

Gas chromatography–electron-capture detection investigation of trihalomethanes produced by chlorination of humic acid in the presence of bromide

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ABSTRACT

Concern over the production of hazardous trihalomethanes (THMs) as byproducts of the chlorination of drinking water prompted the examination of the chlorination of naturally occurring aquatic humic acid in the presence of bromide ion. The effect on THM production of varying reaction conditions such as pH, chlorine-to-bromine ratio, and reaction time was investigated using gas chromatography–electron-capture detection. THMs were formed under all conditions examined, the production of highly brominated compounds being favored.

INTRODUCTION

There is an increasing awareness of the possible dangers inherent in chlorinated drinking water. There are a number of toxic and mutagenic compounds formed in the chlorination process [1,2]. While most studies have concentrated on the detection of chlorinated products, recent research has been directed towards the investigation of alternative reactions occurring due to the presence of other chemical factors in the environment.

Bromide ion, present in aquatic systems at levels of approximately 10 mg/l in ground water and possibly exceeding 100 mg/l in surface water [3], can be considered as a possible coreactant with chlorine. Bromide ion can react with hypochlorous acid to produce hypobromous acid, which then reacts with organic substrates in a manner analogous to hypo-

chlorite [4]. Thus, as Bunn *et al.* [5] have shown, there is the possibility for formation of trihalomethanes containing bromine, which are considered to be more hazardous to human health than their solely chlorinated analogs.

This study concerned the effect of bromide ion upon the products of the reaction of hypochlorite with a humic acid. Conditions of pH, reaction time and chlorine-to-bromine ratios were examined.

EXPERIMENTAL

Materials

Humic acid was obtained from B. Matvienko (Universidade de Sao Paulo, Sao Carlos, Brazil). This material had been obtained from a tropical aquatic source and was extensively purified by a procedure following that of Thurman and Malcolm [6]; this involved adsorption from filtered water on XAD-8 resin, elution with base, reacidification and reconcentration on XAD-8, a second base elution and precipitation at pH 1. Elemental analysis of this humic acid showed 35.08% carbon, 4.51% hydrogen and 7.33% nitrogen. The nitrogen level is great-

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er than typically seen in non-tropical source materials.

Potassium bromide (certified ACS grade) was obtained from Fisher Scientific (Pittsburg, PA, USA). Diethyl ether, ACS reagent grade (Fisher) was double distilled before use. Commercial "Chlorox" was used as the source of HOCl; prior to use it was standardized by sodium thiosulfate-iodine titration. Buffer solutions were prepared from ACS-certified-grade sodium phosphate (Fisher).

Gas chromatography

The gas chromatograph used was a Hewlett-Packard 5730 (Avondale, PA, USA) with an electron-capture detector. The carrier gas was nitrogen, with a detector temperature of 320°C and an injection temperature of 225°C. The temperature program involved an initial temperature hold of 2 min at 40°C, followed by a temperature ramp of 5°C/min to a final temperature of 180°C with a final hold of 1 min.

The column used was 30 m × 0.25 mm internal diameter DB-5 fused-silica capillary column (J & W Scientific, Folsom, CA, USA) with an inlet split ratio of 50:1. The output was to a Perkin-Elmer (Norwalk, CT, USA) Sigma 100 recorder/integrator.

Chlorination/bromination procedures

Halogenated compound formation studies vs. pH. Humic acid samples were prepared at pH values 4–9 in phosphate buffer (0.1 M), containing 400 mg/l of KBr. Samples of humic acid (100 mg) were added to each of five different water sampling jars equipped with crimp top seals. Approximately 160 ml of the buffer solution and 3.5 ml of HOCl (175 mg Cl) were placed in a beaker and the pH adjusted with small amounts of NaOH or HCl; this solution was then added to the 165 ml sampling jar which was then crimp sealed. This procedure ensured that each sample received the defined dose of HOCl and contained an equal amount of bromide ion. It also ensured that the hypochlorite and hypobromite had attained equilibrium before addition to the humic material. After reagent addition, the mixture was allowed to react for 24 h (except for the time-dependent study), then quenched, extracted and analyzed for trihalomethanes (THMs).

For analysis, the sample jar was opened and 25–50 mg of sodium thiosulfate were added to quench

residual reactivity of remaining HOCl and HOBr. A 4-ml aliquot of the solution was then removed, placed in a small vial and extracted with two 2-ml aliquots of diethyl ether. From this extract, 1 ml was diluted into 4 ml of diethyl ether and 2 µl samples were gas chromatographed (with a 50:1 inlet split). THM levels in the various analyzed samples were in the 10–100 ppm range; in all studies reagent and full method blanks were examined and predictably no measurable trihalomethanes were found.

THM formation vs. time. The procedure involved adding 100 mg humic acid, 25 mg KBr and 160 ml of 0.1 M pH 6 phosphate buffer to a 165-ml crimp top vial fitted with a resealable septum top. After adding 3.5 ml of HOCl, the vial was sealed and shaken. In sampling for gas chromatographic quantitation of THMs, 100-µl aliquots were removed and added to 4 ml of diethyl ether which contained 25–50 mg of sodium thiosulfite to quench the reaction. Sampling times during the reaction were after 4 min, 22 min, 45 min, 1.25 h, 2 h, 2.5 h, 5 h and 21 h.

THM formation vs. concentration of bromide ion. Studies were carried out with ca. 100-ml volumes of solutions in pH 6 phosphate buffer (0.1 M), using 165-ml crimp top vials. The total halogen level was kept at 0.021 M and the different molar ratios of Cl/Br were 1:1, 10:1, 50:1 and 100:1; the chlorine-to-carbon ratio was maintained at 5:1 to ensure complete reaction. The appropriate amount of humic acid was added to each of the vials followed by the calculated amount of bromide ion and HOCl, and the sample was allowed to react. After 24 h, 100-µl aliquots were removed and added to 4 ml of diethyl ether containing 25–50 mg of sodium thiosulfate.

RESULTS AND DISCUSSION

Standard compound analysis

Standards of the expected THMs were gas chromatographed to check for retention time (Fig. 1) and linearity of detector. Fig. 2 shows linear responses for the THM standards over the required experimental range.

Compound formation vs. pH

The results from the pH variation study are shown in Fig. 3. It can be seen that at low pH,

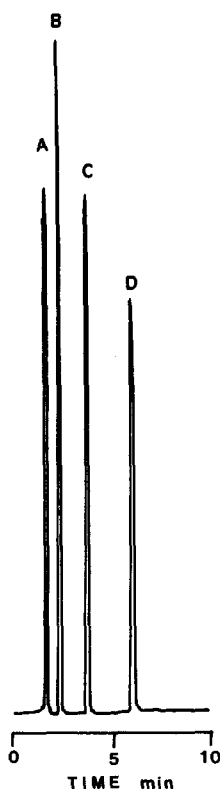
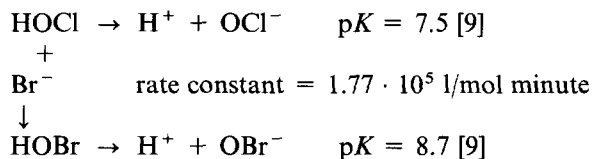


Fig. 1. Gas chromatography (GC)-electron-capture detection (ECD) chromatogram of the standard mixture of (A) chloroform, (B) bromodichloromethane, (C) chlorodibromomethane and (D) bromoform. GC conditions as given in the text. All compounds are at approximately 100- $\mu\text{g/l}$ level.

chloroform formation predominates. As pH is increased, bromoform formation begins to increase and eventually becomes dominant, to the point where it contributes more than 90% of the total trihalomethanes formed. This observation is in contrast to other studies which show chloroform formation to increase with increasing pH [7,8], but these involved only reaction of hypochlorous acid with the humic molecule and did not consider bromide and the impact of the additional hypochlorous/hypobromous equilibrium:



Wong and Davidson [10] showed that this reaction is so predominant that when hypochlorite is added to a bromide-containing mixture in a ratio of less than 1:1, all HOCl is converted to HOBr in under 2.5 min. It has been shown that the reaction of hypobromous acid with many compounds is faster than the hypochlorous acid reaction with the same species [11].

THM formation vs. time. As can be seen in Fig. 4, chloroform was produced to the greatest extent within the first few minutes of reaction, with other THMs being slower to form. However, the formation of each THM then follows the general path of the chloroform formation, with some early reduction in measure levels which is probably due to measurement imprecision, and maintains a constant but lower level for the remaining time period of the study. The order of amount formed is bromoform, chlorodibromomethane and bromodichloromethane. As can be seen, there are no relative changes in compound ratios, implying that once the THM is formed it is not a precursor to further compound formation.

Bromide concentration study

Fig. 5 shows the results of the bromide concentration study. At high levels of bromide ion (Cl as HOCl/Br ratio = 1) bromoform and chlorodibromomethane formation dominate. This is consistent with the hypochlorite-to-hypobromite transformation, producing more hypobromite than hypochlorite. As the concentration of bromide is lowered (increase in Cl/Br ratio) there is a significant drop in the di- and tribrominated species, the chlorinated compounds beginning to predominate. It is noteworthy that the levels of these chlorinated compounds (expressed as mole percents) do not rise to the levels of the brominated compounds. This is presumably because, even when a small amount of bromide is present, the system equilibrium enhances hypobromite production, thus favoring brominated products.

CONCLUSIONS

With the concern over the availability of clean drinking water, and the equal need to determine the level of pollutants in the water supply, it has be-

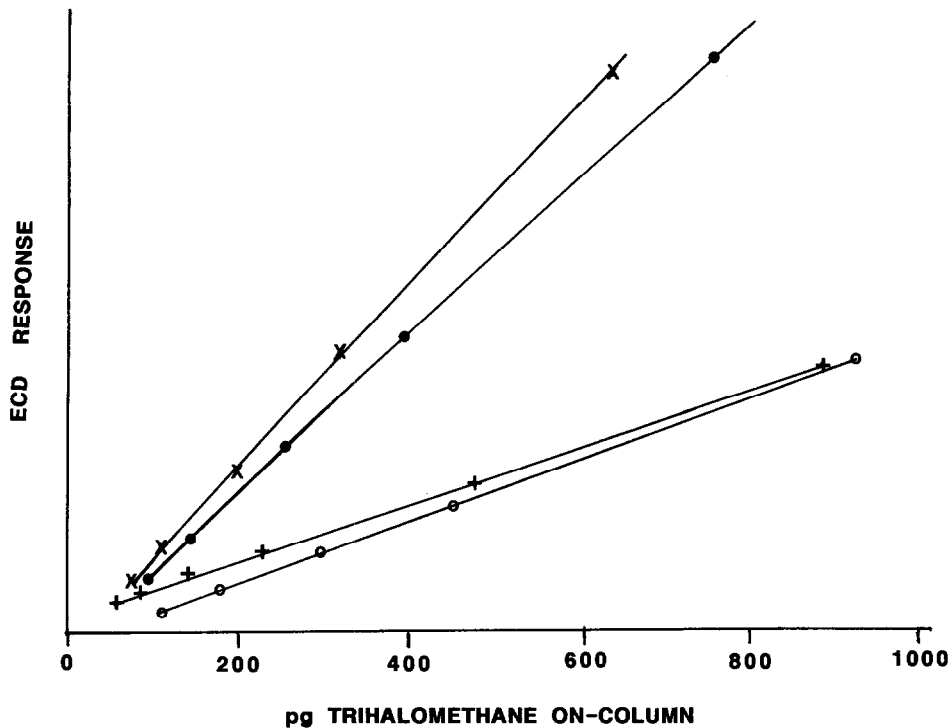


Fig. 2. GC-ECD linearity study and calibration curves for standards: chloroform (+), bromodichloromethane (x), chlorodibromomethane (●) and bromoform (○). All chromatographic conditions are as in the text.

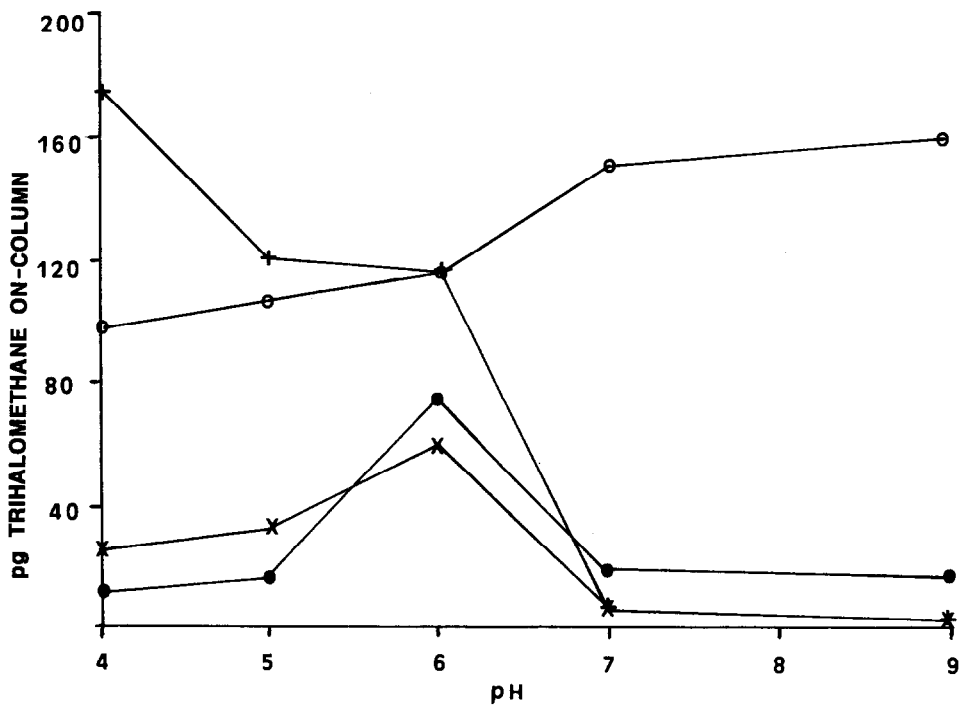


Fig. 3. Study of trihalomethane formation with respect to pH. Plot is of detected quantities of chloroform (+), bromodichloromethane (x), chlorodibromomethane (●) and bromoform (○). Quantitation was performed using GC-ECD with all chromatographic conditions as in the text.

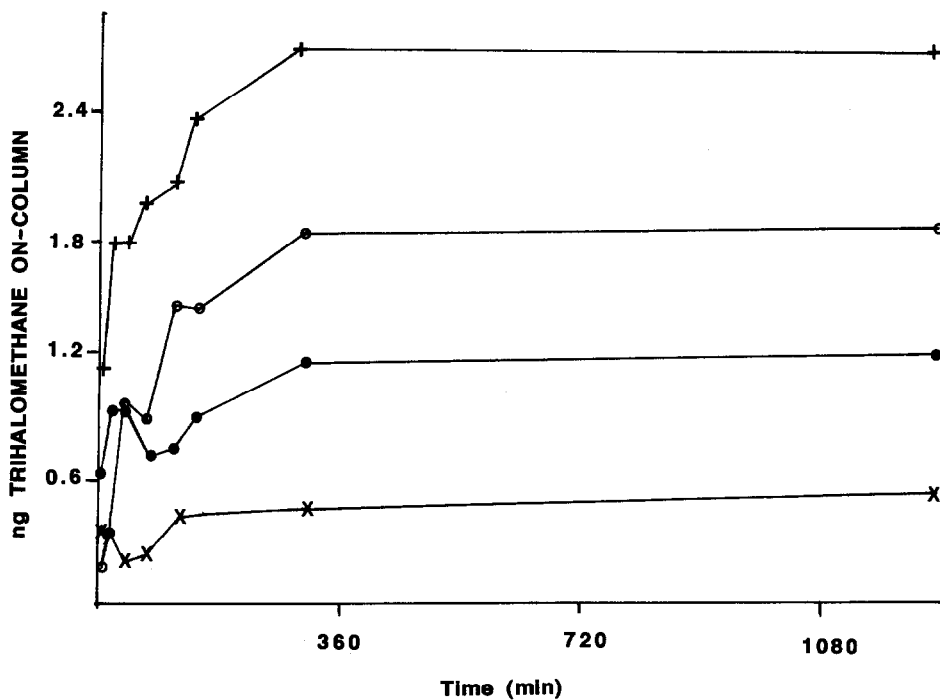


Fig. 4. Time-dependent study of trihalomethane formation with respect to the halogenation of aquatic humic acid. Symbols: + = chloroform; x = bromodichloromethane; ● = chlorodibromomethane; ○ = bromoform. Quantitation was performed using GC-ECD with all chromatographic conditions as in the text.

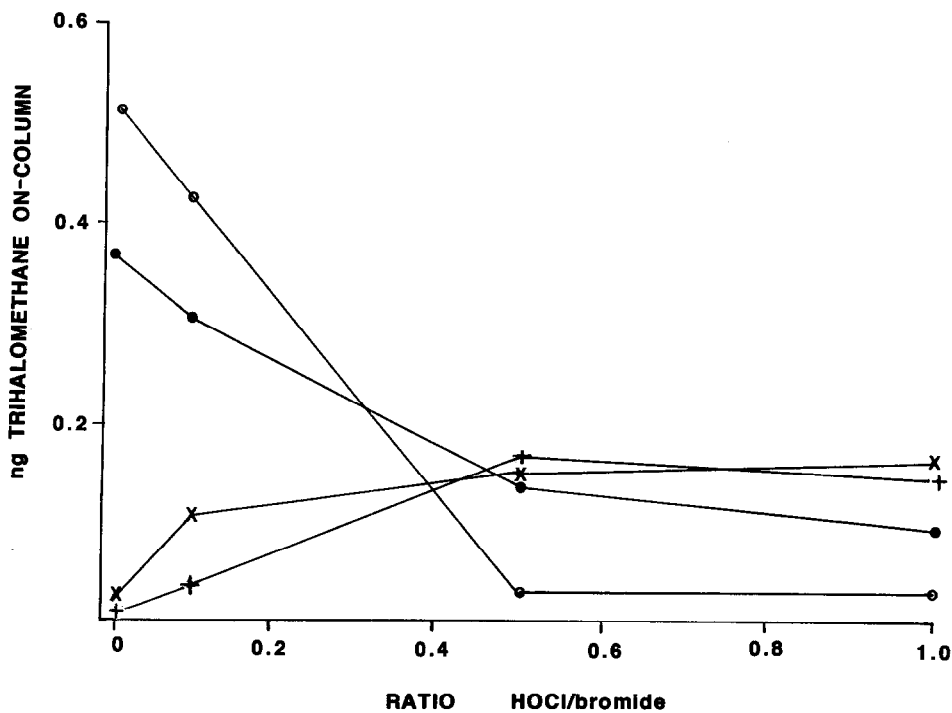


Fig. 5. Chlorine (as HOCl)-to-bromide ratio (M/M) study of trihalomethane formation from the halogenation of humic acid. Symbols: + = chloroform; x = bromodichloromethane; ● = chlorodibromomethane; ○ = bromoform. Quantitation was performed using GC-ECD with all chromatographic conditions as in the text.

come important to identify which pollutants are present from a waste disposal process and which ones may have occurred due to the water purifying process itself. It has long been known that the chlorination process itself is capable of producing chlorinated organic byproducts when water is cleansed. It appears that brominated compounds, which are detrimental to human health, are formed faster than and preferentially to chlorinated compounds. It is also important to note that these compounds are formed in the pH range at which drinking water chlorination occurs.

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