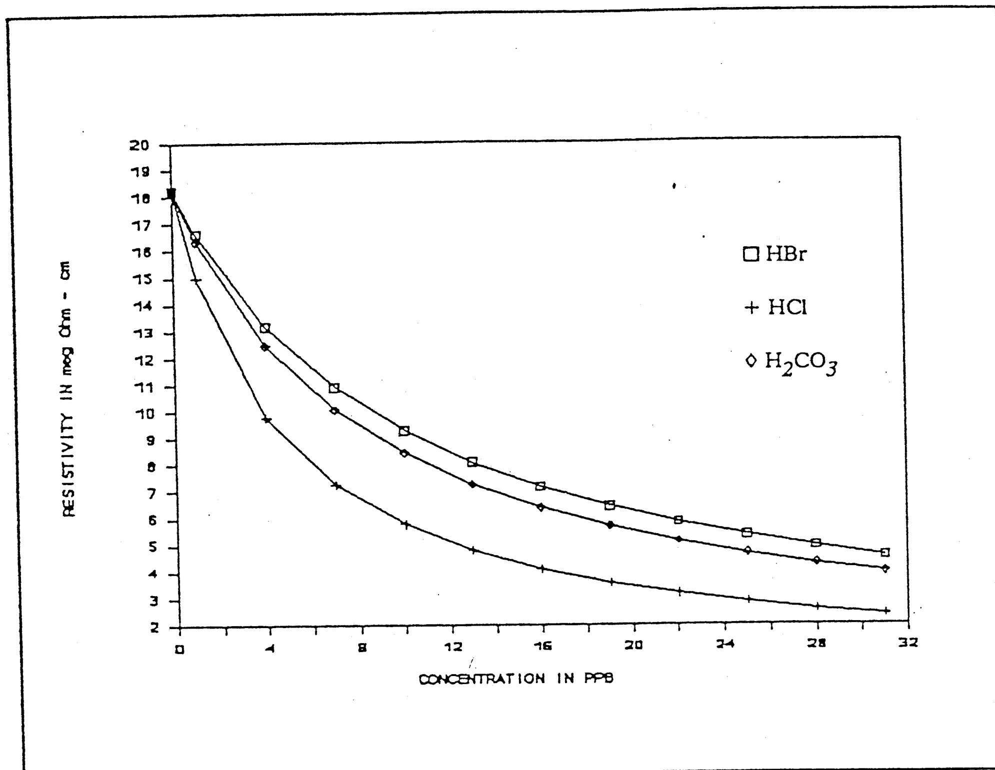


FIGURE 9
SPECIFIC RESISTANCE OF DEIONIZED WATER VS.
ELECTROLYTE CONCENTRATION AT 25°C.

EFFECTS OF THMs AND BROMIDE IONS ON PRODUCT YIELD

The effect of THMs on production yield is not known. Due to THMs' vapor pressure, they may evaporate from the wafer surfaces along with water. However, the halides formed from the UV-induced decomposition of THMs, depending on the types of product and process, can be detrimental. More studies are needed to determine the specific effects of THMs on product yields.

The concentration of bromide ion produced at the UV can exceed the SEMI guidelines.

While bromide ion is not usually thought of as a yield threatening contaminant, its effect can be damaging in the same way as chloride ion. Consider the effect on aluminum metallization, for example. According to current ion theory of corrosion, the anion participates directly in the dissolution of the metal by absorption onto the surface followed by formation of a metal salt, leading to localized dissolution, or pitting (8, 9). Bromide ion, although not as aggressive as chloride ion, reacts similarly to chloride.

CONCLUSION

THMs can cause a resistivity drop across UV sterilizers and the formation of bromide ion. The bromide ion may cause a decrease in product yields.

THMs can cause clumping of the ion exchange resins.

THMs can cause erroneous high TOC results with an on-line TOC analyzer thus leading to the misinterpretation of an organic problem.

Resistivity drop across the UV is a good indication of THMs in the water. However, chloroform can be present at high concentrations and yet not cause a resistivity change. Also, organics other than THMs can cause a resistivity drop. for example, we have detected both acetate and formate ions post UV. Gas Chromatography should be used in the monitoring of THMs.

More specific techniques for monitoring organics in water should be used. The level of organics detected by TOC is highly dependent on the measuring equipment. The TOC results are not always a good indication of the amount of organics present, especially when THMs are present.