Journal of Chromatography, 449 (1988) 326–330
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 677

Note

Comparison of volatile halogenated compounds formed in the chloramination and chlorination of humic acid by gas chromatography–electron-capture detection

M. P. ITALIA* and P. C. UDEN*
Department of Chemistry, Lederle Graduate Research Tower, University of Massachusetts, Amherst, MA 01003-0035 (U.S.A.)

(First received March 23rd, 1988; revised manuscript received May 24th, 1988)

In recent years there has been a great deal of concern over the formation of trihalomethanes (THMs) from the chlorination of organic compounds in drinking water supplies[1,2]. An area of particular interest has been the chlorination of aquatic humic and fulvic acids[3,4]. Since Rook[5] first showed that THMs were formed from the chlorination of these substances, there have been hundreds of additional chlorinated compounds identified that are also formed from these humic precursors in the chlorination process[6–8]. The range of compounds identified includes halogenated aliphatic acids and aldehydes, haloacetonitriles, ketones and phenolic compounds. The latter aromatic compounds comprise a major non-volatile portion of the total organic chlorine content produced in the chlorination process which may also act as THM precursor material[9–11].

In the search for alternate methods of water disenfection, a popular alternative to chlorination is chloramination[12]. Because chloramine is a less vigorous chlorinating agent, the extent of trihalomethane formation is decreased. The production of chloramine involves addition of ammonia during the chlorinating procedure, according to the following reaction[13]:

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$

To determine what effect this change in the chlorinating processes had on the formation of halogenated substances from humic precursors, a comparison of the major products of chlorination and chloramination of a high-nitrogen humic acid was undertaken.

EXPERIMENTAL

Materials

Humic acid was obtained from Dr. Matvienko of the Universidad de Sao Paulo (Sao Carlos, Brazil), and had a composition of 35.08% carbon, 4.51% hydrogen and

---

* Present address: Union Carbide Co., Bound Brook, NJ 08805, U.S.A.

7.33% nitrogen. Hypochlorous acid (as 5% sodium hypochlorite), concentrated sulfuric acid, ammonia (as 3 *M* ammonium hydroxide), and diethyl ether were obtained from Fisher Scientific (Pittsburgh, PA, U.S.A.). A pH 7 phosphate buffer was prepared and used in all humic acid solutions. A 14% boron trifluoride–methanol solution, used as a derivatizing agent, was obtained from Supelco (Bellefonte, PA, U.S.A.).

Gas chromatography (GC) was performed using a Hewlett Packard 5794 instrument equipped with an electron-capture detector and a J&W Scientific (Folsom, CA, U.S.A.) 30 m × 0.2 mm I.D. DB-5 fused-silica capillary column.

Methods

Humic acid (100 mg) was added to each of two separate nitric acid washed 165-ml jars with crimp tops. To each was added 125 ml of 0.1 *M* phosphate buffer and the solutions were sonicated for 5 min to complete dissolution of the humic material.

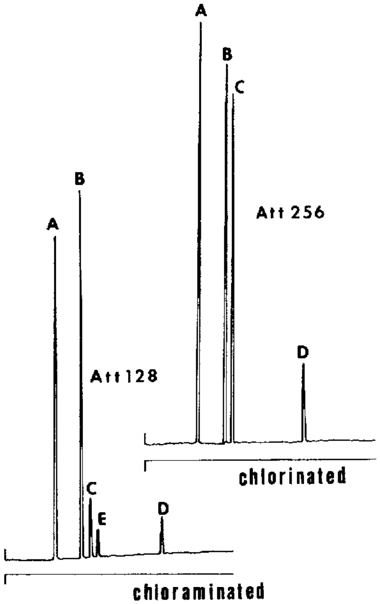
A solution of chloramine was made by adding 25 ml of hypochlorite to 11 ml of 3 *M* ammonium hydroxide to obtain a chlorine to ammonia molar ratio of 1:1.1. This procedure minimized dichloroamine formation and mimicked typical treatment at the chlorinating plant. This mixture was then iodometrically titrated to determine the amount of chlorinating agent present. Both the chloramine and hypochlorite chlorinating agents were then added to separate vials of the previously prepared humic solutions in quantities that would add equal amounts of reactive chlorine to each sample, and give a chlorine to carbon ratio of 5:1. The samples were then crimp sealed, placed in the dark and allowed to react for 24 and 48 h.

To determine the neutral compounds present after each time period a 4-ml aliquot of the solution was removed, placed in a small vial, quenched with a few granules of sodium thiosulfate and extracted with two 2-ml portions of diethyl ether. From this extract, 1 μl was diluted to 4 ml with diethyl ether and an injection of 2 μl made into the gas chromatograph. When acidic compounds were to be analyzed, the procedure was modified somewhat. A 4-ml aliquot was again removed, quenched, and placed in a small vial. At this point, a few drops of concentrated sulfuric acid was added to reduce the pH to less than 1 and the mixture was extracted with 4 ml of diethyl ether. Derivatization using boron trifluoride–methanol was carried out following the procedure described by Young[14]. The organic layer recovered was diluted (1 μl with 4 ml of diethyl ether) and a 2-μl injection made to the gas chromatograph.

In all analyses the GC conditions were as follows: nitrogen carrier gas, an injection port temperature of 225°C and an electron-capture detector temperature of 320°C. For the neutral fraction, the initial temperature was 40°C with a hold of 2 min, a temperature ramp of 5°C/min to a final temperature of 180°C followed by a 1-min final hold. For acidic analyses all conditions were identical except for a 50°C initial temperature. Injections were made on a DB-5 capillary column with a 50:1 split ratio and a 1-ml/min flow-rate. All output was to a Perkin Elmer Sigma 10 recorder/integrator.

RESULTS AND DISCUSSION

A GC comparison of the chlorination and chloramination of humic acid is shown for neutrals and acids (Figs. 1 and 2). The neutral fraction of both reactions



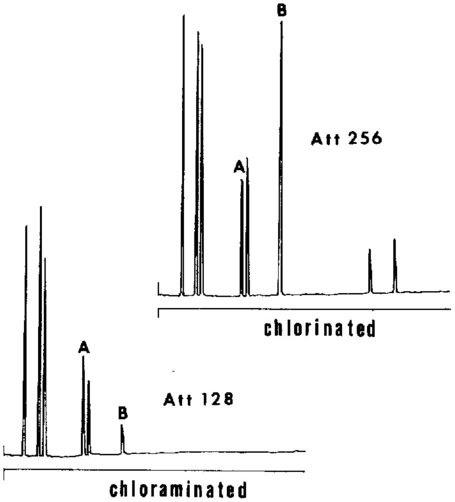


Fig. 1. GC with electron-capture detection of the neutral fraction of humic acid chlorination and chloramination. GC conditions: 40°C initial temperature, 2 min initial hold, 5°C/min temperature increase, 180°C final temperature and 1 min final hold. Column was a 30 m × 0.2 mm I.D. J&W DB-5 fused-silica capillary column with a flow-rate of 1 ml/min and a split ratio of 50:1. Attenuation of chlorinated (top) chromatogram is 256 and chloraminated (bottom) is 128. Peaks are identified as (A) chloroform, (B) dichloroacetonitrile, (C) trichloroacetaldehyde, (D) trichloroacetone and (E) unknown.

Fig. 2. GC with electron-capture detection of the acidic fraction of humic acid chlorination and chloramination after derivatization. All GC conditions are the same as in Fig. 1 with the exception of a 50°C initial temperature. Peaks are identified as methyl esters of (A) dichloroacetic acid and (B) trichloroacetic acid.

contained four chlorinated compounds formed from the chlorination of the humic material; chloroform, dichloroacetonitrile, trichloroacetaldehyde, and trichloroacetone. Upon examination of the neutral fraction (Fig. 1) it is seen that there is an overall decrease in the total halogenated material in the chloraminated sample (the attenuations were 512 for chlorination, 256 for chloramination). The most striking difference was the amount of trichloroacetaldehyde present; in the chloraminated fraction this was much reduced. It is also clear that dichloroacetonitrile is the predominant species in the chloraminated sample.

Examination of the chromatogram of the acidic fraction (Fig. 2) also shows a small amount of trichloroacetic acid (B, methyl ester), with dichloroacetic acid (A, methyl ester) as the dominant substance in chloramination. This is in contrast to the relative magnitudes of these compounds seen in chlorination. Quantitative results are given in Table I. After 24 h, chloramination has generated less than 40% of the total amount of these major halogenated compounds as produced by chlorination. This observation agrees well with the concept of chloramination; since it is a less vigorous chlorinating reagent, the multi-chlorinated species should not be produced as

TABLE I

COMPARISON OF THE AMOUNTS OF THE MAJOR CHLORINATED PRODUCTS OF HUMIC ACID CHLORINATION *VS.* CHLORAMINATION AT 24 AND 48 h

Values in parentheses are percentages of respective compounds to total chlorinated organics in that fraction.

	Chlorination		*Chloramination*		*Chlorination*	*Chloramination*
	24 h	*48 h*	*24 h*	*48 h*		
Neutrals						
Chloroform	0.177 (44)	0.48 (27)	0.036 (24)	0.081 (23)		
Dichloroacetonitrile	0.230 (56)	1.32 (73)	0.115 (76)	0.262 (77)		
Acids						
Dichloroacetic acid					0.094 (27)	0.092 (81)
Trichloroacetic acid					0.244 (73)	0.021 (19)

extensively. As can be seen, the amount of highly chlorinated compounds (as evidenced by trichlorinated species) in both the acidic and neutral fraction has decreased under chloraminating conditions. Trichloroacetaldehyde was not quantified in this study, but it is clear that there is a large decrease in the amount produced under chloraminating conditions.

If the quantitation of the neutral fraction is considered in terms of the relative proportions (peak heights) of chlorinated materials, there are further interesting observations. When the chlorinated humic acid sample was examined, the relative levels of chloroform and dichloroacetonitrile showed each to be present at approximately the same level (45 and 55%, respectively of the total level of these two compounds). However, the same computations performed on the chloraminated humic acid sample showed the relative proportions of dichloroacetonitrile as 76% and chloroform 24%. After 48 h the levels of both chloroform and dichloroacetonitrile in the chlorinated sample approached that of the chloraminated sample (in terms of relative compound proportions) but this is probably due to the greater continuing persistence of the chlorinating reagent. It is significant that while the absolute level of chlorinated species is diminished with chloramination, there is an increase in the fraction of neutral chlorinated organics present as the potentially harmful dichloroacetonitrile. There are two ways to explain these results. The first is that the additional dichloroacetonitrile is produced by direct action of the chloraminating reagent functioning to reduce the generation of trichlorinated species but still producing dichlorinated compounds at the same level. The second possibility is that alternative chemical reactions occur which are making the chloramine into a source of reactive nitrogen to produce dichloroacetonitrile. This study merits further investigation fully to evaluate chloramination as an alternative to chlorination. It must be confirmed that chloramination not only reduces the level of THMs, as is apparently the case, but that it does not cause other, potentially more hazardous, halo-organics to be formed.

ACKNOWLEDGEMENTS

This research was supported in part by the Geological Survey, US Department of the Interior through the Massachusetts Water Research Institute, by the 3M Corporation and the Dow Chemical Company.

REFERENCES

1 *The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Mehod,* U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, September, 1977.

2 J. Symons, T. A. Bellar, J. K. Carswell, J. DeMarco, K. L. Kropp, G. C. Robek, D. R. Seeger, C. J. Slocum, B. L. Smith and A. A. Stevens, *J. Am. Water Works Assoc.*, 67 (1975) 634.

3 J. J. Rook, in R. L. Jolley, W. A. Brungs and R. B. Cumming (Editors). *Water Chlorination: Environmental Impact and Health Effects*, Vol. 3, Ann Arbor Science Publishers, Ann Arbor, MI, 1979, pp. 85–98.

4 B. D. Quimby, M. F. Delaney, P. C. Uden and R. M. Barnes, *Anal. Chem.*, 52 (1980) 259.

5 J. J. Rook, *Water Treat. Exam.*, 23 (1974) 234.

6 R. F. Christman, J. D. Johnson, D. I. Norwood, W. T. Liao, J. R. Hass, F. K. Pfaender, M. R. Webb and M. J. Bobenrieth, *Chlorination of Aquatic Humic Substances*; U.S. Environmental Protection Agency Project Summary, EPA-600/s2-81-016, March, 1981.

7 K. P. Kringstad, P. O. Ljungquist, F. deSousa and L. M. Stromberg, *Environ. Sci. Technol.*, 17 (1983) 553.

8 E. W. B. de Leer, J. S. Damste, C. Erkelens and L. de Galan, *Environ. Sci. Technol.*, 19 (1985) 512.

9 S. Onodera, N. Iino, M. Matsuda and S. Ishikura, *J. Chromatogr.*, 265 (1983) 201.

10 S. Onodera, K. Yamada, Y. Yamati, S. Ishikura and S. Suzuki, *J. Chromatogr.*, 354 (1986) 293.

11 S. Boyce and J. Hornig, *Environ. Sci. Technol.*, 17 (1983) 202.

12 J. M. Symons, in R, L. Jolley, H. Gorchev and D. H. Hamilton, Jr. (Editors), *Water Chlorination: Environmental Impact and Health Effects*, Vol. 2, Ann Arbor Science Publishers, Ann Arbor, MI, 1978, pp. 555–560.

13 S. D. Faust and O. Aly, *Chemistry of Water Treatment*, Butterworth, Boston, MA, 1983, pp. 616–632.

14 M. S. Young, *Ph.D. Dissertation*, University of Massachusetts, Amherst, MA, 1988.