Environ. Sci. Technol. 1994, 28, 592–599

Multispectral Identification of Chlorine Dioxide Disinfection Byproducts in Drinking Water

Susan D. Richardson,* Alfred D. Thruston, Jr., and Timothy W. Collette

Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia 30605-2720

Kathleen Schenck Patterson and Benjamin W. Lykins, Jr.

Drinking Water Division, Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

George Majetich and Yong Zhang

Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556

This paper discusses the identification of organic disinfection byproducts (DBPs) at a pilot plant in Evansville, IN, which uses chlorine dioxide as a primary disinfectant. Unconventional multispectral identification techniques (gas chromatography combined with high- and low-resolution electron-impact mass spectrometry, low-resolution chemical ionization mass spectrometry, and Fourier transform infrared spectroscopy) were used to identify more than 40 DBPs in finished water at a chlorine dioxide pilot plant in Evansville, IN. Treatment variations included the use of liquid versus gaseous chlorine dioxide and the use of residual chlorine. Among the more unusual compounds identified were a series of maleic anhydrides, which are believed to have been formed from maleic acids during the extraction and concentration process, and halopropanones.

Introduction

Due to concern over trihalomethanes (THMs) in chlorinated drinking water (*1*), the U.S. Environmental Protection Agency (EPA) established a maximum contaminant level (MCL) of 0.10 mg/L for total THMs (*2*). To comply with this regulation, many drinking water utilities have had to alter their treatment methods (*3*). Consequently, many alternative disinfectants, including chlorine dioxide (ClO_2), are being explored. Primarily because chlorine dioxide does not produce the high levels of THMs observed with chlorine treatment, it has been listed by the EPA in a subsequent amendment to the THM regulation as a suitable alternative treatment method (*4*). Chlorine dioxide currently is used in more than 300 drinking water treatment plants in the United States and in several thousand plants in Europe (*5*).

In addition to reducing the levels of THMs significantly below the MCL, chlorine dioxide also is an excellent disinfectant; its biocidal efficiency is equal to or superior to chlorine. Also, chlorine dioxide is effective over a wide pH range and is five times more soluble in water than chlorine. Moreover, chlorine dioxide is effective for controlling taste and odor, which is the primary reason for its widespread use in Europe. Chlorine dioxide is effective for removing iron and manganese, and it does not react with amines to form chloramines. Finally, chlorine dioxide produces much lower total organic chlorine levels, as compared to those obtained with chlorination (*6*). Two excellent reviews on chlorine dioxide can be found in a journal publication by E. M. Aieta and J. D. Berg (*7*) and in a book by W. J. Masschelein (*5*).

Although the inorganic byproducts and volatile organic byproducts are reasonably well understood, very little is known about the semivolatile organic disinfection byproducts (DBPs) that are produced by chlorine dioxide treatment. Many laboratory reactions of chlorine dioxide with individual compounds and with fulvic acid have been carried out to propose possible DBPs (*5, 8,* 9), but few studies have been carried out at actual water treatment plants, where potentially many different organic precursors are present simultaneously. In the few studies conducted at actual treatment plants or pilot plants, only a very few DBPs have been reported (*10, 11*); in some cases, investigators reported that no detectable DBPs were formed by chlorine dioxide treatment (*3, 12*).

Because THMs and other volatile DBPs have been studied thoroughly, the goal of our work was to identify semivolatile, organic DBPs produced by chlorine dioxide treatment. To this end, samples were taken from a pilot plant in Evansville, IN, that uses various forms of chlorine dioxide treatment. These treatment variations included (1) liquid ClO_2, (2) liquid $ClO_2 + FeCl_2 + Cl_2$ + dual media filtration (sand and anthracite), (3) gaseous ClO_2, and (4) gaseous $ClO_2 + FeCl_2 + Cl_2$ + dual media filtration. Multispectral identification techniques were used to identify nonderivatized semivolatile byproducts in sample extracts. These multispectral techniques included gas chromatography combined with high- and low-resolution electron-impact mass spectrometry (GC/EI-MS), low-resolution chemical ionization mass spectrometry (GC/CI-MS), and Fourier transform infrared spectroscopy (GC/FT-IR). To our knowledge, this is the first such comprehensive study of its kind.

Rather than attempting to identify a few expected target byproducts, our objective was to identify every compound that was detected in the sample extracts. In most cases, the multispectral techniques afforded very precise identifications for the semivolatile byproducts. For those identifications not confirmed by standards, our confidence in the assignments is high, due to the wealth of spectral information used to make the identifications. More than 40 different DBPs were identified. Among the more unusual compounds identified were a series of maleic anhydrides, which are believed to have been formed from maleic acids during the extraction and concentration process, and halopropanones. Mutagenicity studies also were performed on these samples; the results from that work will be the focus of a separate publication.

0013-936X/94/0928-0592$04.50/0

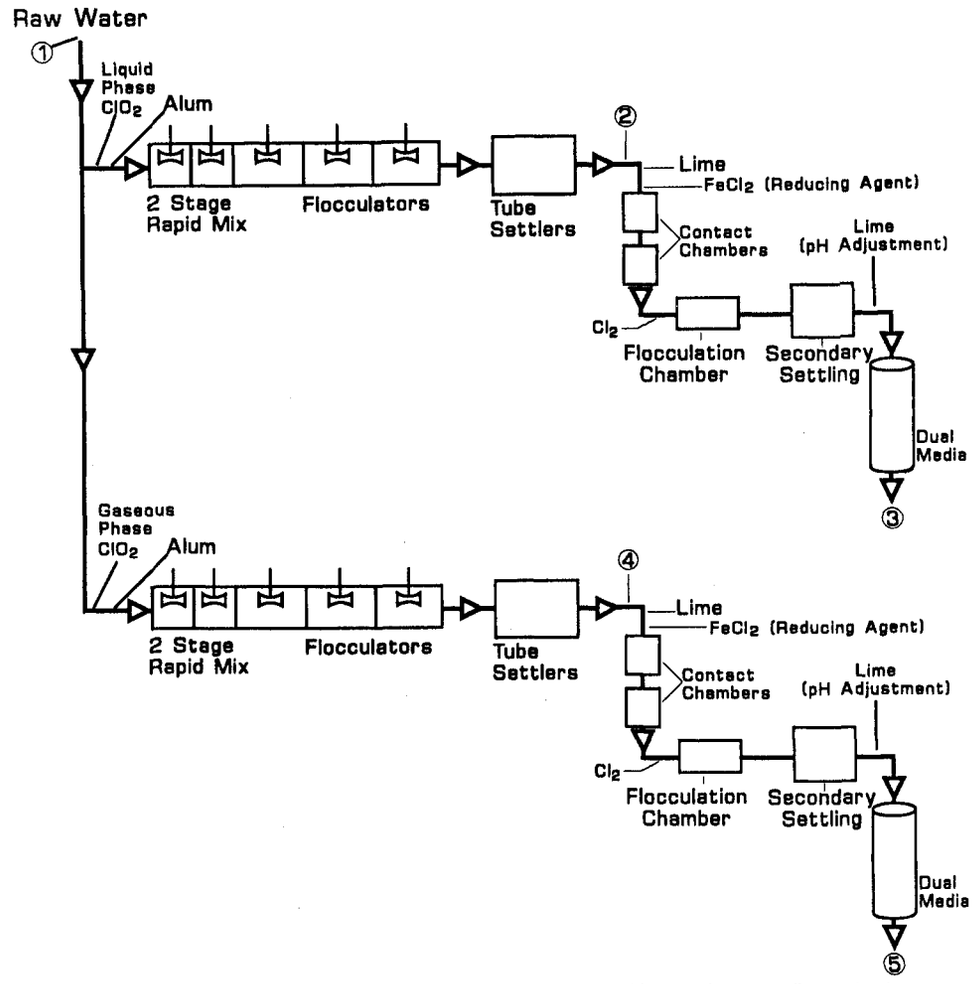


Figure 1. Chlorine dioxide treatment process at Evansville, IN, pilot plant (numbers identify five sampling points).

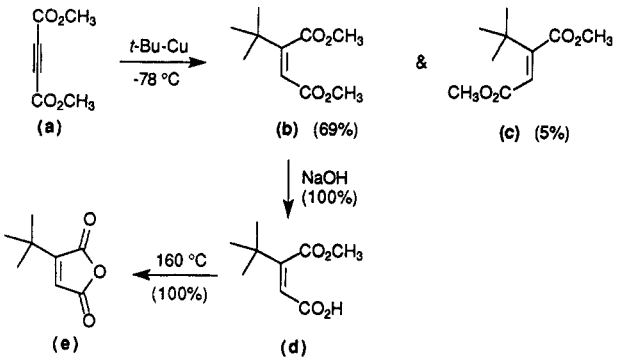
Experimental Section

Chlorine Dioxide Treatment and Sample Preparation. The treatment process and sampling points are shown schematically in Figure 1. At a pilot-scale drinking water treatment plant in Evansville, IN, raw river water (TOC = 1.5 mg/L) was sampled before disinfection (sample 1) and then after treatment with liquid chlorine dioxide (3 mg/L) (sample 2) or gaseous chlorine dioxide (3 mg/L) (sample 4). Chlorine dioxide residuals were 1.21 and 1.14 mg/L for samples 2 and 4, respectively. In the treatment process, both streams were clarified by the addition of alum and were treated with lime to maintain pH at 8.2–8.5. A reducing agent, $FeCl_2$ (0.1–1 mg/L) was added to control chlorite and chlorine dioxide concentrations. Sufficient chlorine was introduced to achieve a free chlorine residual ranging from 2 to 3 mg/L. A residual oxidant is needed to maintain disinfection in the distribution system. Samples 3 and 5 were collected following a final pH adjustment (pH 8.2–8.5) and filtration through dual media (sand and anthracite). Chlorine residuals for samples 3 and 5 were 2.0 and 2.4 mg/L, respectively. Chlorine dioxide was produced at the Evansville, IN, plant using an electrochemical generator (Olin Corp.).

The water samples were concentrated by adsorption on Amberlite XAD resins. Preparation of the resins included consecutive washes with 0.1 N NaOH, distilled water, and methanol. After washing, the resins were purified by consecutive, 24-h Soxhlet extractions with methanol, ethyl acetate, and methanol. Resins were stored in methanol at room temperature. Prior to use, the methanol was replaced by distilled water. After packing each column with resin, the columns were rinsed twice with 0.1 N HCl, followed by a single rinse with 0.1 N NaOH. A third acid rinse was followed by a distilled water rinse.

At the treatment plant, the water samples were acidified to pH 2 by the addition of HCl prior to passage through columns containing a combination of XAD-8 resin (65 mL) over XAD-2 resin (65 mL). Each column was eluted with approximately 400 mL of ethyl acetate. Residual water was removed from the ethyl acetate eluents by using separatory funnels to drain off the water layers, followed by the addition of sodium sulfate. After removal of a 100-mL aliquot for mutagenicity testing, the ethyl acetate eluents (equivalent to approximately 90 L of treated water) were shipped on cold packs to the Environmental Research Laboratory—Athens. At the laboratory, the samples were concentrated to 2 mL by Kuderna–Danish evaporation. Sample extracts were analyzed by GC/MS and GC/FT-IR after concentration and were stored under refrigeration when not in use. In addition to the raw water control, two solvent blanks also were analyzed: (1) 300 mL of ethyl acetate concentrated to 2 mL by Kuderna–Danish and (2) 400 mL of ethyl acetate passed through the XAD resins (followed by removal of a 100-mL aliquot for mutagenicity testing) and then concentrated to 2 mL by Kuderna–Danish. All chemicals and standards used were of the highest available purity.

Scheme 1



Synthesis of 2-*tert*-Butylmaleic Anhydride. The route for synthesizing 2-*tert*-butylmaleic anhydride (**e**) is shown above in Scheme 1 (*13*). Addition of the cuprate reagent derived from *tert*-butyllithium was added to dimethyl acetylenedicarboxylate to give diesters **b** and **c**, which were readily separable using silica gel column chromatography. Diester **b** was then saponified to give acid-ester **d** in high yield. Finally, heating **d** to 160 °C resulted in anhydride formation.

TOC and TOX Determinations. Total organic carbon (TOC) concentrations were determined using the persulfate–ultraviolet oxidation method, and the adsorption–pyrolysis–titrimetric method was used for total organic halide (TOX) analyses (*14*).

GC/MS Analysis. High-resolution GC/EI-MS analyses were performed on a VG 70-SEQ high-resolution hybrid mass spectrometer, equipped with a Hewlett Packard Model 5890A gas chromatograph. The mass spectrometer was operated at an accelerating voltage of 8 kV and at a resolution of 10 000. Low-resolution GC/MS analyses (EI and CI) were performed on a Finnigan 4500 mass spectrometer. Positive chemical ionization experiments were accomplished by using methane gas. Injections of 1–2 μL of the extract were introduced via a split/splitless injector onto a J&W Scientific DB-5 chromatographic column (30 m, 0.25 mm i.d., 0.25 μm film thickness). The GC temperature program consisted of an initial temperature of 35 °C, which was held for 4 min, followed by an increase at a rate of 9 °C/min to 285 °C, which was held for 30 min. Transfer lines were held at 280 °C, and the injection port was controlled at 250 °C.

GC/FT-IR Analysis. GC/FT-IR analyses were performed on a Hewlett Packard Model 5890 Series II GC interfaced to a Hewlett Packard Model 5965B infrared detector (IRD). Spectra were generated at 8 cm^{-1} resolution with a useful range of 4000–700 cm^{-1}. Injections of 2 μL of the extracts were introduced onto a Restek Rtx-5 column (30 m, 0.32 mm i.d., 0.5 μm film thickness) with a heated on-column injector (280 °C). The GC temperature program consisted of an initial temperature of 35 °C, which was held for 4 min, followed by an increase at a rate of 9 °C/min to 280 °C, which was held for 30 min. Transfer lines were held at 280 °C, and the light pipe was controlled at 280 °C.

Results and Discussion

Multispectral Identification. An example of one of the GC/MS chromatograms is shown in Figure 2 (sample 2, liquid phase ClO_2 treatment). Compounds that were found in the solvent blanks are labeled with asterisks. Most of these labeled compounds were due to ethyl acetate impurities and not due to artifacts obtained from the resin and equipment used. Although the ethyl acetate was of high purity, the large concentration factor of the solvent (150×) magnified the levels of impurities present. Evident from these chromatograms are the numerous byproducts that were produced by chlorine dioxide treatment. Table 1 lists the identifications we obtained and shows the different spectral techniques applied to identify each compound.

Although library database searching (both NIST and Wiley databases) was very useful for obtaining a "first guess" at an identification, it did not usually suffice by itself. Often, many similar library entries were obtained for a single unknown spectrum, preventing a definite assignment. For those cases, high-resolution EI mass spectrometry (HREI) was useful for determining empirical formulas for molecular ions and fragments, and IR defined functional groups present in the molecules. Other times, spectra did not contain molecular ions. Methane CI was necessary in those instances to determine molecular weights. When available, standards were purchased to confirm difficult identifications and to precisely determine a particular isomer, when spectra were not conclusive. In this way, GC retention times and spectra were matched with those of the unknowns.

Carboxylic Acids. Because GC/FT-IR is not commonly used together with MS techniques, several items are worth noting about its use for identifying compounds in these samples. First, it helped to uncover the 2-ethylhexanoic acid spectrum from an overlapping benzyl cyanide spectrum. By EI-MS, most carboxylic acids exhibit the characteristic ions m/z 60 and 73; however, carboxylic acids branched at carbon-2 do not show these distinctive ions, thus hindering an assignment of a branched acid when it is not well resolved from another co-eluting compound. Because IR spectra of carboxylic acids exhibit intense C=O stretching peaks in the 1785–1755 cm^{-1} range, we could easily distinguish 2-ethylhexanoic acid from the co-eluting benzyl cyanide. In addition to 2-ethylhexanoic acid, several other carboxylic acids were also identified. Although they were also present in the raw water, they appeared to be in greater concentration in the treated samples. In fact, carboxylic acids have been reported as byproducts of the reaction of fulvic acid with chlorine dioxide (*9*).

Maleic Anhydrides. GC/FT-IR also helped to identify an unusual series of maleic anhydrides. Their structures are shown below, and key IR absorbances are given in

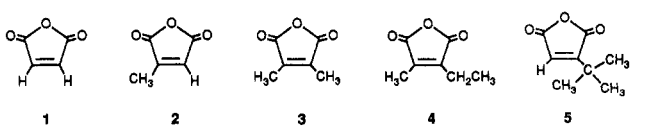


Table 2. By mass spectrometry, we had tentatively identified maleic anhydride (**1**), 2-methylmaleic anhydride (**2**), 2,3-dimethylmaleic anhydride (**3**), and 2-ethyl-3-methylmaleic anhydride (**4**). All four of these compounds were present in our mass spectral library database, and interpretation of high-resolution fragment ions, as well as molecular ions obtained by CI, was consistent with these assignments. In confirming the maleic anhydride (furandione) functional group for these four compounds, IR revealed an additional maleic anhydride in samples 2 and

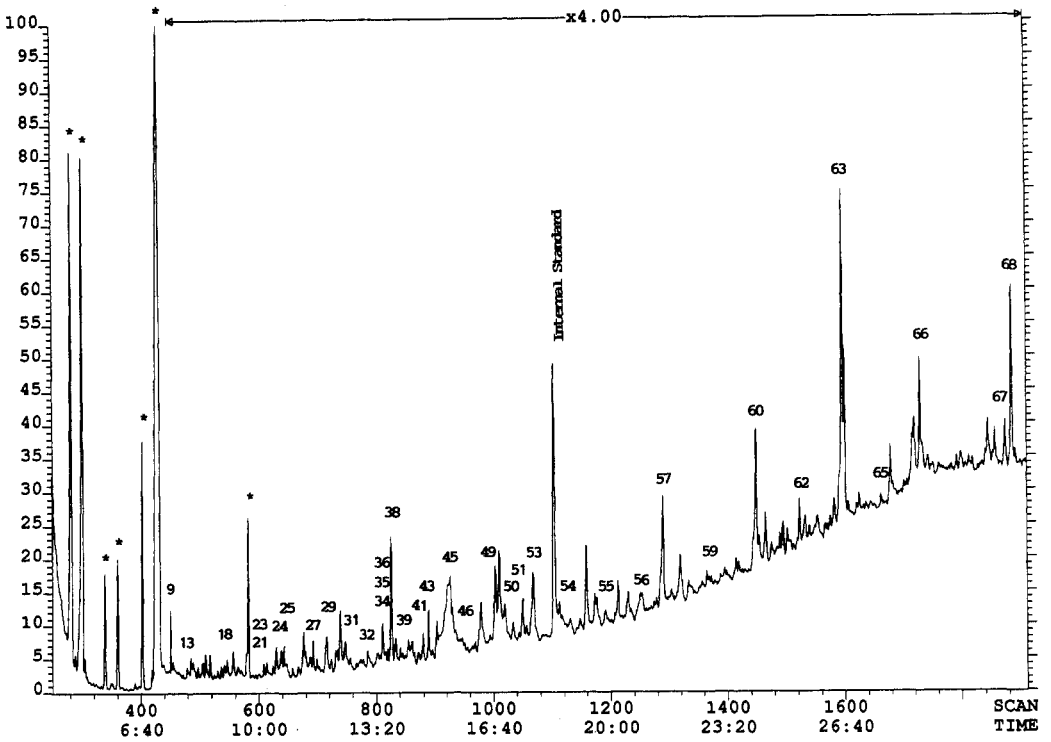


Figure 2. GC/MS chromatogram for sample 2 (raw water + liquid ClO_2).

4, subsequently identified as 2-*tert*-butylmaleic anhydride (**5**). Because there are no EI-MS ions that are consistent and characteristic for this series of anhydrides and because this compound was not in the library database, mass spectrometry could not by itself provide an identification. However, with additional information provided by IR and by the chromatography observed, we could identify this compound.

This anhydride, identified as 2-*tert*-butylmaleic anhydride (**5**), will serve to illustrate how we used multispectral techniques and spectral interpretation to identify compounds in these samples. Figure 3a shows the EI-MS spectrum obtained for this compound, the empirical formula assignments for fragment ions determined by HREI, and the molecular weight, as determined by CI-MS. Figure 3b shows the accompanying IR spectrum obtained, with key absorbances noted. Because the *m/z* 139 ion in the mass spectrum results from a loss of 15 mass units—a methyl group—from the molecular ion (*m/z* 154), the empirical formula for the molecular ion must be $C_8H_{10}O_3$.

Next, from the IR spectrum, we were able to determine the functional group. The two C=O stretching peaks noted in Figure 3b (1844 and 1787 cm^{-1}) are unusual and are very indicative of an anhydride in a five-membered ring (furandione). These two peaks are due to symmetrical stretching [ν_{sym} $(C{=}O)_2$] and asymmetrical stretching [ν_{asym} $(C{=}O)_2$] of the carbonyl groups in the planar O=C—O—C=O system. The loss of CO in the mass spectrum (*m/z* 154 → 126) is indicative of a carbonyl group and supports the functional group assignment by IR.

With the furandione base structure, there only remains the placement of four methylene/methyl groups. This limits the structure to a diethylmaleic anhydride, a methylpropyl- (or methylisopropyl-) maleic anhydride, a butylmaleic anhydride (*n*-butyl, isobutyl, *sec*-butyl, or *tert*-butyl), or a cyclohexane ring fused to the furandione ring. The latter structure was eliminated as a possibility after analysis of the commercially available standards, *cis*- and *trans*-1,2-cyclohexanedicarboxylic anhydride, showed different mass spectra and GC retention times.

From additional IR information, we were able to determine whether the furandione ring was monosubstituted or disubstituted. We have noted from the first four entries in Table 2 that, when X and Y substituents are similar electronically, the ratio of the intensities of the symmetric and asymmetric carbonyl stretching peaks (I_{sym}/I_{asym}) is considerably less than when X and Y are very different electronically. For example, when $X = Y = CH_3$ (**3**), $I_{sym}/I_{asym} = 0.06$; however, when $X = CH_3$ and Y = H (**2**), $I_{sym}/I_{asym} = 0.17$. As a result, monoalkyl-substituted maleic anhydrides have significantly higher I_{sym}/I_{asym} values than do dialkyl-substituted maleic anhydrides. Consequently, because **5** shows a $I_{sym}/I_{asym} = 0.15$, we propose that it is monoalkyl-substituted.

Knowing the structure must be a monoalkyl-substituted maleic anhydride, we must only determine the arrangement of carbons in the butyl substituent. Fortunately, we could gather additional information from an unusual chromatographic finding. This 4-carbon-substituted maleic anhydride eluted *before* the 3-carbon-substituted maleic anhydride (2-ethyl-3-methylmaleic anhydride, **4**) on a DB-5 column. When a less polar DB-1 column was substituted, these compounds co-eluted. The only reasonable explanation for this elution order is that **5** must be heavily branched, as branched compounds typically have lower boiling points and elute before their unbranched counterparts. A *tert*-butyl branch could sufficiently reduce the boiling point of this 4-carbon-substituted maleic anhydride, allowing it to co-elute with the unbranched 3-carbon-substituted maleic anhydride (**4**) on a DB-1 column, or to elute before Compound **4** on a DB-5 column. Also, a *tert*-butyl branch would be consistent with the lack of a significant molecular ion in the EI mass spectrum, as *tert*-butyl-substituted compounds commonly lose CH_3 groups to form the $(M - CH_3)^+$ ion and, consequently, do

Table 1. Compounds Identified in Samples 1–5

compound identified	EI-MS library match	HREI-MS	LRCI-MS	IR	standard confirmation	EPA regulated	sample 1[a]	2[b]	3[c]	4[d]	5[a]
1. bromodichloromethane	x				x	x	x		x		x
2. 1-chloroethanol acetate		x	x	x					x		x
3. dichlorobutanal[f]			x								x
4. carbon tetrachloride	x	x				x			x		
5. dibromochloromethane	x					x			x		x
6. 2,3,4-trimethylcyclopent-2-en-1-one	x	x								x	
7. 2-methylphenol	x						x				
8. 2-chloroethanol acetate	x								x		
9. butanoic acid	x			x				x	x	x	x
10. 3-methylphenol	x						x				
11. 1,1,1-trichloro-2-propanone	x	x	x	x	x	x			x		x
12. 4-methylphenol	x						x				
13. maleic anhydride	x	x		x	x	x	x	x	x	x	x
14. 3-bromopropyl chloromethyl ether[f]									x		x
15. 1-chloro-2-ethoxy-2-methoxy ethane	x								x		
16. bromoform	x					x			x		x
17. cyclohexanone	x					x			x		x
18. pentanoic acid	x			x				x	x	x	x
19. dibromochloroacetonitrile		x	x								x
20. dibromoacetonitrile	x								x		x
21. dimethylphenol	x						x	x		x	
22. 1-bromo-1,1-dichloro-2-propanone		x	x	x					x		x
23. 2-methylmaleic anhydride	x	x		x	x		x	x	x	x	x
24. 1,2,3,4-tetrachlorobutane	x						x	x	x	x	x
25. benzaldehyde	x						x	x	x		
26. chlorotribromomethane		x							x		x
27. hexanoic acid	x			x				x	x	x	x
28. 3,3,3-trichloro-2-methyl-1-propene	x								x		
29. 1,4-dichlorobenzene	x					x	x	x			x
30. 2-ethylhexanol	x				x				x		x
31. 2,3-dimethylmaleic anhydride	x	x		x	x		x	x	x	x	x
32. 1,1,3,3-tetrachloro-2-propanone	x	x	x	x				x	x	x	x
33. 2-chlorocyclohexanone	x		x						x		x
34. heptanoic acid	x			x				x	x	x	x
35. 3-ethyl styrene		x						x		x	
36. 4-ethyl styrene	x	x			x			x		x	
37. 1,1,1,3,3-pentachloro-2-propanone	x	x	x	x	x				x		x
38. 2-*tert*-butylmaleic anhydride		x	x	x	x			x		x	
39. 2-ethyl-3-methylmaleic anhydride	x	x	x	x				x		x	x
40. *tert*-butylphenol	x						x				
41. 2-ethylhexanoic acid	x			x				x	x	x	x
42. benzyl cyanide	x				x	x			x		x
43. 2,6,6-trimethyl-2-cyclohexene-1,4-dione	x	x		x				x		x	
44. ethylbenzaldehyde[f]	x									x	
45. octanoic acid	x			x				x	x	x	x
46. benzoic acid	x			x		x		x	x	x	x
47. naphthalene	x					x				x	
48. 2-methyl-3,3-dichloro-2-propenyl dichloromethyl ether		x	x	x					x		x
49. (1-chloroethyl)dimethylbenzene[f]	x							x	x	x	x
50. nonanoic acid	x			x				x	x	x	x
51. 2-methylnaphthalene	x							x		x	
52. 1-methylnaphthalene	x									x	
53. phthalic acid	x			x			x	x	x	x	x
54. decanoic acid	x			x				x	x	x	x
55. undecanoic acid	x			x				x	x	x	x
56. nonylphenol	x						x	x			
57. dodecanoic acid	x			x			x	x	x	x	x
58. octylphenol	x						x				
59. tridecanoic acid	x		x					x	x	x	x
60. tetradecanoic acid	x			x			x	x	x	x	x
61. decylphenol	x					x					
62. pentadecanoic acid	x			x			x	x	x	x	x
63. hexadecanoic acid	x			x			x	x	x	x	x
64. 4-dodecyl-5-ethyl-2(5*H*)furanone[f]		x	x	x					x		x
65. heptadecanoic acid	x			x			x	x	x	x	x
66. octadecanoic acid	x			x			x	x	x	x	x
67. hexanedioic acid, dioctyl ester	x							x	x	x	x
68. tris-(2-butoxyethyl)phosphate	x						x	x	x	x	x

[a] Raw water. [b] Raw water + liquid ClO_2. [c] Raw water + liquid ClO_2 + $FeCl_2$ + Cl_2 + dual media filtration. [d] Raw water + gaseous ClO_2. [e] Raw water + gaseous ClO_2 + $FeCl_2$ + Cl_2 + dual media filtration. [f] Tentative identification.

not usually exhibit molecular ions. Along with the previously discussed IR information, this MS and chromatographic information led us to identify **5** as 2-*tert*-butyl maleic anhydride.

Table 2. Important IR Absorbances for Maleic Anhydrides

compd no.	name	ν_{sym} (C=O)$_2$, cm^{-1}	ν_{asym} (C=O)$_2$, cm^{-1}	ν_{sym} C–O–C, cm^{-1}	ν_{asym} C–O–C, cm^{-1}	I_{sym}/I_{asym} (C=O)$_2$
1	maleic anhydride	1860 broad shoulder	1799	1284/1269/1231 multiplet	890	0.10
2	2-methylmaleic anhydride	1851	1793	1239	892	0.17
3	2,3-dimethylmaleic anhydride	1870	1786	1273	932	0.06
4	2-ethyl-3-methylmaleic anhydride	1853	1785	1280/1254 doublet	917	0.08
5	2-*tert*-butylmaleic anhydride	1844	1787	1249	900	0.15

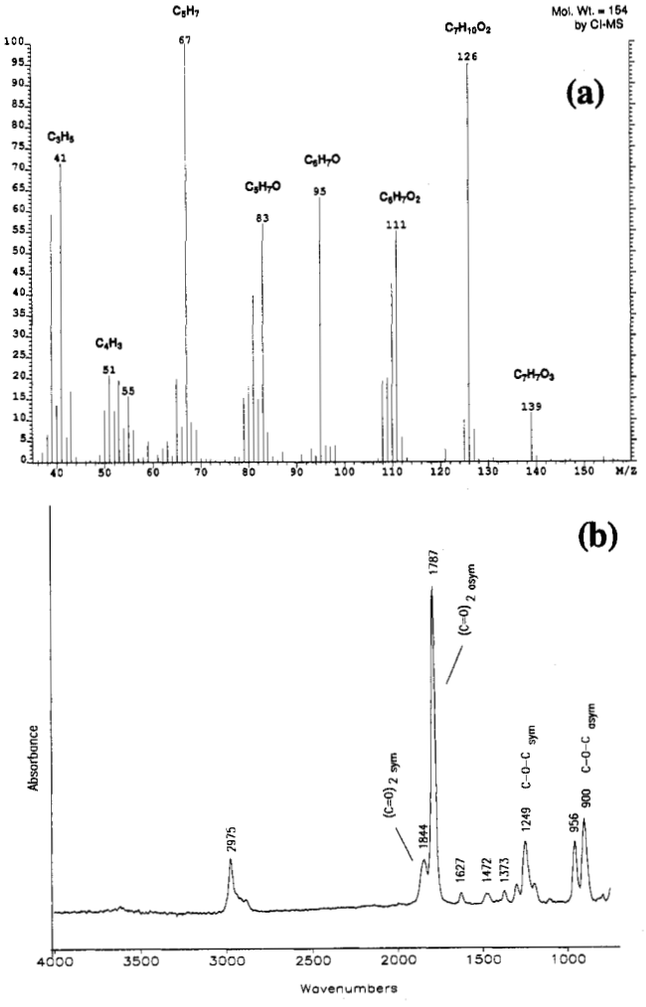


Figure 3. (a) EI mass spectrum and (b) FT-IR spectrum of compound identified as 2-*tert*-butylmaleic anhydride (**5**).

To confirm the identification of this unusual compound, we synthesized 2-*tert*-butylmaleic anhydride according to the procedure described earlier. The EI mass spectrum, FT-IR spectrum, and GC retention time of the synthesized standard perfectly matched that of **5**. Thus, its identity was confirmed.

Because maleic acids can be converted to maleic anhydrides when heated in a GC injection port, experiments were performed to determine whether 2-*tert*-butylmaleic acid was the actual DBP, and if so, at what stage it was converted to the anhydride. First, because anhydrides are generally not stable in water, the actual DBP would be expected to be the corresponding acid. To test this assumption, 2-*tert*-butylmaleic anhydride was dissolved in water (with methanol as a cosolvent) under acidic, neutral, and basic pH. As expected, this anhydride opened to 2-*tert*-butyl maleic acid at each pH within 2 h. Therefore, it is more likely that the actual DBP was 2-*tert*-butylmaleic acid. The common method for confirming the presence of an acid—methylation by diazomethane or BF_3/methanol—was ineffective in this case. Diazomethane was very effective for methylating the aliphatic carboxylic acids in the samples, but failed to methylate the maleic acids, probably due to the lack of solubility of the acids in the reaction solvent (ether). BF_3/methanol did methylate the maleic acids to form dimethyl esters, but unfortunately, methylation of the corresponding anhydrides produced the same dimethyl esters. Thus, the common methylation techniques could not be used to confirm that the actual DBP was the acid; however, it is likely that the actual DBP is the acid, due to its stability in water.

To determine at what stage the acid was converted to the anhydride, a cool on-column GC injection of the sample extracts (samples 2 and 4) was performed. Because this injection still yielded the anhydride and because solution phase IR and nuclear magnetic resonance (NMR) spectra indicate that the acid quickly converts to the anhydride at room temperature in ethyl acetate, we believe that the anhydride was formed during the sample workup, prior to injection onto the GC.

It is interesting to note that phenols are known to react with chlorine dioxide to form dicarboxylic acids, including maleic acid (*7*, *15*). Because phenols (including *tert*-butylphenol) were identified in the raw water, it is possible that phenols or phenolic groups attached to humic acid are the precursors to these maleic acids.

Halogenated Byproducts. Many halogenated byproducts also were identified in these samples (Table 1). Although we were not using specific methods to analyze for volatile compounds, we did observe a few trihalo- and tetrahalomethanes–bromodichloromethane, carbon tetrachloride, dibromochloromethane, bromoform, and chlorotribromomethane. It must be emphasized, however, that we cannot address concentrations of these halomethanes with any certainty, as the semivolatile method used here does not allow a complete recovery of volatiles. However, as is evident from Table 1, these halomethanes were only observed when a chlorine residual was added after ClO_2 treatment (samples 3 and 5) and were not observed when ClO_2 treatment was used alone (samples 2 and 4). This finding is consistent with previous studies that have shown that THMs were not produced when chlorine dioxide was reacted with humic acid (*7*) (without residual chlorine added).

In addition to halomethanes, a series of halopropanones also were observed—1,1,1-trichloro-2-propanone, 1-bromo-1,1-dichloro-2-propanone, 1,1,3,3-tetrachloro-2-propanone, and 1,1,1,3,3-pentachloro-2-propanone. Except for 1,1,3,3-tetrachloro-2-propanone, which was also produced by ClO_2 treatment (without residual chlorine added), all of the halopropanones were only observed when a chlorine residual was added after ClO_2 treatment. In fact, three of these halopropanones—1,1,1-trichloro-2-propanone, 1,1,3,3-tetrachloro-2-propanone, and 1,1,1,3,3-pentachloro-

2-propanone—have also been observed as byproducts of chlorination of drinking water (*16–18*) and humic acid (*19, 20*).

Effect of Chlorine Dioxide Treatment. Table 1 also shows the compounds present in the untreated raw water (sample 1). The TOC of the raw water was 1.5 mg/L and did not change much with treatment (1.6, 1.5, 1.5, and 1.3 mg/L for samples 2–5, respectively). Compounds that were not degraded by the chlorine dioxide treatment are evident in Table 1. The most noticeable of these compounds are the carboxylic acids. In fact, carboxylic acids have been shown to be generally unreactive toward ClO_2 in aqueous solution (*5*).

One observation that can be made, with regard to the different variations on chlorine dioxide treatment, is the striking similarity of byproducts produced in samples 2 and 4 and also the similarity of byproducts produced in samples 3 and 5 (Table 1). The types of byproducts produced, the relative amounts of byproducts produced, and the concentrations of TOX are very similar for these two sets of samples. TOX concentrations were 0.05 mg/L for samples 2 and 4 and were 0.11 and 0.10 mg/L for samples 2 and 4, respectively. As a result, it appears that the form of ClO_2 used is not important; both liquid and gaseous ClO_2 have the same effect, with respect to the formation of DBPs. However, the effect of adding residual chlorine, along with the reducing agent, $FeCl_2$, and dual media filtration is evident. A greater variety of byproducts appear to be produced for those samples (Table 1), including halomethanes, that can be attributed to the addition of residual chlorine.

Toxicity and Regulation. Of the compounds we identified that are regulated by the U.S. EPA, only two compounds—carbon tetrachloride and 1,4-dichlorobenzene—are regulated under the Safe Drinking Water Act and Amendments. Both compounds are known to be toxic and carcinogenic. Although many other compounds we identified are also toxic (e.g., benzyl cyanide) and mutagenic/carcinogenic (e.g., trichloro-, tetrachloro-, and pentachloropropanone) (*21–22*), they are not regulated by the U.S. EPA with respect to drinking water. Therefore, following EPA guidelines for drinking water analyses, these other toxic compounds would not be identified. Many of these compounds are regulated under other categories, including hazardous substances (Comprehensive Environmental Response, Compensation and Liability Act), extremely hazardous substances (Superfund Amendment and Reauthorization Act), wastewater (Resource Conservation and Recovery Act), hazardous substance discharge (Federal Water Pollution Control Act), and acute/chronic toxicity to freshwater organisms (Federal Water Pollution Control Act).

In addition, it is evident from Table 1 that numerous compounds identified in this study are not found on any list of EPA-regulated compounds. Although many of the compounds identified are known to be nontoxic, e.g., the fatty acids, there are many in Table 1 whose toxicity and mutagenicity/carcinogenicity are not known. If only two compounds present in the sample are identified—as would have been done using the list of compounds regulated for drinking water—proper risk assessments cannot be made. Proper risk assessments can only be made when all compounds present in the sample are identified.

Although many compounds identified in this chlorine dioxide-treated drinking water are known to be toxic, and many others are of unknown toxicity, all of the semivolatile compounds identified appear to be of extremely low concentration. It should be noted, however, that the methods used did not permit individual quantitation of very polar compounds (e.g., the maleic acids), which would require derivatization for accurate quantitation. Using the internal standard 2,2′-difluorobiphenyl, semiquantitative results indicated approximate concentrations of 1–10 ng/L (ppt) in the treated water for the DBPs. These levels appear to be much lower than those levels typically found for chlorinated drinking water samples (*23*). TOX concentrations (which would include volatile as well as semivolatile halogenated byproducts) were also lower for those samples treated with ClO_2 only (TOX = 0.05 mg/L for samples 2 and 4) than for those samples treated with ClO_2 + residual chlorine (TOX = 0.11 and 0.10 mg/L for samples 3 and 5).

Summary and Conclusions

Using multispectral identification techniques, we identified many byproducts produced by chlorine dioxide treatment of drinking water. To our knowledge, this is the first such comprehensive study of its kind. Because THMs and other volatile DBPs have already been thoroughly studied, the goal of our work was to identify semivolatile DBPs. We chose not to derivatize these samples because we wanted to determine precisely what the actual byproducts were, and we wanted to eliminate any speculation about what was actually formed as a DBP and what was formed after derivatization. Also, our goal was not to look at a few targeted DBPs but to identify every detected byproduct in the samples. It is likely that extremely polar compounds (as well as thermally labile and higher molecular weight compounds) escaped detection. However, we did identify several relatively polar acids, including phthalic acid (pK_{a1} = 2.89), benzoic acid (pK_a = 4.19), and butanoic acid (pK_a = 4.82). Thus, highly polar compounds that may not have been detected would be more polar than these, at similar concentration levels.

Overall, among the more interesting compounds identified were a series of maleic anhydrides, which are believed to have been formed from maleic acids during the extraction and concentration process, and halopropanones. In addition, several other halogenated byproducts were identified, including a few halomethanes that were produced when residual chlorine was used in treatment. Because these halomethanes were only formed when chlorine residuals were used, it is possible that the halomethanes can be totally eliminated by using a different residual disinfectant, e.g., monochloramine. Many of the byproducts identified in these samples are known to be toxic, carcinogenic, or mutagenic. However, the levels of all of the semivolatile byproducts appeared to be extremely low.

Acknowledgments

The authors wish to acknowledge the assistance of Mark Griese, manager of water quality and research for the Evansville Water and Sewer Utility, and Stevan Wells, pilot-plant operator. We would also like to acknowledge Robert Miller, John Glass, Sr., and David Cmehil for their efforts in the concentration of the water samples; George Yager for assistance with GC/FT-IR analyses; and Terrance Floyd for his assistance with diazomethane reactions.

Special appreciation is extended to Karen Wheless for experimental assistance in synthesizing 2-*tert*-butylmaleic anhydride. In addition, we wish to thank Dr. Don Gates of Rio Linda Chemical Co. and Dr. Robert Romano of the Chemical Manufacturers Association for providing considerable background information on chlorine dioxide treatment.

Literature Cited

(1) *National Cancer Institute Report on Carcinogenesis Bioassay of Chloroform.* Carcinogenesis Program, Division of Cancer Cause and Prevention: Bethesda, MD, Mar 1976.
(2) Symons, J. M.; Stevens, A. A.; Clark, R. M.; Geldreich, E. E.; Love, O. T., Jr.; DeMarco, J. *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*; U. S. Environmental Protection Agency: Cincinnati, OH; Sep 1981; EPA-600/2-81-156.
(3) Lykins, B. W.; Goodrich, J. A.; Hoff, J. C. *Aqua* **1990**, *39*, 376–386.
(4) *Fed. Registr.* **1983**, 48:40:8406.
(5) Masschelein, W. J. *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds*; Ann Arbor Science: Ann Arbor, MI, 1979; p 156.
(6) Eul, W. L. Applications of Chlorine Dioxide Produced from Sodium Chlorite in Europe. Presented at the conference on Chlorine Dioxide: Scientific, Regulatory and Application Issues, Denver, CO, Nov 1989.
(7) Aieta, E. M.; Berg, J. D. *J. Am. Water Works Assoc.* **1986**, *78*, 62–72.
(8) Gordon, G.; Kieffer, R. G.; Rosenblatt, D. H. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1972; Vol. 15, pp 201–286.
(9) Colclough, C. A.; Johnson, J. D.; Christman, R. F.; Millington, D. S. In *Water Chlorination, Environmental Impact and Health Effects*; Jolley, R. L., Brungs, W. A., Cotruvo, J. A., Cumming, R. B., Mattice, J. S., Jacobs, V. A., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; Vol. 4, Chapter 15.
(10) Stevens, A. A. *EHP, Environ. Health Perspect.* **1982**, *46*, 101–110.
(11) de Greef, E.; Morris, J. C.; van Kreijl, C. F.; Morra, C. F. H. In *Water Chlorination, Environmental Impact and Health Effects*; Jolley, R. L., Brungs, W. A., Cumming, R. B., Eds.; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 3, Chapter 79.
(12) Lykins, B. W., Jr.; Griese, M. H. *J. Am. Water Works Assoc.* **1986**, *78*, 88–93.
(13) Additional details are available upon request.
(14) *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; American Public Health Association: Washington, DC, 1989.
(15) Wajon, J. E.; Rosenblatt, D. H.; Burrows, E. P. *Environ. Sci. Technol.* **1982**, *16*, 396–402.
(16) Krasner, S. W.; McGuire, M. J.; Jacangelo, J. G.; Patania, N. L.; Reagan, K. M.; Aieta, E. M. *J. Am. Water Works Assoc.* **1989**, *81*, 41–53.
(17) Suffet, I. H.; Brenner, L.; Silver, B. *Environ. Sci. Technol.* **1976**, *10*, 1273–1275.
(18) Horth, H. *Aqua* **1989**, *38*, 80–100.
(19) Coleman, W. E.; Munch, J. W.; Kaylor, W. H.; Streicher, R. P.; Ringhand, H. P.; Meier, J. P. *Environ. Sci. Technol.* **1984**, *18*, 674–681.
(20) Reckhow, D. A.; Singer, P. C.; Malcolm, R. L. *Environ. Sci. Technol.* **1990**, *24*, 1655–1664.
(21) Bull, R. J.; Robinson, M. *Carcinogenic Activity of Haloacetonitriles and Haloacetone Derivatives in the Mouse Skin and Lung*; U.S. Environmental Protection Agency: Cincinnati, OH, Jul 1984; EPA-600/D-84-185.
(22) Theiss, J. C.; Stoner, G. D.; Shimkin, M. B.; Weisburger, E. K. *Cancer Res.* **1977**, *37*, 2717–2720.
(23) Keith, L. H.; Garrison, A. W.; Allen, F. R.; Carter, M. H.; Floyd, T. L.; Pope, J. D.; Thruston, A. D., Jr. In *Identification & Analysis of Organic Pollutants in Water*; Keith, L. H., Ed.; Ann Arbor Science: Ann Arbor, MI, 1976; Chapter 22.

Received for review May 17, 1993. Revised manuscript received October 20, 1993. Accepted January 7, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1994.