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THE REACTION OF DECHLORINATING AGENTS WITH SOME NON-VOLATILE HALOGENATED ORGANICS

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ABSTRACT

Chlorination of various wastewaters as well as drinking water produces an abundance of non-volatile halogenated organics. Many of these compounds are unsaturated and contain chlorine and oxygen atoms. Dechlorination with sodium sulfite prior to extraction changes the concentration of the halogenated organics. Certain types of halogenated compounds are reduced more than others. This observation implies that laboratory dechlorination should only be practiced if the compounds of interest (e.g., THM's) are unreactive with the added reducing agents. The potential use of dechlorination as a treatment for halogenated byproducts is explored.

INTRODUCTION

There has been continued concern over the health effects of chlorinated organic compounds produced during the chlorination process (1,2). These chlorinated organic compounds are produced by the reaction of aqueous chlorine with organic carbon in water. The chlorinated organic compounds which have received the most attention thus far, are the trihalomethanes (THM's) (3-6).

The presence of THM's in water indicates that carbon sources in sufficient quantities to react with chlorine were present in the water prior to chlorination. This in turn implies that other halogenated, oxidized and potentially harmful chlorination byproducts are also present.

Non-volatile halogenated compounds can be analyzed collectively as a lump parameter by microcoulometry and labeled as total organic halogen (TOX) (7-11). Alternately, a subset of these compounds can be examined in detail by a chromatographic procedure. Gas chromatography (GC), gas chromatography/mass spectroscopy (GC/MS) and high pressure liquid chromatography (HPLC) have been used by various researchers (7,12-21) to study some of the individual components of TOX.

It has been commonplace to add a dechlorinating agent such as sodium sulfite to quench the residual chlorine before GC, GC/MS and TOX analysis of the organic compounds in a chlorinated water sample. This is usually done in order to arrest the further reaction of chlorine with the carbon sources in the water or the extraction solvent. Since dechlorinating agents are not reactive with THM's, this protocol has gained widespread acceptance with researchers who studied the kinetics of THM formation. The recent interest in the analysis of other halogenated chlorination byproducts also use the residual chlorine quenching step from the THM analytical protocols. The effects of dechlorinating agents on these non-volatile halogenated organics has been partially addressed. Cheh (22,23) demonstrated that sulfite treatment of chlorinated water reduces the mutagenic activity of the sample. Wilcox and Horth (24) have also demonstrated that sulfite can reduce the mutagenic activity of chlorinated water. Stanbro and Lenkevich (25) have shown that sodium sulfite slowly reacts with certain organic chloramines.

This paper shows that dechlorinating agents (sodium sulfite) are reactive with several of the gas chromatographable non-volatile chlorination byproducts. The analysis and identification of some of these compounds are presented along with discussion of their reactivity with sodium sulfite and the implications of these observations.

Our overall study has examined the nature of the precursors which react with aqueous chlorine to produce these halogenated compounds (26,27). We have also studied the effects of chlorination parameters such as pH (4-10), chlorine dose (carbon to chlorine ratio of 0.25-40), reaction time (15 minutes to 24 hours), and ammonia to chlorine ratio (0-7) on the formation of non-volatile chlorination byproducts, as well as possible treatment alternatives. These investigations involved approximately 500 different GC analyses, most of which were analyzed in duplicate. Due to the large number of samples analyzed GC/MS data was used sparingly.

EXPERIMENTAL METHODS

Water Samples

Most of the water samples used in this work were collected at a tertiary wastewater treatment plant in San Diego, CA. Water hyacinths, small fish and other aquatic organisms provide secondary treatment. Tertiary treatment includes reverse osmosis (RO) and granular activated carbon adsorption (GAC). Chlorination is only performed after GAC treatment. Details about the San Diego plant are presented elsewhere (27). Our data base is mostly comprised of samples collected at the San Diego plant, but are not limited to the San Diego plant and have been applied to other waters (26,27).

The chlorination byproducts and the effects of reducing agents on the these compounds were examined using four different types of samples. First, the chlorinated final effluent from the San Diego plant was analyzed before and after sulfite addition. Second, the carbon adsorption effluent (pre-chlorination water) was chlorinated in the laboratory with successful reproduction of most of the halogenated compounds observed in the plant's chlorinated final effluent. This laboratory chlorinated water was analyzed before and after sulfite addition. Third, concentrated aquaculture effluent extracts (concentrated by XAD8 adsorption) were chlorinated in the laboratory as 15 mL solutions (1 mg TOC). This chlorinated concentrated solution also reproduced most of the halogenated compounds observed in our study. Fourth, aqueous solutions of reagent grade halogenated compounds (purchased from chemical manufacturers) were reacted with sodium sulfite and analyzed by GC.

Collection of Organics

A modification of an extraction procedure previously developed to quantify total extractable organics in runoff waters was used (28). Details of the procedure are presented elsewhere (26,27). The water samples were adsorbed on XAD8 resin purchased from Rohm and Haas. The procedure used was a modified version of a protocol described by Thurman and Malcolm (29) for the collection of fulvic and humic acids. No humic/fulvic split was made. XAD8 collectible organics were used in the extract chlorination experiments.

In brief, the organics were extracted with methylene chloride and analyzed without derivitization on a 30 metre Supelcowax 10 fused silica capillary column. GC analysis was performed with a Varian Vista 6000 instrument equipped with both a flame ionization and an electron capture detector in a splitless mode. The two detectors work in parallel by means of an SGE fused silica splitter. GC/MS samples were run using the same capillary column. The MS instrument was a Finnigan 4000 series.

Chlorination of Samples

One litre volumes were used for all water sample chlorinations. The appropriate amount of calcium hypochlorite solution was added from a prepared and calibrated solution. A 4 mg/mL stock solution of $CaOCl_2$ was prepared in distilled water. The pH of the chlorinated water was then immediately adjusted with 1N HCl or 1N NaOH to the desired acidity. The pH adjustment was done in less than one minute.

The chlorinated solution was stirred in a constant temperature (25°C) bath for the appropriate time before extraction. The extraction and GC analysis proceeded as previously described. Sodium sulfite was only added in experiments where its potential effects were being tested. In such instances a 6 mg/mL solution was used.

Solvent extractable organics and XAD8 adsorbable organics from the test samples were subjected to chlorination as concentrated 15 mL solutions. One mg (measured as TOC) of XAD8 extract (procedure described below) was added to an appropriate amount of distilled water so that after addition of chlorine solution, the total volume was 15 mL. Chlorine was added as a 4 mg/mL solution followed by pH adjustment. The 25 mL flask was then stirred for the appropriate time before extraction.

Extractions were done in 60 mL separatory funnels. After the addition of NaCl and sulfuric acid, the reaction flask was rinsed with 25 mL of methylene chloride. The wash was added to the separatory funnel. The funnel was violently shaken by hand for one minute. The combined three extracts were evaporated and dried as previously described.

Addition of Sodium Sulfite to Pure Compounds

Approximately 5 mg of each pure compound was dissolved in 2.5 mL of water. Water insoluble compounds were dissolved in methanol and methanol solutions yielding 5 mg of the compound (usually 20 µl) were added to the water. A control (no sodium sulfite addition) sample was extracted with 5.0 mL CH_2Cl_2 for compounds eluting at temperatures higher than 75°C, and in 5.0 mL of pentane for early eluting compounds. The extraction was done in a 10 mL vial.

Sodium sulfite (greater than ten-fold excess) was added to an identical sample vial and the vial was allowed to stand at room temperature for 15 minutes before extraction. The control and sulfite containing sample were chromatographed at the previously described conditions. All samples were analyzed in triplicate.

RESULTS AND DISCUSSION

Extractable organics from various points around the San Diego wastewater treatment plant were initially analyzed, both gravimetrically and by gas chromatography. It became apparent that the treatment scheme at the plant performs quite well up to the point of chlorination. After chlorination one observes a significant increase in both flame ionization detector (FID) and electron capture detector (ECD) peak areas. The increase in ECD areas signifies the uptake of chlorine by carbon sources and the increase in FID area denotes that chlorination has broken down larger molecules which prior to chlorination were not amenable to GC.

These initial observations stimulated interest in investigating these non-volatile halogenated organics produced by chlorination, and the literature was more closely examined to determine the most well established analytical protocols. It is common practice to dechlorinate samples prior to their analysis. In an effort to conform to this practice, sodium sulfite was added to chlorinated samples prior to extraction. This practice, however, produced dramatically different chromatographs.

The two experiments using the chlorinated San Diego effluent and the laboratory chlorinated carbon adsorption effluent will be discussed together since they showed similar results. The chlorination of the XAD8 extracts and sulfite addition to pure compounds are discussed separately.

Chlorinated water samples

An abundance of new (not present in the unchlorinated water samples) halogenated organics were detected by GC and GC/MS after chlorination. Some of the compounds were identified by name, others were identified by molecular formula, and several other compounds were only identified by molecular weight or number of halogenated atoms in the molecule. Each sizeable ECD peak produced after disinfection, regardless of its level of identification, is given a reference number. Table I lists some of these compounds and their average approximate concentrations (calculated based on area responses of similar classes of compounds) throughout our two year sampling period at the San Diego plant (these concentrations should only be regarded as within one degree of magnitude). The identification of these compounds is tentative and our confidence in the identification is listed in Table I. Additional GC/MS analyses are currently underway to better identify these halogenated molecules.

Figure 1 (bottom) shows the GC output of the total extractable organics from the chlorinated San Diego final effluent without addition of sodium sulfite prior to extraction. Only new (formed during chlorination) peaks are labeled. Dichlorobenzenes and other chlorinated organics were present prior to chlorination (27) and are consequently not listed in Table I. Figure 1 (top) shows the GC output of a similar sample which was dechlorinated prior to extraction. The "A #" peaks are reactive with the sulfite ion and show considerable reduction in peak magnitude. The "D #" peaks, furan structures and phenols, are not affected. On several occasions, probably due to different chlorination conditions at the treatment plant, most of the compounds in the plant's chlorinated effluent were "A # " peaks. Under these latter conditions, dechlorination has a more pronounced effect.

The following generalizations can be made about the produced halogenated organics. First, in agreement with Coleman (14) and others (17-21) chlorinated aromatic compounds were observed. Second, many of the observed halogenated compounds are unsaturated and contain oxygen atoms. Some unsaturated halogenated compounds are reactive with dechlorinating agents which precludes their chromatographic identification.

Third, many of the compounds contain more than one chlorine atom and consequently produce much more response in the ECD than in the FID. Although the FID responds to all molecules, it gives the best response to carbon-hydrogen bonds. Since many of the observed halogenated organics are unsaturated (fewer carbon-hydrogen bonds) and are poly-chlorinated, this magnifies the difference between the response of the two detectors.

Fourth, the identified halogenated compounds most closely resemble the structures identified by Coleman, et al. (14). This probably results because Coleman did not add any dechlorinating agents to his samples prior to extraction.

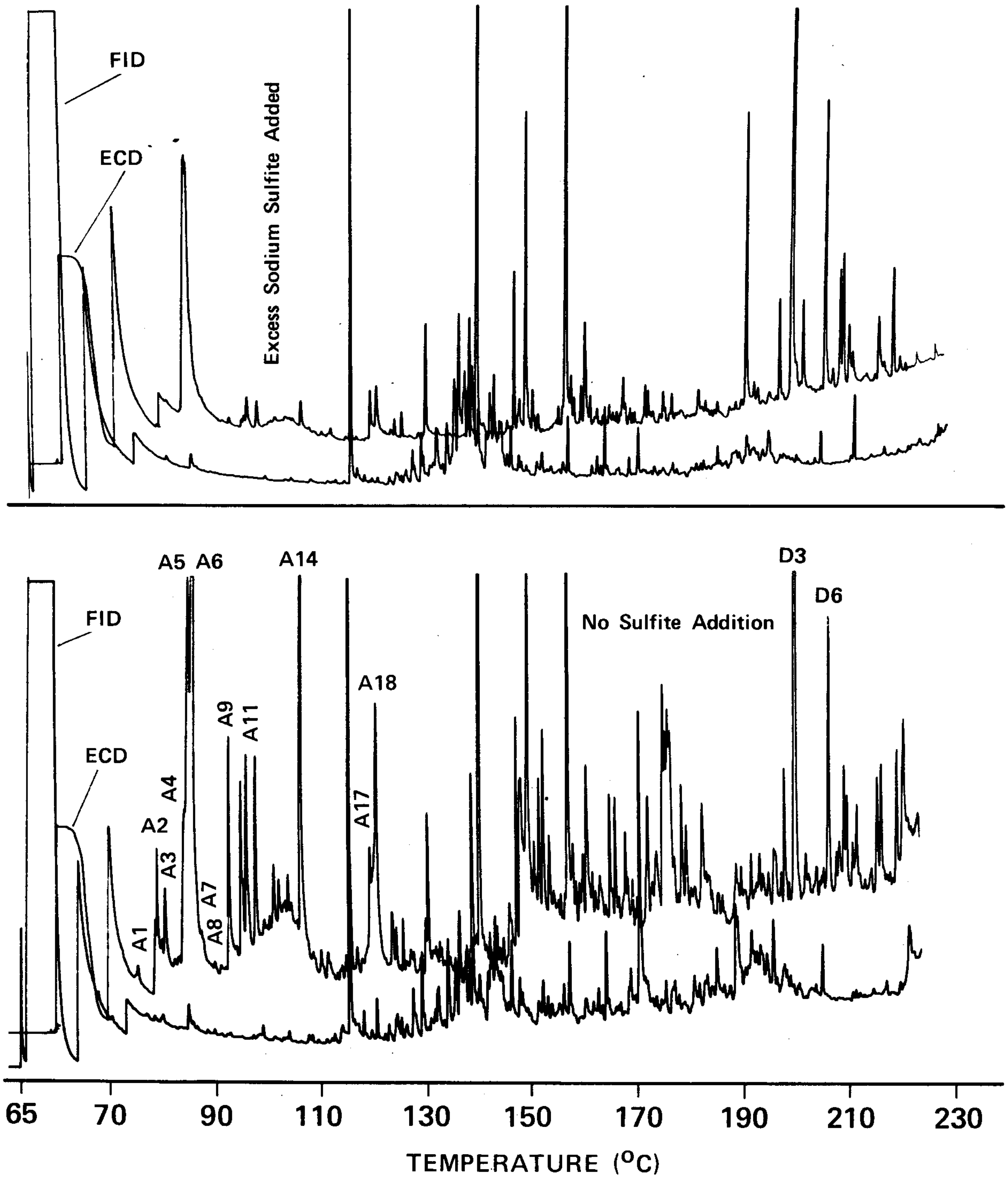

Fig. 1 GC's showing the effect of sodium sulfite on the chlorinated San Diego Wastewater Treatment Plant effluent. Top: excess sulfite added; bottom: no sulfite addition. GC conditions as previously specified. Axes labeled for ECD.

Table I Halogenated Compounds Produced during Disinfection

Identification	RT (min.)	Method of ID	% Confidence in ID	ref.	Concentration in chlorinated SD final effluent average (ppb)
chloroform	-	1,2,3	>95	E1	ND
chloro-bromomethane	-	1,2,3	>95	E2	ND
dichloro-propane	-	1,2	90	E3	ND
dichloro-cyclohexene	5.52	1,2	60	A1	3.1
unknown unsaturated chlorinated compound	6.39	-	-	A2	5.0
unknown	6.67	-	-	A3	0.5
chloro-iodo methane	7.80	1	>95	A4	0.8
2-propanone 1,1 dichloro	8.00	1,2	90	A5	5.7
2-propanone 1,1,1 trichloro	8.28	1,2	90	A6	10.0
C_3NCl_3	9.17	1	60	A7	0.7
1-propene 1,2,3,3 tetrachloro	9.46	1,2	80	A8	<.5
unknown	9.85	-	-	A9	<.5
unknown	9.91	-	-	A10	0.4
$C_4H_6Cl_3N$	10.64	1	60	A11	1.0
$C_5H_8Cl_2$	11.17	1	90	A12	2.9
MW 152, 2 chlorines $C_4H_2O_2Cl_2$	11.94	1	60	A13	0.3
$C_5H_3Cl_3O$	13.25	1	70	A14	4.6
cyclopentanol 1,2 methyl	14.24	1,2	90	A15	1.5
$C_5H_5Cl_3O$	15.25	1	90	A16	<.5
pentachloropropene	15.83	1	90	A17	1.5
$C_5Cl_3H_5O$	16.49	1	90	A18	3.3
MW 146, 1 chlorine	17.21	1	60	A19	3.1
benzaldahyde	17.63	1,2	90	A20	1.2
unknown	19.36	-	-	A21	4.2
1-hexanone,5 methyl,1-phenyl	22.48	1,2	70	A22	3.1
unknown halogenated aliphatic acid	22.64	-	-	A23	<.5
unknown	23.43	-	-	A24	<.5
unknown halogenated aliphatic. Formed mostly at high pH and low chlorine dose	25.54	-	-	A25	<.5
$C_4H_4Cl_4O$ (may be fragment of larger molecule) molecule	36.23	1	60	D1	ND

Table I Halogenated Compounds Produced during Disinfection (Continued)

Identification	RT (min.)	Method of ID	% Confidence in ID	ref.	Concentration in chlorinated SD final effluent average (ppb)
$C_4H_2Cl_4O$ (may be fragment of larger molecule)	36.25	1	60	D2	ND
C_4Cl_4O (may be fragment of larger molecule)	36.55	1	80	D3	8.9
2,4, dichloro-6-methyl phenol	37.43	1,2	90	D4	<.5
$C_8Cl_2OH_{14}$	38.60	1	30	D5	1.9
$C_8H_9Cl_2NO_2$	38.87	1	30	D6	7.6
$C_{10}Cl_2H_{12}NO_2$	39.55	1	30	D7	1.0
2,4,6 trichiophenol	40.61	1,2,3	>95	D8	2.8
dichloro-propyl phenol	41.61	1	70	D9	0.6
trichloro benzoic acid	42.89	1	60	D10	33.2
MW 232, 3 chlorines	44.12	1	60	D11	0.8
MW 230, 3 chlorines	45.15	1	60	D12	5.1
trichloro-phenol ethoxy	46.03	1	80	D13	5.8
unknown	47.59	-	-	D14	<.5

Key:

RT = retention time in minutes
ND = not determined
ref = reference number for compound for discussion in upcoming chapters
Scan No. = MS scan number
1 = manual interpretation of MS scan
2 = computer matched interpretation of MS scan
3 = GC retention time match with known standard
% confidence in ID = personal judgement
concentration = based on 10,000 area counts/ng for FID area. Concentration is the average for all samples collected at the San Diego plant. Concentration values should be regarded as ±100%.

Chlorination of XAD8 extracts

It was observed that XAD8 adsorbable organics from the the aquaculture effluent yield a very similar pattern of halogenated organics upon laboratory chlorination as the San Diego effluent. The chlorinated San Diego effluent contains many background organics as well as the chlorination byproducts. Since the XAD8 extract does not contain any background halogenated organics (they are not collected by the adsorption/desorption procedure), but contain most of the chlorination byproducts upon chlorination, it provides a simpler chromatographic system for the identification of the organic compounds produced during disinfection. In addition, it dramatizes the effects of dechlorinating agents. Figure 2 illustrates this observation.

The XAD8 extract was chlorinated under various pH conditions and with addition of bromide ion (1.0 mg TOC, 10.0 mg free chlorine, four hour contact time). Table II summarizes the results. The early eluting, "A #" peaks, are more affected by dechlorination. Although the percentage drop in total ECD area caused by dechlorination in the presence of bromide ion is less than the drop caused without bromide addition, the magnitude of the drop was more than twice that without bromide addition. It should be noted that the ECD detector does not give a linear response to compound concentrations nor to different halogenated compounds of the same concentrations. The observation that some compounds completely disappear after sulfite addition (Figure 2) however, renders the simplifying assumptions used in generating Table II forgivable.

Addition of Sodium Sulfite to Pure Halogenated Compounds

Eight classes of halogenated organics were treated with sodium sulfite prior to extraction from a prepared aqueous solution. Control samples were extracted under identical conditions minus the sodium sulfite addition step. Table III lists the classes of compounds used, the compound name and the average percent decrease in the integrator area of the compound caused by the addition of sodium sulfite. The decrease in the area of the compound implies that the compound reacted with the sulfite ion and consequently the area of the original compound (reactant) decreased.

The two unsaturated aliphatics (3-chloro-1-butene, and 3-bromo-propene) as well as chlorobenzene were the only three compounds which were reactive with sodium sulfite. Although this list of compounds is not exhaustive, it is still very informative.

It was predictable that chlorophenols, and halogenated saturated aliphatics would not be reactive with the sulfite ion since they have been successfully analyzed in the past by numerous workers. The presence of oxygen (aldehydes, phenols, and alcohols) or nitrogen atoms does not lead to reactivity with the sulfite ion. The three reactive molecules are unsaturated. Other unsaturated compounds, however, were unreactive (dichlorobenzenes) which means that the presence of a carbon double bond may be necessary, but is not sufficient to render the compounds reactive with the sulfite ion.

Although the exact reaction mechanism is unknown, stoichlometrically it is hypothesized that the sulfite ion displaces the halogen atom, forming a sulfonic acid (or possibly a di-sulfonic acid). Sulfonic acids are not methylene chloride extractable (too polar) and consequently do not appear in the gas chromatograms after sulfite addition. It is postulated that the reaction is a substitution and not an addition reaction because brominated compounds are more reactive with sulfite than chlorinated compounds. This is seen with 3-bromopropene and with the brominated compounds produced by the reaction with the XAD8 extracts. Bromide is a better leaving group than chlorine and is consequently more likely to undergo substitution reactions (30) A leaving group is the moeity in a molecule which is displaced during a reaction. The alkyl bromide ion is a fifty times better leaving group than the alkyl chloride ion. Figure 3 is a schematic of the postulated reaction between 3-bromopropene and sodium sulfite.

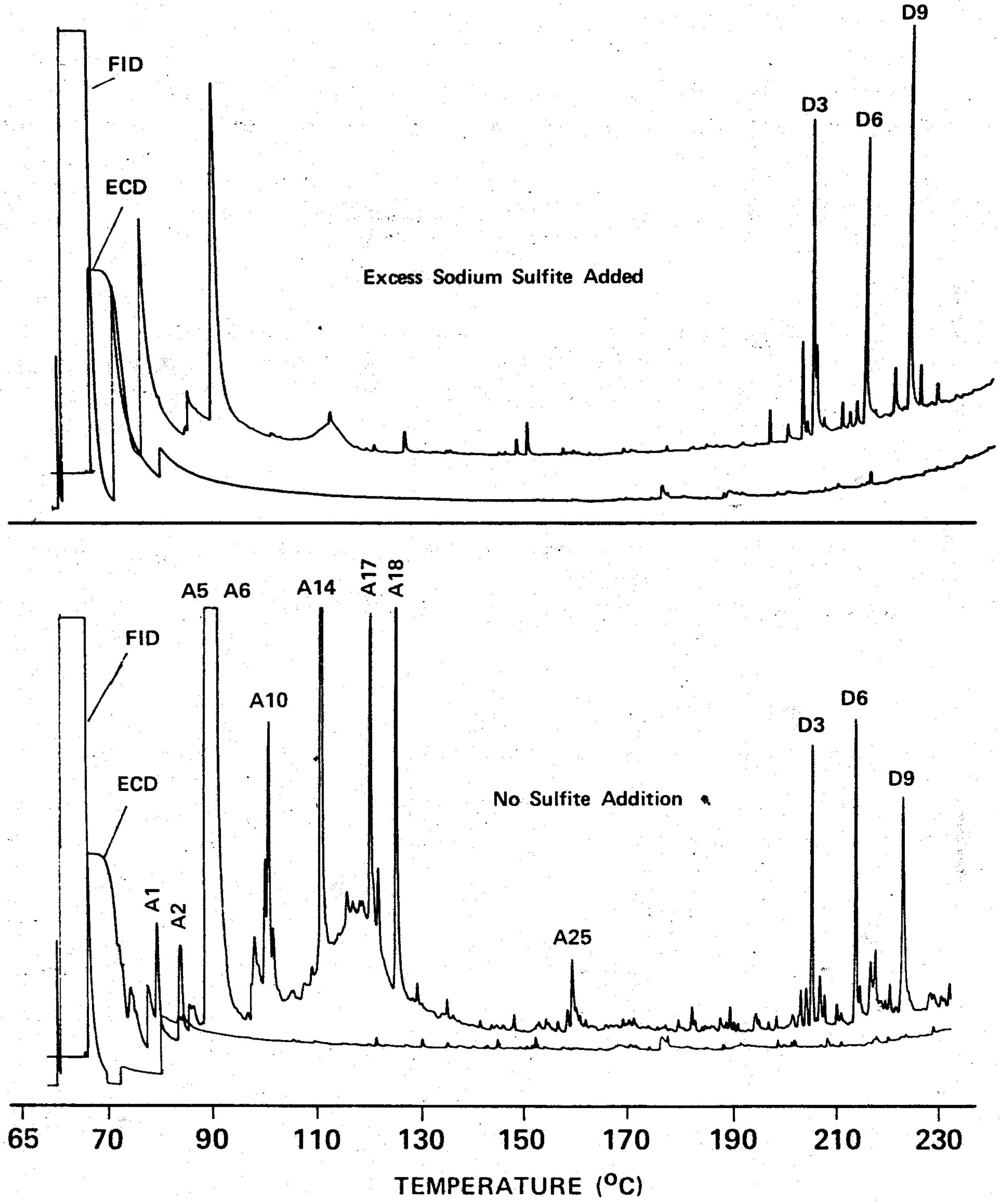

Fig. 2 GC's showing the effect of sodium sulfite on the chlorinated aquaculture XAD8 extract. Top: excess sulfite added; bottom: no sulfite addition. GC conditions as previously specified. Axes labeled for ECD.

Table II. Effects of Sodium Sulfite on Chlorinated XAD8 Extract

Conditions	Total ECD Area		Total ECD Area Eluting Before 20 minutes		Total ECD Area Eluting After 20 minutes	
(all for 4 hr contact and 10 mg Cl_2)	minus sulfite x 10^7	plus sulfite x 10^7	minus sulfite x 10^7	plus sulfite x 10^7	minus sulfite x 10^7	plus sulfite x 10^7
pH 3	6.0	1.7	4.5	1.1	1.5	0.6
pH 7	6.5	2.1	5.6	1.3	1.0	0.9
pH 11	6.9	1.8	4.1	0.9	2.7	0.9
5 mg Br, pH 7	22.0	12.0	18.0	9.2	4.0	3.4

Table III. Addition of Sodium Sulfite to Pure Compounds

Compound Name	Compound Class	% Drop Caused by Sulfite
o-chlorophenol	phenol	0
2,4,5-trichloro-phenol	phenol	0
2,4,6-trichloro-phenol	phenol	0
chloro-cyclohexane	cyclic aliphatic	0
bromo-cyclohexane	cyclic aliphatic	0
trichloroethane	straight aliphatic	0
chloroform	straight aliphatic	0
chloro-ethanol	alcohol	0
chloro-pyridine	nitrogen containing	0
bromo-analine	nitrogen containing	0
2,4-dichlorobenzaldehyde	aldehyde	0
2,4-dichlorobenzene	aromatic	0
1,3-dichlorobenzene	aromatic	0
1,4-bromochlorobenzene	aromatic	0
chloro-benzene	aromatic	31
3-chloro-1-butene	unsaturated aliphatic	26
3-bromo-propene	unsaturated aliphatic	95

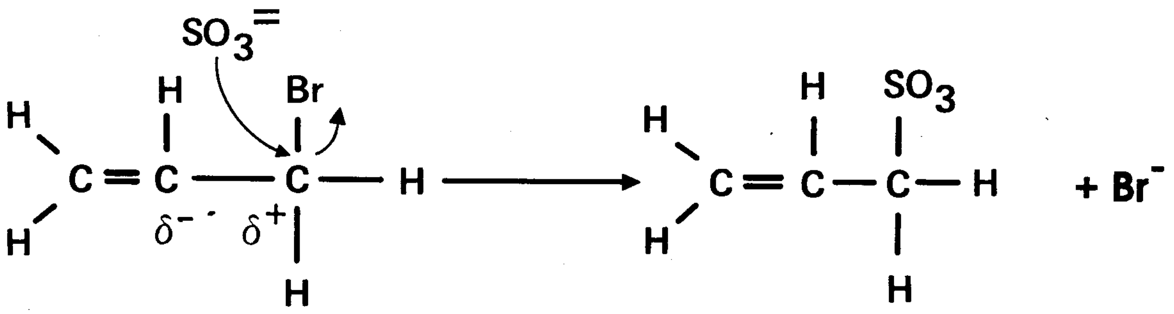

Fig. 3 Reaction of Sodium Sulfite with 3-Bromopropene

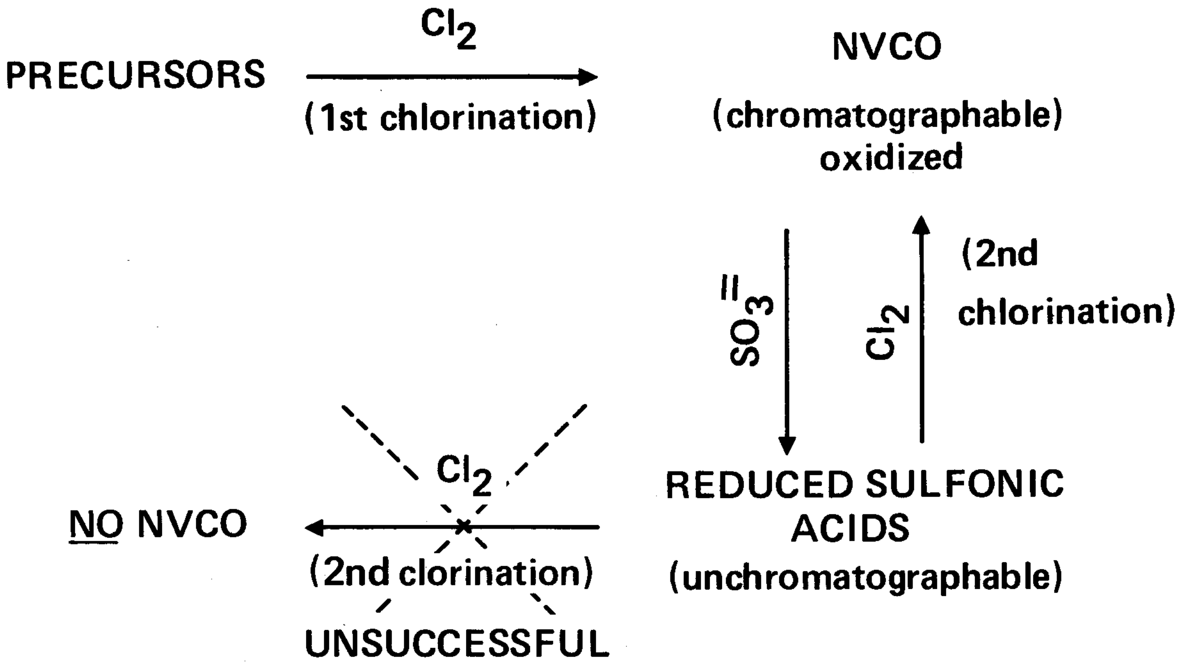

Fig. 4 Schematic of the Proposed 2-Stage Chlorination
(NVCO = non-volatile chlorinated organics)

The fast reaction of the sulfite ion with unsaturated carbonyl compounds was reported as early as 1966 (31) for applications of sulfur dioxide in the food processing and pharmaceutical industries. The reactions reported in this paper are very similar to these early observations.

Dechlorination as a Treatment Alternative

The discovery that sodium sulfite is reactive with some of the observed halogenated organics was initially very exciting as it appeared to be a method for their elimination. A two stage chlorination procedure was envisioned, whereby the first chlorination would produce the halogenated byproducts which would be partially eliminated by dechlorination. The second chlorination should not produce any chlorination products since the precursors would have been eliminated. This technique, however, has only been marginally successful. Apparently, the chlorination byproducts are reduced by sodium sulfite and rendered unchromatographable, but a subsequent chlorination oxidizes them to their previous chromatographable state. Figure 4 is a schematic of proposed reactions.

This procedure has been attempted many times with marginal success. The carbon adsorption effluent from the San Diego Wastewater Treatment Plant, as well as the aquaculture XAD8 extract were chlorinated. The initial chlorination (the precursor consumption step) was attempted at pH 3, 7 and 11. High chlorine doses (10, 20, 40 and 100 mg/L) were used as well as long contact times (4 to 24 hours). The high chlorine doses and long contact times were intended to maximize the reaction of the precursors with chlorine. The second chlorination was always done for two hours at pH 7 using a 10 mg/L chlorine dose. The second chlorination was also attempted using monochloramine. The chromatograph of this twice chlorinated extract was then compared to a sample which was chlorinated for two hours at pH 7 using a 10 mg/L chlorine dose. The sodium sulfite addition step was done at various pH values since the sulfite ion has different redox potentials at the various pH's. In summary, no set of conditions using either free chlorine or chloramine in the second chlorination step yielded any significant level of improved treatment.

Dechlorination has been shown to be a viable treatment for reducing the levels of the some of the produced halogenated compounds. Since it is often necessary to maintain a chlorine residual in drinking water and reclaimed wastewater, the effect of partial dechlorination on the observed halogenated organics was investigated. One litre of carbon adsorption effluent from the San Diego Wastewater Treatment plant was chlorinated using a 10 mg/L dose at pH 7 for two hours. The extractable organics were analyzed after partial and full dechlorination. Partial dechlorination (4 mg/L total available chlorine) resulted in a 65% decrease in the total ECD area and total dechlorination resulted in a 90% decrease in total ECD area. Partial dechlorination is consequently a desirable unit operation which is capable of significant reduction in the observed halogenated organics levels. This observation may be of practical value. If the sulfonated compounds are less of a health hazard than their halogenated counterparts, it may be advantageous to chlorinate under conditions which produce sulfite reactive compounds that may be partially reacted with dechlorinating agents. Cheh (22,23) has demonstrated the sulfite treated chlorinated waters show decreased mutagenic activity.

SUMMARY AND CONCLUSIONS

It was observed that many of the halogenated compounds produced during disinfection are reactive with dechlorinating agents. It is postulated that the sulfite ion undergoes a substitution reaction with halogen atoms. The most reactive group of compounds with the sulfite ion was found to be the unsaturated, halogenated aliphatics. The sulfite ion was shown to be reactive with aqueous solutions of pure unsaturated halogenated compounds.

If knowledge of the exact reaction time between chlorine and the TOC in the water samples is not required, then use of dechlorinating agents is unnecessary. Researchers who require exact knowledge of reaction times in their analytical laboratory experiments may remove residual chlorine by rotoevaporation (19) or perform the extraction in a time period which is small compared to the studied reaction times. Dechlorinating agents should only be added if the compounds of interest are not reactive with the sulfite ion. These results indicate that the TOX analysis underestimates the total halogenated organics concentration. Further analysis is being performed in the laboratory to quantify the underestimates.

The potential use of dechlorinating agents for reducing chlorinated organics in chlorinated water may be promising if the sulfonated compounds are not found to be a health hazard.

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