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CATALYTIC DEGRADATION OF TRIHALOMETHANES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The chlorination of waters containing humic and other organic substances leads to the formation of trihalomethanes (THMs). These compounds are suspected carcinogens and pose a health hazard. Their formation and removal after chlorination is of interest to the Army because of the exclusive use of hypochlorite for disinfection. This paper describes studies on the removal of trihalomethanes from water using catalytic degradation. Of the several metals and metal oxides studied, Zn was found to be a superior catalyst. In the presence of Zn powder and $2.5 \times 10^{-4}$ M $H_2$ gas.		

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20. Abstract (continued)

four THMs ( $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$ ) all appear to dehalogenate in a relatively short period of time. The formation and degradation of reaction intermediates are discussed. Originator supplied keywords include:

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## INTRODUCTION

In the past several years, it has become apparent that trihalomethanes (THMs) are present in our water resources. The main sources of these compounds are from industrial spills and wastes, and through the chlorination of drinking water and sewage effluent. A median concentration of total THMs in drinking water of 28  $\mu\text{g/L}$  and concentrations as high as 427  $\mu\text{g/L}$  have been reported.<sup>1</sup> The reason for so much concern over THMs in drinking water stems from the fact that they are considered carcinogens and, hence, pose possible adverse health effects.<sup>2,3</sup> According to Rook,<sup>4</sup> THMs are formed from the chlorination of naturally occurring humic substances found in surface waters. Several possibilities exist for eliminating THMs in drinking water:

- Reduce the amount of humic and other organic precursors before chlorination. Examples of this are coagulation procedures<sup>5</sup> and chemical addition for oxidation of humic substances.<sup>6,7</sup>

- Use nonhalogen disinfectants such as ultraviolet light or ozone. Although these methods work well, they tend to be expensive and they do not leave a protective residual.

- Remove the THMs after the chlorination step by using activated carbon, resins, or aeration procedures.

Since chlorination of drinking water seems to be the most cost effective and easiest method of disinfection, methods for the physical and chemical removal of THMs may be the most practical. In reviewing some of these methods, Symons et al.<sup>8</sup> report powdered activated carbon as not effective for THM removal, granular activated carbon has a short service life, and resins are not readily available commercially; however, aeration is a feasible and effective method for THM removal.

The approach studied in this laboratory for removing THMs from water involved catalytic degradation by replacement of halogen atoms with hydrogen atoms.

## EXPERIMENTAL

### CHEMICALS

Stock solutions of THM were prepared by dissolving a weighed amount of THM into 10 mL of pesticide-grade methanol (Burdick-Jackson). Reagent grade chloroform,  $\text{CHCl}_3$ , (99.5%) was obtained from J.T. Baker Chemical Co. Bromodichloromethane,  $\text{CHCl}_2\text{Br}$  (97%), dibromochloromethane,  $\text{CHClBr}_2$  (98%), and bromoform,  $\text{CHBr}_3$  (96%) were supplied by Aldrich Chemical Company. Aliquots of the stock THM solutions were diluted in double-distilled water and extracted with nanograde pentane (Mallinckrodt, Inc.). Several metal catalysts which reduced all of the THMs, except  $\text{CHCl}_3$ , were  $\text{TiO}_2$ , Pt (foil), and Sn (mossy); however, early experiments indicated Zn to be the best choice for

degrading THMs. Thus, the degradation study used 200 mesh Zn obtained from the J.T. Baker Chemical Co.

#### PROCEDURE

The pH of a 1 liter 0.05 M  $\text{NaH}_2\text{PO}_4$  solution was adjusted to 7 with NaOH in a 1 liter volumetric flask. Hydrogen was bubbled through the buffered solution for 20 minutes at the rate of 100 cc/min using a gas dispersion tube. The concentration of  $\text{H}_2$  in this solution was calculated from solubility data<sup>9</sup> to be  $7.5 \times 10^{-4}$  M.

To this solution 100  $\mu\text{L}$  of THM standard was injected beneath the surface. The volumetric flask was immediately stoppered and inverted three times. This THM solution was then used to fill 40 mL reaction vials (Pierce Chemical Company #13510) containing 0.1 g of catalyst. Teflon-faced silicone septa were carefully placed on the vials with the teflon side toward the solution and the caps were screwed on so that no air bubbles remained inside the vial.

The reaction vials were clamped to a long rod which was rotated axially at 60 RPM with a low-speed motor. This produced a tumbling effect and provided uniform mixing in all the reaction vials. The reaction vials were then quenched at various times to obtain the degradation data. All experiments were conducted at room temperature (approximately 25°C).

The liquid-liquid extraction procedure recommended by the U.S. Environmental Protection Agency<sup>10</sup> was used to determine THMs in the reaction vial. When the reaction vial was opened, the contents were poured into a 10 mL glass syringe. The syringe plunger was inserted and the volume was adjusted to 10 mL. This volume was then carefully injected into a 13 mL culture tube to prevent aeration. Two mL of n-pentane were pipetted into the culture tube, the teflon-lined cap was screwed on, and the tube was shaken vigorously for 60 seconds. Upon phase separation THMs were determined by injecting 3  $\mu\text{L}$  of the pentane layer into a Hewlett Packard 5830A gas chromatograph equipped with an electron capture detector. The column was 5 percent SP 1,000, 100/120 Supelcoport with 5 percent methane/95 percent Argon as carrier gas. The oven temperature was programmed from 65°C to 90°C at 25°/min after a 2.3 min hold at 65°C.

#### RESULTS AND DISCUSSION

As indicated in Figure 1, the four THMs,  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$  are well resolved under the chromatographic conditions stated previously.

Figure 2 shows the Zn catalyzed degradation of  $\text{CHCl}_3$  to be faster at low pH and negligible at high pH. This effect is due to the ability of Zn to reduce hydrogen ion to hydrogen gas. No  $\text{H}_2$  was added to the reaction mixture. To study this degradation process without forming a large concentration of zinc ion, the reaction mixture was buffered at pH 7 and saturated with  $\text{H}_2$ . From the results of Figure 2, 0.1 g of zinc powder was arbitrarily chosen as the amount of catalyst to use for further studies.

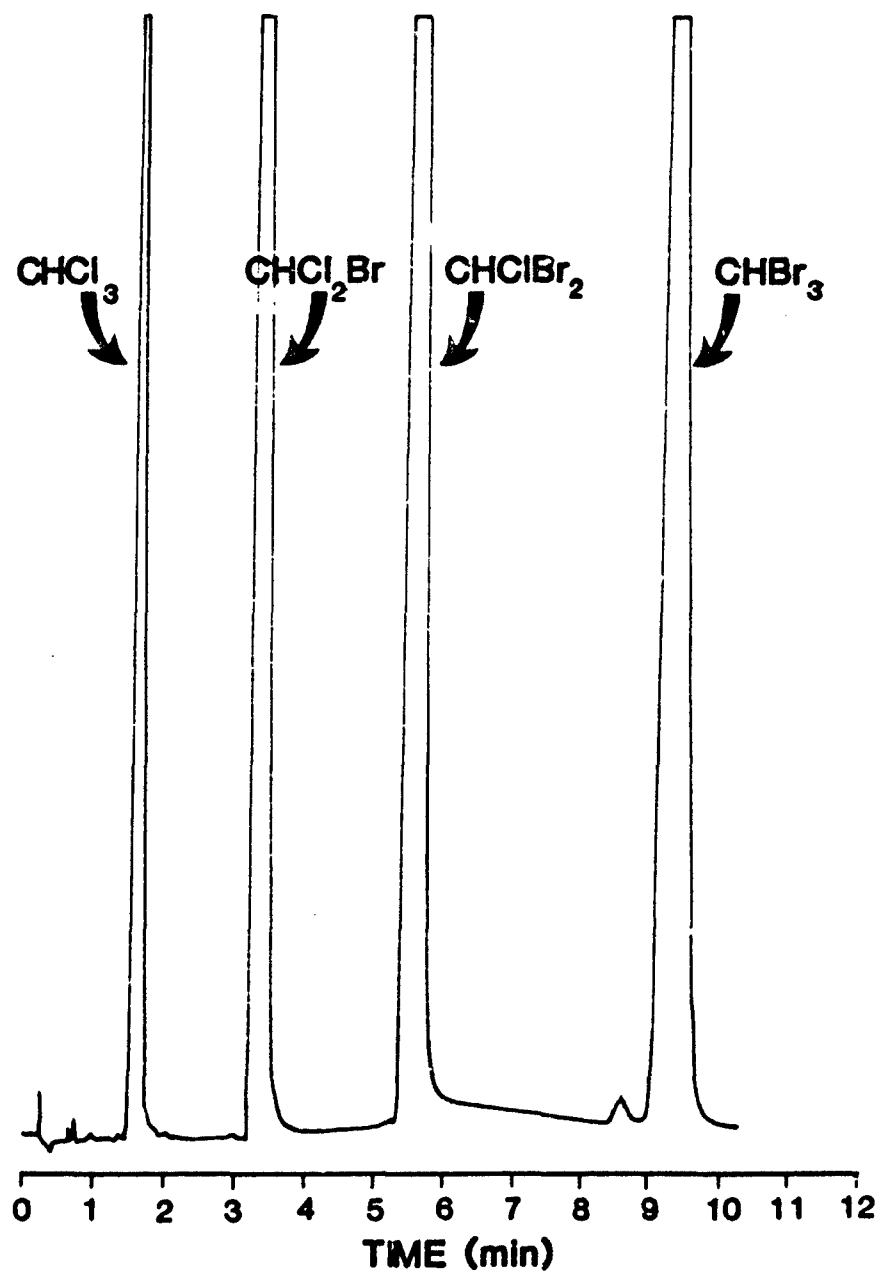


Figure 1. Chromatogram of four trihalomethanes.



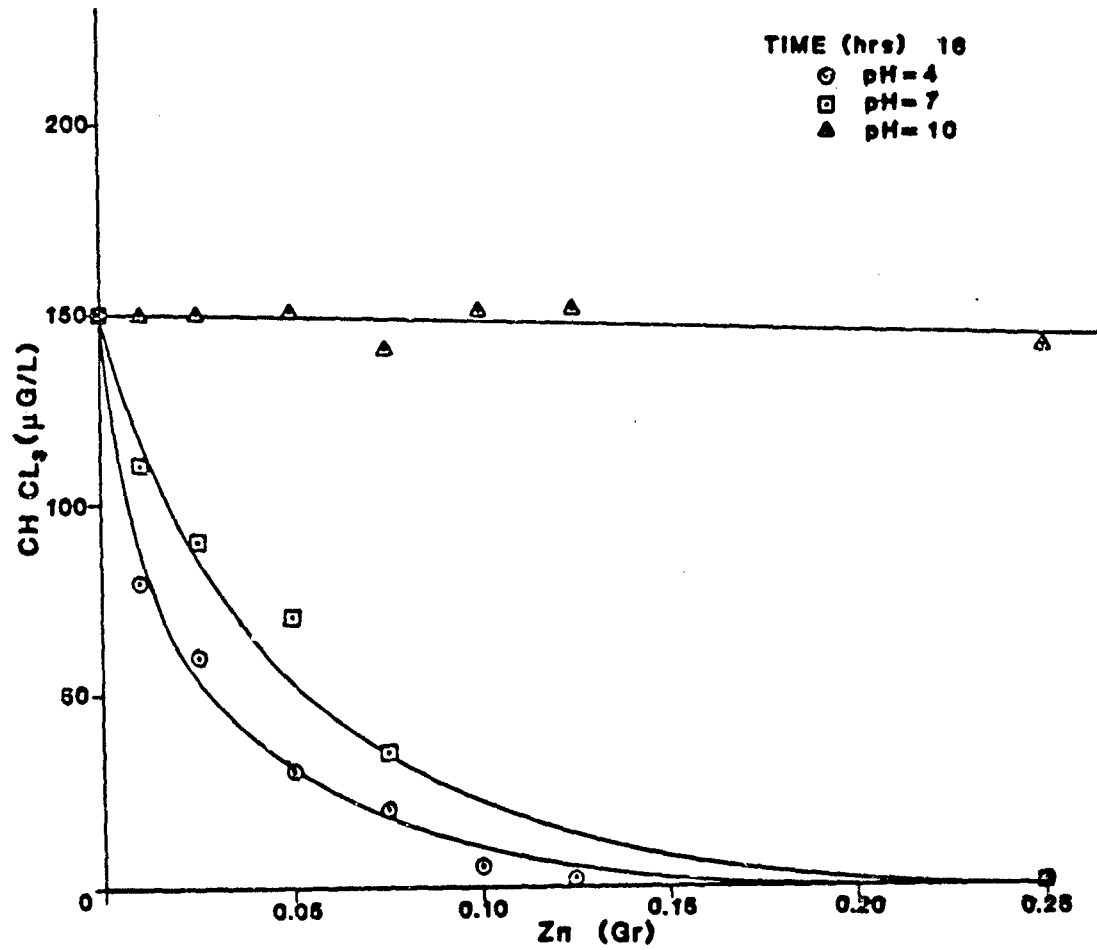


Figure 2. Effect of pH and Zn surface area on rate of degradation of  $\text{CHCl}_3$ .

Under these conditions, as shown in Figure 3,  $\text{CHCl}_3$  is much more difficult to degrade than the other three THMs. The possibility of THM adsorption onto the surface of the Zn powder was considered. When the Zn powder from several of the reaction vessels was washed with n-pentane and analyzed for THMs, none was found.

When the  $\text{H}_2$  concentration was reduced by 1/2 with all other parameters constant, there was a noticeable decrease in the rate of degradation of  $\text{CHCl}_3$  (Figure 4). The other three THMs also degraded more slowly under these conditions; however, degradation was complete after 1 hour of reaction time. First order degradation rates were observed for each of the THMs studied.

In the early stage of a 7-hour degradation experiment, two extra peaks appeared on the chromatogram. These were assumed to be intermediate degradation products since they too disappeared with time. To determine the origin of these intermediate compounds, solutions of each of the four THMs were prepared and degraded separately.

Chloroform and bromodichloromethane showed no evidence of intermediates. However, upon degrading  $\text{CHClBr}_2$  under the same conditions for several minutes, a new peak appeared at 1.85 min (Figure 5). This retention time is identical to that of chlorobromomethane. One would assume, therefore, that the first step in the degradation process is the substitution of a hydrogen atom for a bromine atom as shown below.



Figure 6 shows the degradation of  $\text{CHClBr}_2$  with time and the formation and subsequent degradation of  $\text{CH}_2\text{ClBr}$ .

Bromoform degradation also yielded a new peak having a 3.46 min retention time after only 2 min of reaction time (Figure 7). Dibromomethane has a 3.46 min retention time, again lending strong evidence for the stepwise substitution mechanism. Figure 8 shows the degradation of  $\text{CHBr}_3$  and the formation and subsequent degradation of  $\text{CH}_2\text{Br}_2$ . Although monobromomethane could be resolved under these chromatographic conditions, none was found during the course of the reaction.

The zinc ion concentration during the course of the experiment was measured at 5.2 mg/L by atomic absorption spectroscopy. Although the toxicity of zinc has not been well defined, an upper limit of 5 mg/L has been recommended.<sup>11</sup>

In order to maintain quality control for the THM determination, standards were obtained from the U.S. Environmental Protection Agency and run intermittently with samples. In all cases, our values fell well within the acceptable ranges for each of the THM quality control standards.

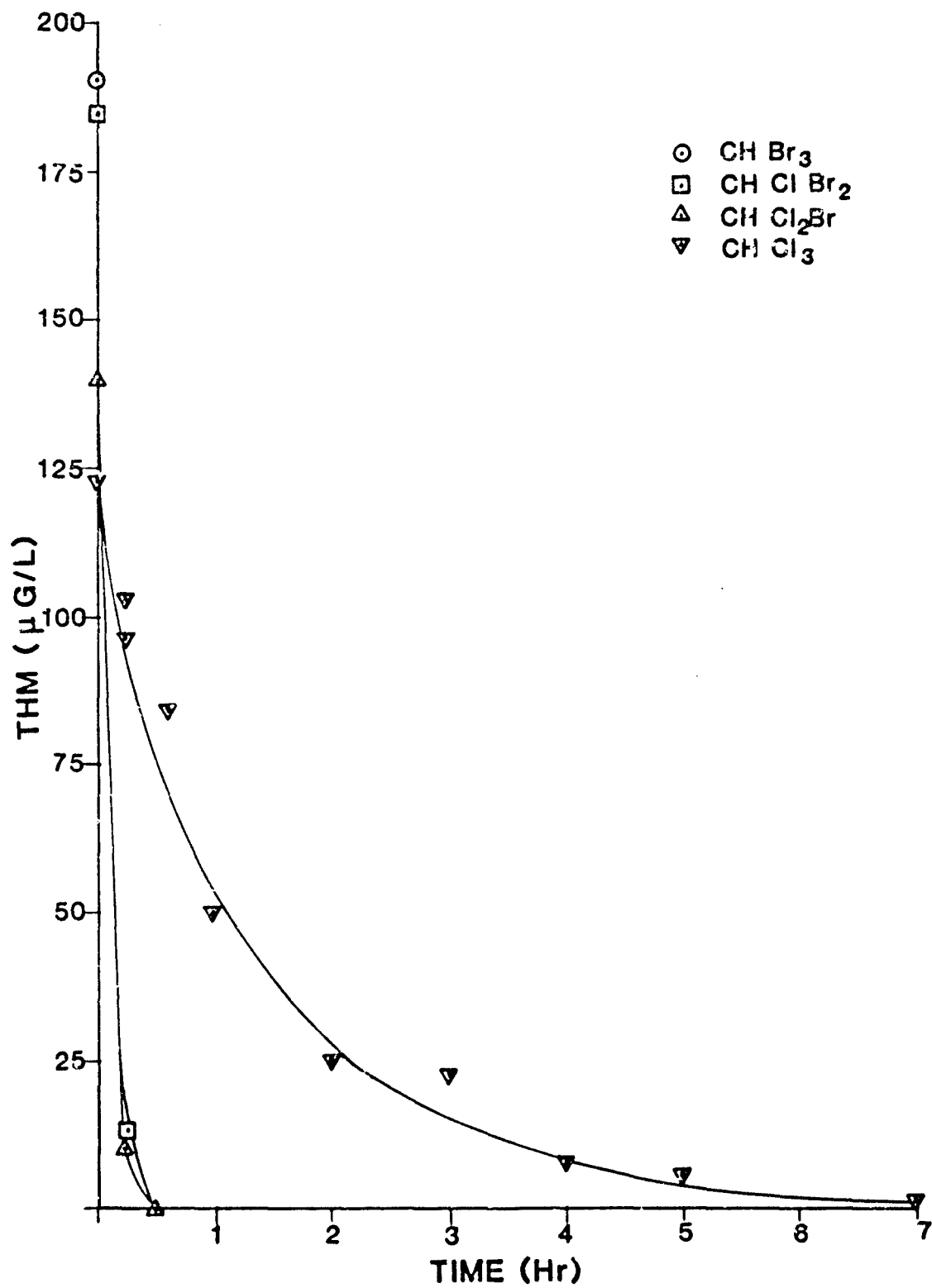


Figure 3. Relative degradation rates of four trihalomethanes.

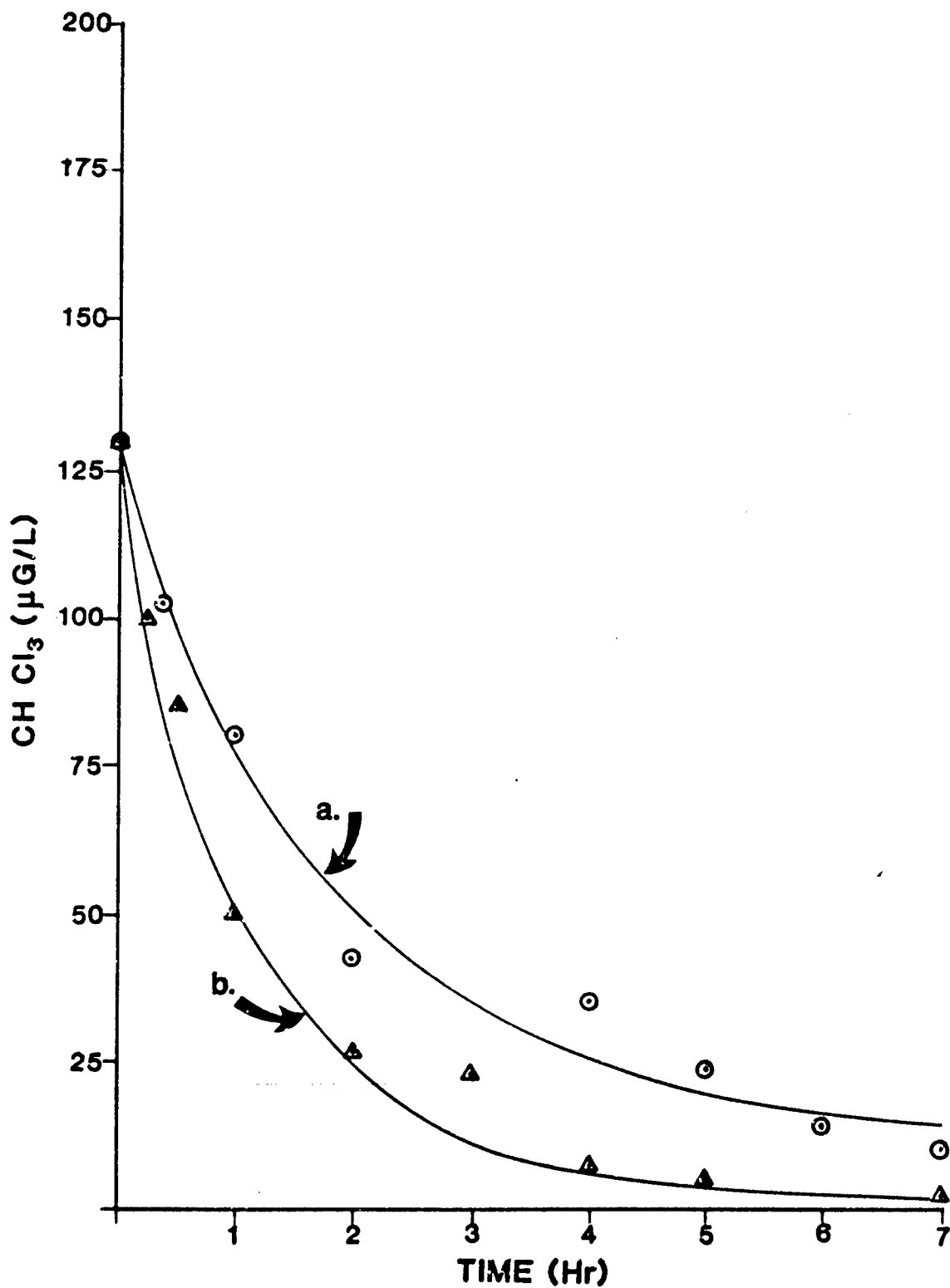


Figure 4. Degradation rate of  $\text{CHCl}_3$  in (a)  $3.7 \times 10^{-4} \text{ M H}_2$  and (b)  $7.5 \times 10^{-4} \text{ M H}_2$ .

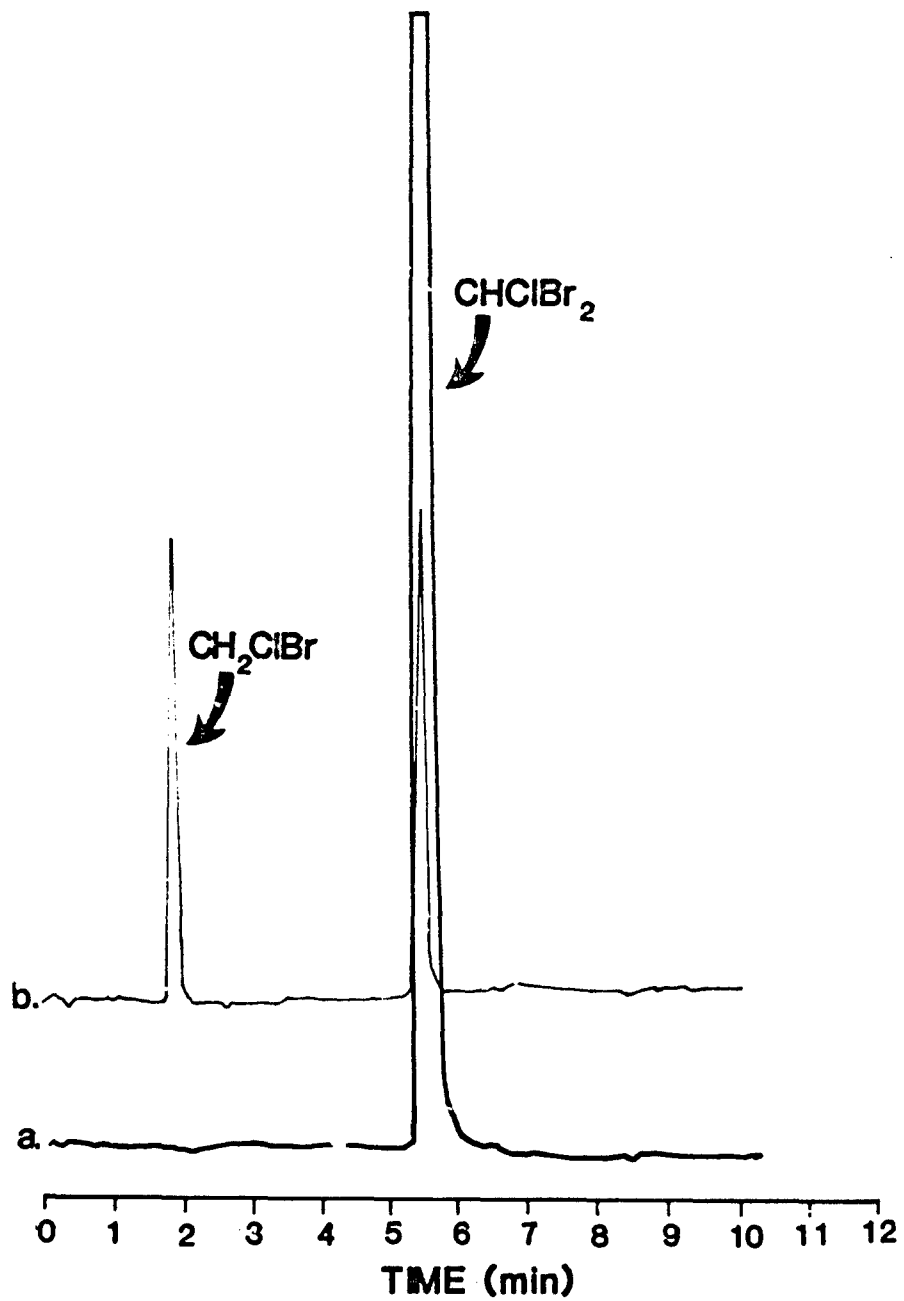


Figure 5. Chromatogram of  $\text{CHClBr}_2$  sample (a) before and (b) after degradation.

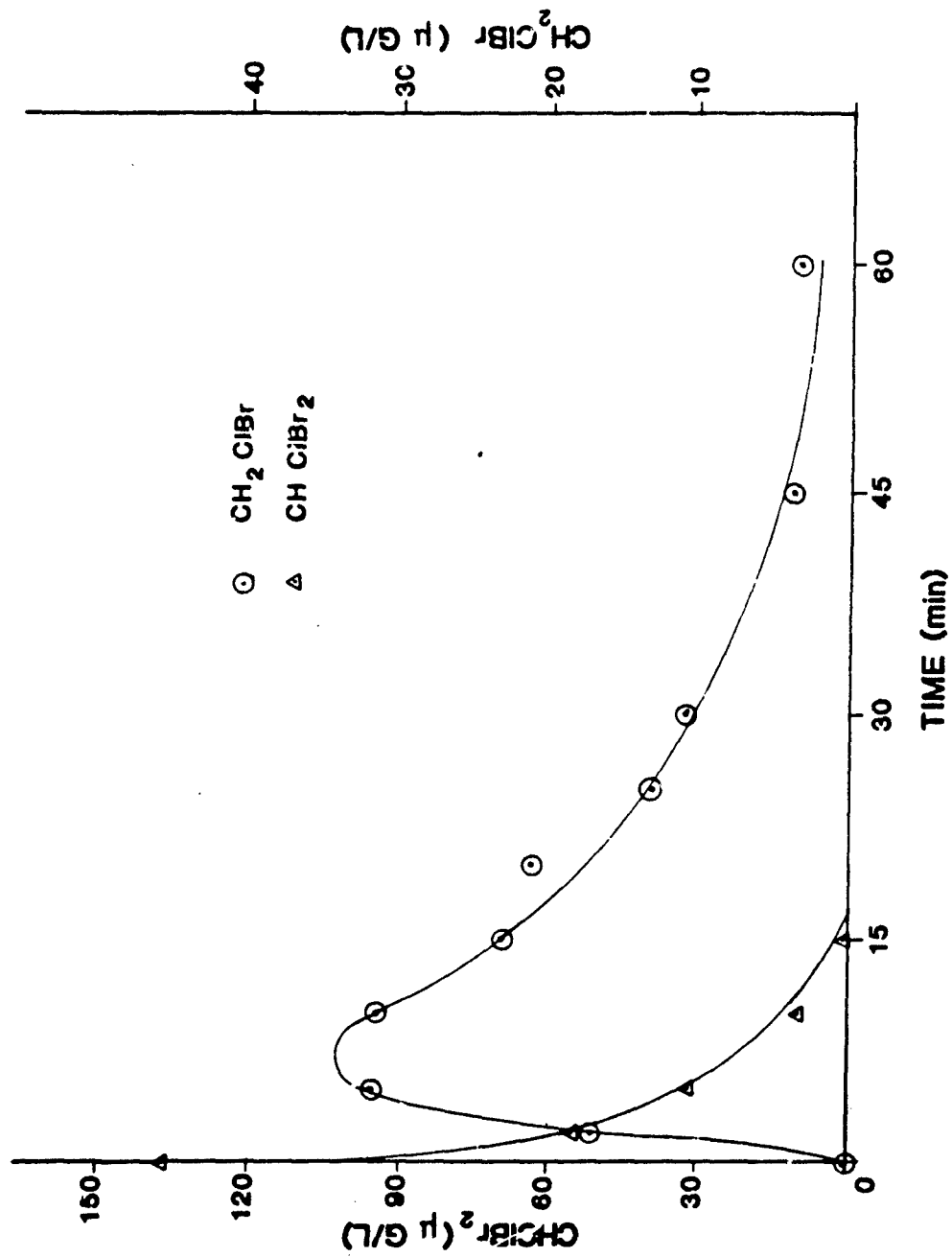


Figure 6. Degradation of CHClBr<sub>2</sub> and formation and degradation of CH<sub>2</sub>ClBr.

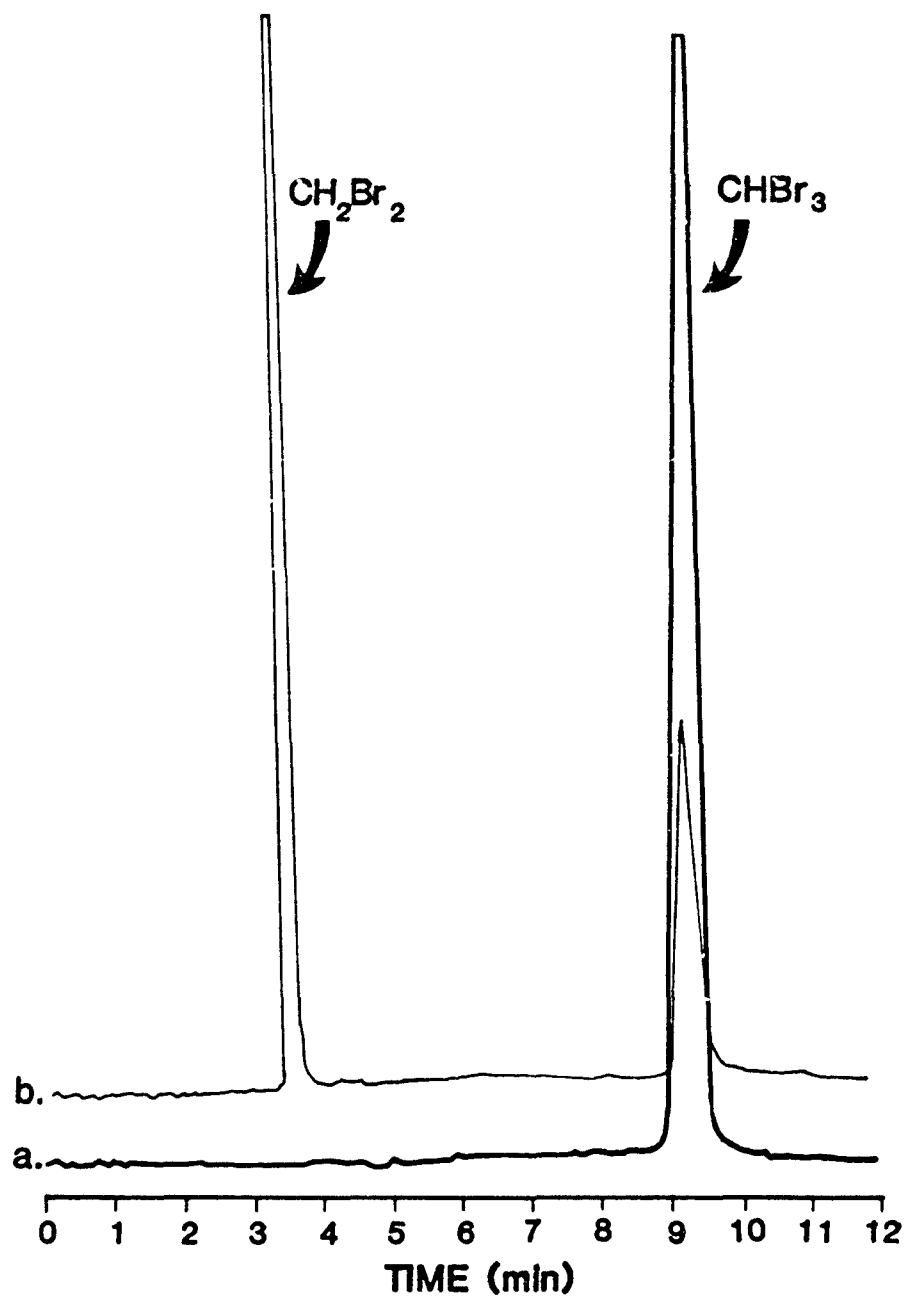


Figure 7. Chromatogram of CHBr<sub>3</sub> sample (a) before and (b) after degradation.

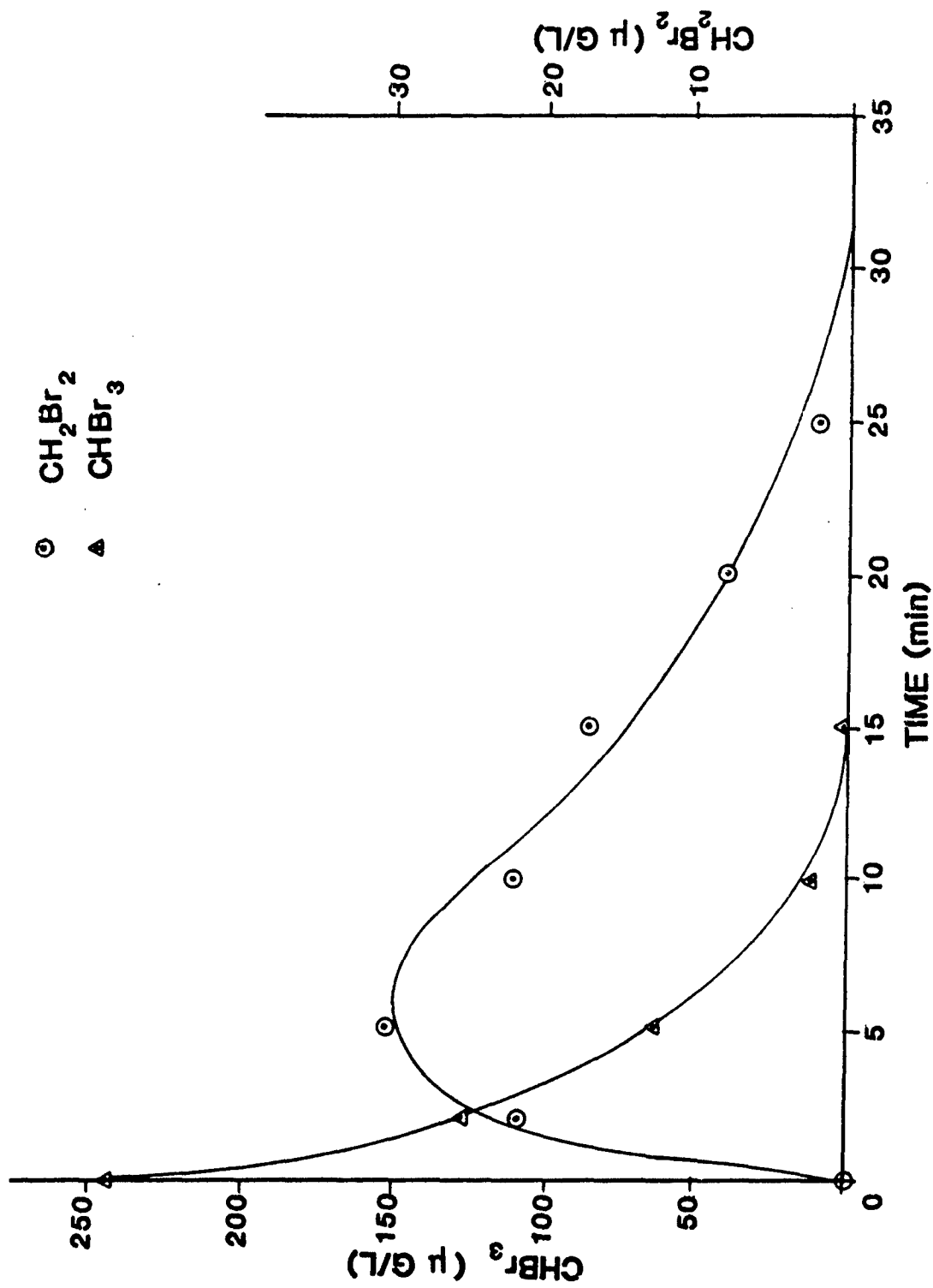


Figure 8. Degradation of CHBr<sub>3</sub> and formation and degradation of CH<sub>2</sub>Br<sub>2</sub>.



### CONCLUSION

We have clearly demonstrated that drinking water levels of THMs can be catalytically dehalogenated using Zn as a catalyst. Although the addition of H<sub>2</sub> greatly enhances the rate of the reaction, we feel the same effect could be obtained by passing finished drinking water through galvanized pipe with no H<sub>2</sub> addition.

It is expected that this study will encourage further research in the area of catalytic dehalogenation, so that our drinking water will some day be free from hazardous substances like THMs.

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