

## The Decomposition of Chlorinated Hydrocarbons in Aqueous Solution by Ultrasonic Irradiation

Cary L. DeMoss

### Abstract

Dilute aqueous solutions of methylene chloride were irradiated with intense ultrasound. The decomposition of the methylene chloride by as much as 73.4% was observed. The most favorable conditions for decomposition occurred at short frames using high rates of power. The primary chlorine containing product was hydrogen chloride.

### Introduction

In recent years, the environmental hazards of chlorinated hydrocarbons have been increasing, due in part to its accumulation in surface and ground water. The contamination of water by agricultural and industrial uses of chlorinated hydrocarbons is significant. These hydrocarbons have been scientifically linked to endocrine disruption of various species, as well as having carcinogenic properties.

In the last two decades methods for cleaning water contaminated with chlorinated hydrocarbons have varied from lime based solidification to incineration and photochemical destruction (Bunce, Environmental Chemistry). Attempts to clean up these hazards have been slow, which has created an increased level of need to discover new methods that reduce their effects.

Since the 1950's ultrasound in the range of 20-100kHz has been used with the aid of the ultrasonic bath for, metallurgy, emulsification, and promoting chemical reactivity (Wilkinson, K.J., Chemical Society Reviews). Sonocatalysis causes a reaction process known as cavitation. Cavitation is caused by intense pressure waves generated as the result of high intensity, high frequency sound waves. An ultrasound's transducer converts a high frequency (20kHz) electrical sound to sound waves with energy of 20,000 cycles per second. Under these conditions bubbles (cavities) are formed from negative pressure excursion, and are imploded during positive excursion. This reaction agitates liquids and promotes chemical reactivity. Although localized temperatures can reach 4000 degrees celsius, the bulk liquid temperature will not be affected greatly. This process of cavitation enhances chemical reactivity, and promotes chemical reactions, including chemical decomposition.

Recently, studies conducted by Cheung and Inazu with Nagata and Maeda discovered that only a simple aqueous solution is needed for the decomposition of chlorinated hydrocarbons to take place. All research concluded that cooler temperatures (10-20 degrees celsius) are needed to be maintained during the reaction process, although any change in temperature

would be caused by the cavitation process, its increase would be minimal. A separate study conducted by Cheung indicated that the chlorine from the hydrocarbon is cleaved and converted to HCl, which can be monitored by a pH change.

(Cheung, Environmental Science Technology)

The purpose of this was to determine whether intense, high frequency sound waves would be effective in destroying chlorinated hydrocarbons by breaking the bond between Cl and C atoms. With chlorine being cleaved from the hydrocarbon, its hazardous effects will be diminished.

### Materials and Methods

Dilute aqueous solutions methylene chloride were prepared by diluting 0.80-ml and 1.75-ml of methylene chloride with a purity level of 99%+ to 1000.0-ml with water. This produces an 800 and 1750 ppm solution respectively. Material setup consisted of a Vibracell 600-Watt dual output ultrasonic processor, working at a maximum output of 360-Watts (60%). A Perkin-Elmer Sigma 3B Gas Chromatograph with a 10ft x1/8in, 100/120 Supelcoport column was used for determination of methylene chloride concentrations. The GC parameters were set for an isothermal column temperature of 65 degrees celsius, and an injector temperature of 150 degrees celsius. An F.I.D. detector was used and set at 200 degrees.

The protocol for analyzing diluted samples of methylene chloride, involved combining 20.0 ml of sample with 2.0 ml of hexane in a separatory funnel and shaken for 2-3 min by hand. After 5 min of equilibration time, .3ul of the hexane phase was injected into the GC. A calibration curve utilizing aqueous samples of known methylene chloride concentration was developed by using the same protocol. The curve was linear over the range of 250-1750 ppm range. The methylene chloride in solution prior to and after sonocatalysis was determined using the peak height relative to that of n-hexane (major component of the extraction solvent).

Sonocated samples were prepared by placing 100

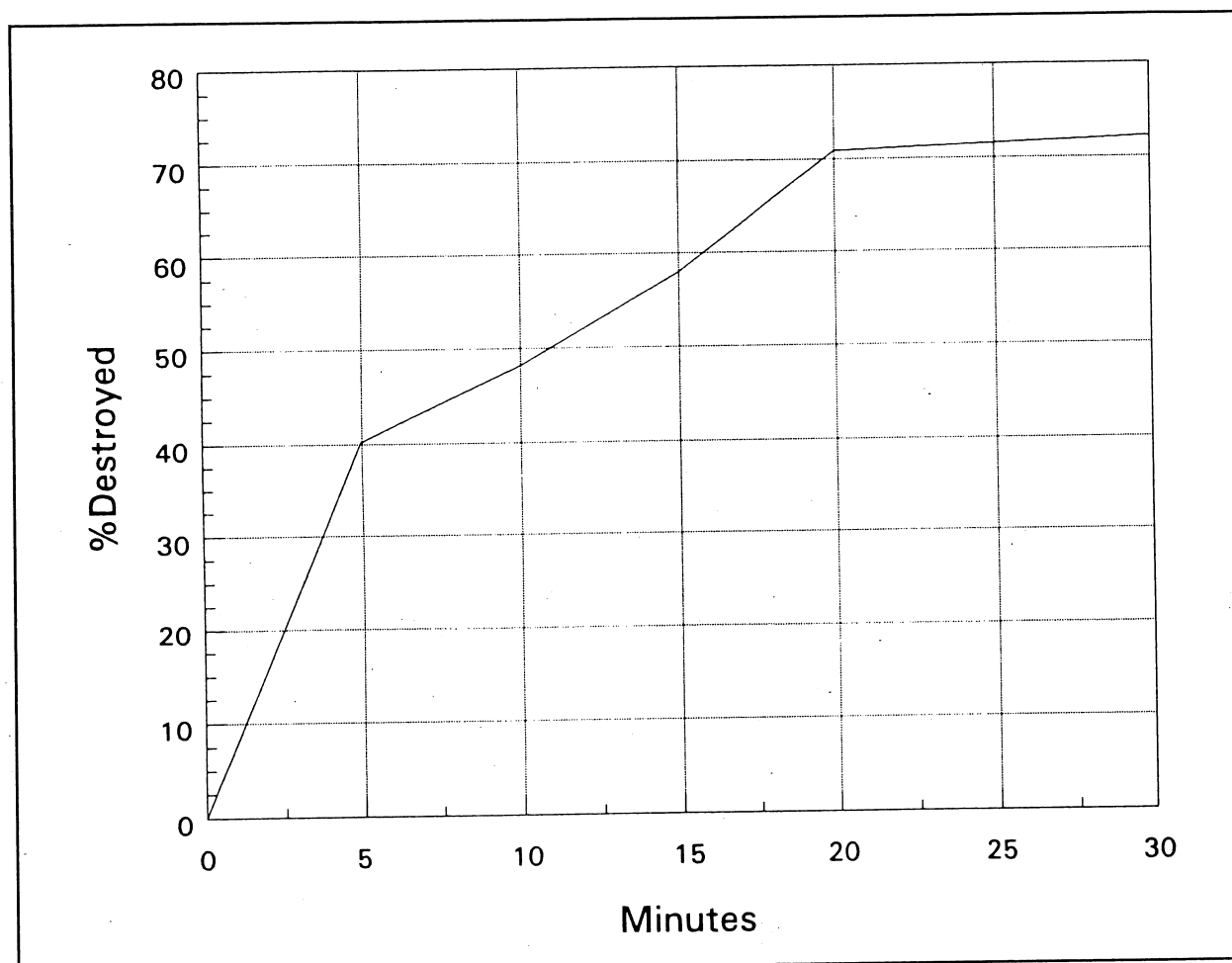


Figure 1. Amount of destroyed (converted) chloride for a 800ppm solution while varying time.

ml of desired sample in a 250-ml conical flask under the sonocator, and sealing the open area with parafilm, to reduce evaporation. The 800ppm and the 1750ppm solutions were initially sonocated at 60% maximum level for; 5, 10, 15, 20, and 30 minutes, and their results were compared by % destruction. The 800ppm solution was performed in duplicate to determine ruggedness. Once analyzed by GC, a chloride test was performed by transferring 15-ml of the water phase to a 250-ml flask. Five milliliters of glacial acetic acid and 50-ml of methanol was added, and titrated with 0.1 N silver nitrate VS to a rose colored end point, using eosin Y TS as the indicator. By performing the titration, the concentration of free chlorine can be calculated, and compared to the amount of bound chlorine in methylene chloride, and there by determine the amount of methylene chloride destroyed. The 1750ppm aqueous solution of methylene chloride was also decomposed by sonocation for 20-min using various power levels: 10%, 25%, 30%, 50%, and 60%; analyzed by GC, and the % decomposition calculated.

### Results

The success of destroying the chlorinated hydrocarbon was dependent upon three variables: concentration, power, and time. When varying the time in which the samples were sonocated, methylene chloride was decomposed most rapidly in the first five minutes. The 1750ppm(38.78mg of Cl) solution had converted 60%(15.12mg) (Table 2) of the total amount of decomposed chloride, while the 800ppm(17.73mg) solution was slightly lower at 56%(6.34mg).(Figs. 1,2) After 30 min of sonocation the 1750ppm soln. had converted 69.78%(25.36mg) of the chlorine. The total amount of converted chloride for the 800ppm solution was comprable at 72.24%(12.68mg) (Table 1), for the same amount of time. The efficiency of the reaction (total energy/mg of Cl converted) for the 800ppm solution decreased as time was increased, ranging from 249.8-Watts/mg of chloride for 5 min of sonocation to 845.0-W/mg for 30 min, while the 1750ppm soln. ranged from 111.3-W/mg to 399.2-W/mg.

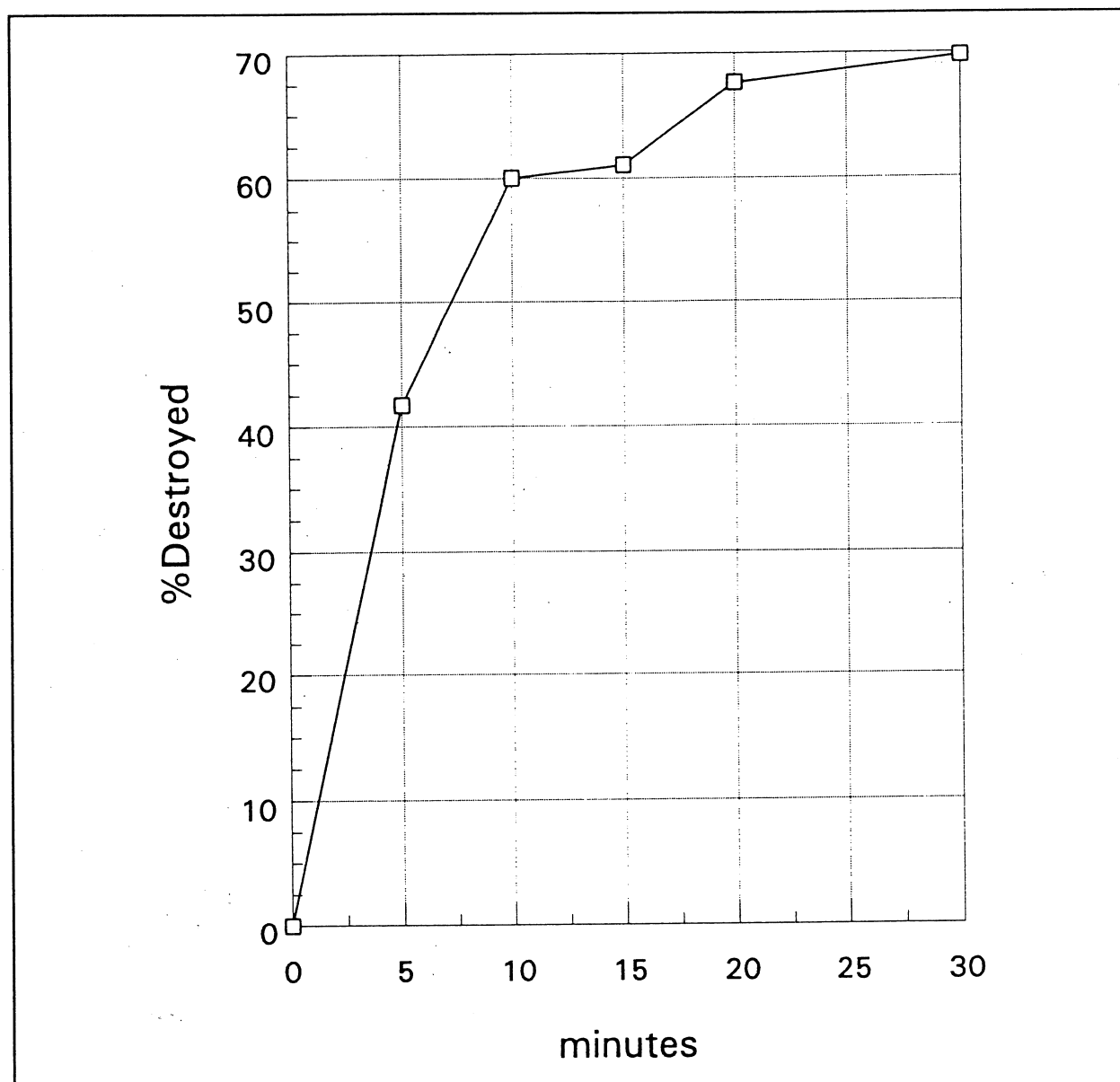


Figure 2. Amount of destroyed (converted) chloride for a 1750ppm solution while varying time.

The chloride titration yielded comparable results to that of the GC. On average, there was a -5.4% (0.96mg) difference between the predicted value from the GC to that of the titration for the 800ppm. The 1750ppm solution was slightly higher with a percent difference of -5.8 (2.25mg).

Concentration variations did not influence the overall percent conversion of chloride greatly, although the 800ppm solution had a less dramatic change. (Figs. 1,2) After 10 min of sonocation, the 1750ppm solution was 86.1% complete, while the 800 ppm soln. was only 66.8%. The chloride titration varied slightly from that of the GC analysis. Although there was only a 0.4% difference variation between

concentrations, there was a 1.29mg of actual chloride difference. When comparing the efficiency ratings between the concentration levels, the 1750ppm solution had better overall efficiency ratings, but it also had a slower decline in efficiency at 38.7% as compared to the 800ppm's 42.0%.

Varying the power levels produced a less dramatic conversion of methylene chloride, making a near linear curve (Fig. 3). The values ranged from 5.5%(2.1mg) (Table 3) at 10% of full power, to 69.8%(25.4mg) at 60% full power. The greatest increase in chloride conversion occurred between the 50-60% power levels(9.4%). The smallest increase was between 10 to 25 percent range(4.6%). By

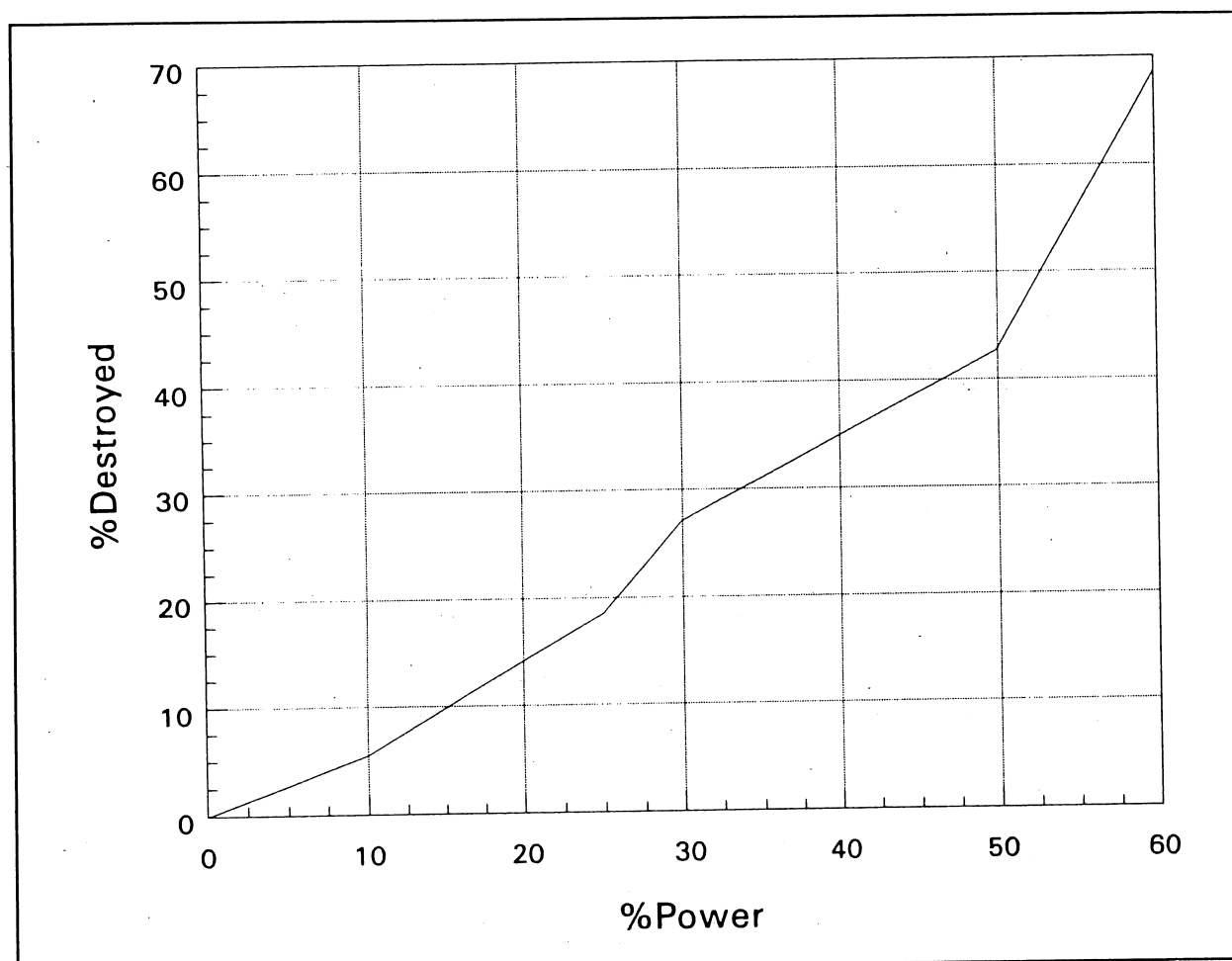


Figure 3. Amount of destroyed (converted) chloride for a 1750ppm solution while varying power.

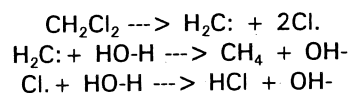
increasing power levels, the efficiency of the chloride conversion increased. This was an increase of 106.6%, from 567.1-W/mg(10%) to 274.6 W/mg(60%).

### Discussion

Sonocation proved to be a valid process for destroying methylene chloride, although it may not be a very viable method, due to the energy costs. The sonocation of methylene chloride at higher power levels for shorter periods of time proved to be the most efficient process for removing chlorine from chlorinated hydrocarbons, where higher concentration of methylene chloride are slightly more efficient than lower concentrations.

The chloride titration proved to be a viable, useful, and independent method of analysis. By comparing the two methods of analysis, it showed that approximately 94.6 of the chlorine removed became free chloride ions as HCl. This is consistent with that observed by Cheung. This suggests the following

mechanism:



Evaporation, and/or other mechanisms that do not produce free chloride could account for the lack of the remaining 5.4%. With increased improvements to power conversions, sonocation may play an important role in cleaning polluted water ways and the growing volume of chemical waists in the future.

### Literature Cited

- Agriculture and Groundwater Quality (C.A.S.T), May 1985. report no. 103, pp.10.
- Bunce,Nigel. 1991. Environmental Chemistry. Wuerz Publishing. 1ST edition pp.262-294.
- Hileman, Bette, April 19,1993. Concerns Broaden

Tables 1, 2, and 3.

	GC value	T. value	% Diff.	% Dest.	Eff.
5 min	7.207mg	5.853mg	18.8%	40.6%	250 W/mg
10 min	8.567mg	8.929mg	3.2%	48.3%	420 W/mg
15 min	10.264mg	9.756mg	5.0%	57.9%	526 W/mg
20 min	12.657mg	11.219mg	11.4%	71.4%	569 W/mg
30 min	12.787mg	12.68mg	0.8%	72.1%	845 W/mg

	GC value	T. value	% Diff.	% Dest.	Eff.
5 min	16.175mg	15.122mg	6.5%	41.7%	111 W/mg
10 min	23.292mg	21.463mg	7.9%	60.1%	155 W/mg
15 min	23.688mg	21.951mg	7.33%	61.1%	228 W/mg
20 min	26.220mg	24.390mg	7.0%	67.6%	275 W/mg
30 min	27.057mg	21.365mg	6.3%	69.8%	399 W/mg

	GC value	% Dest.	Eff.
10 %	2.116mg	5.5%	567 W/mg
25 %	7.180mg	18.5%	418 W/mg
30 %	10.518mg	27.2%	342 W/mg
50 %	18.916mg	48.8%	317 W/mg
60 %	26.220mg	67.6%	275 W/mg

Over Chlorine and Chlorinated Hydrocarbons,  
Chemistry and Engineering, pp.11-20.

Cheung, H. Michael, August 1991. Sonochemical  
destruction of chlorinated hydrocarbons in dilute  
aqueous solution, Environmental Science &  
Technology, V.25, pp.1510-12.

Cheung, H. Michael; K. Inazu, Y. Nagata, Y. Maeda,  
Jan. 1993. Decomposition of Chlorinated  
Hydrocarbons in Aqueous Solutions by  
Ultrasonic Irradiation, Chemistry Letters, pp.57-  
60.

Lorimar, J.P.; Mason Mistry, Jan. 1987. Effect of

Ultrasound on the Solvolysis of 2 chloro, 2  
methylpropane in Aqueous Alcoholic Solvents,  
Ultrasonics, v.25, pp.23-28.

Schantz, Michele M.; Reenie M.Parris, Jan. 5,1993.  
Comparison of methods for gas-chromatographic  
determination of PCB congeners and chlorinated  
pesticides in marine reference materials,  
Fresenius' Journal of Analytical Chemistry,  
pp.766-778.

Wilkinson, K.J.. 1987. Sonochemistry, Synthetic  
Applications. Chemical Society Review, v.16,  
pp.275-309.