

EPA-660/2-75-017
JUNE 1975

Environmental Protection Technology Series

Radiation Treatment of High Strength Chlorinated Hydrocarbon Wastes



**National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
Corvallis, Oregon 97330**

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RADIATION TREATMENT OF HIGH STRENGTH
CHLORINATED HYDROCARBON WASTES

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EPA Project R800312
Program Element 1BB036
ROAP 21AZR, Task 009

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ABSTRACT

The possible use of gamma radiation for the treatment of waste effluents containing chlorinated hydrocarbons, particularly pesticides, has been investigated. Significant destruction was obtained of representative compounds such as pentachlorophenol, 2,4,5-trichlorophenoxyacetic acid, and 2,4-dichlorophenoxyacetic acid. Radiation treatment had little effect on polychlorinated biphenyls or mixtures of compounds, including actual manufacturing effluents.

It was found that the addition of a material of high atomic weight, such as barium, increased the efficiency of radiation utilization. No other materials were found which increased the desired destruction. G-values were calculated for pentachlorophenol, 2,4,5-trichlorophenoxyacetic acid, and 2,4-dichlorophenoxyacetic acid.

It is concluded from the magnitude of these values that radiation treatment of chlorinated hydrocarbons is not economically feasible at the present level of radiation costs.

This report was submitted in fulfillment of Grant No. R800312 by the Engineering Experiment Station of the Georgia Institute of Technology under the partial sponsorship of the Environmental Protection Agency. Work was completed as of November 1974.

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ACKNOWLEDGEMENTS

This project was funded by the United States Environmental Protection Agency, Grant Number R800312 to the Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia.

The support of this work by the Environmental Protection Agency is greatly appreciated. The contribution of Project Officer Dr. Robert R. Swank, Jr. (Southeast Environmental Research Laboratory) to the project involved both scientific and managerial matters. His genuine interest and assistance are acknowledged with sincere thanks.

SECTION I

CONCLUSIONS

The following conclusions can be drawn concerning the compounds and mixtures on which experimental work was performed:

1. Gamma radiation from cesium-137 and cobalt-60 destroys individual compounds with varying degrees of efficiency in aqueous solutions.
2. Little or no radiation destruction occurs when the compound is dispersed on an inert substrate.
3. Destruction can occur when the compound is dissolved in a non-aqueous solvent such as hexane or benzene.
4. The presence of extraneous material is most likely to diminish the destruction of the compound in question.
5. Destruction of mixtures is likely to be much less efficient than destruction of single compounds.
6. The utilization of radiation in the destruction of these materials is not very efficient as shown by the calculated G-values.
7. Radiation treatment of wastes containing chlorinated hydrocarbons such as those resulting from manufacturing processes is unlikely to be economically feasible at present levels of radiation costs unless a very effective means of radiation utilization enhancement can be found.

SECTION II

RECOMMENDATIONS

Ionizing radiation is a very effective agent for treating organic waste constituents that are resistant to biological degradation. The efficiency, however, depends on the radiation sensitivity of the pollutant materials and their concentration in the waste stream. Under present economic conditions, radiation treatment is somewhat more expensive than the ordinary biological processes. Nevertheless, it appears very useful for treatment of wastes containing obnoxious bio-resistant components, particularly when the pollutant concentration of these refractories is not too low.

There are two major factors that have hindered the adoption of radiation waste treatment processes. The first is the insensitivity to radiation of some compounds. Radiation ruptures chemical bonds, but this is of no benefit if the fragments recombine in their original configuration. It is recommended that a search be carried out for effective, low-cost scavenging agents which will damp out the recombination reaction.

A second factor is the low concentration at which refractory pollutants occur in the usual industrial waste stream. Much energy is expended on the irradiation of large volumes of water in order to degrade the small amount of obnoxious matter present. It is therefore recommended that means be sought to produce more concentrated wastewater streams through changes in waste-generating operations, or through procedures for concentrating these refractory pollutants produced in normally dilute solutions or suspensions.

It is specifically recommended that tests be conducted of waste treatment systems that provide for retention of the refractory material in a radiation zone while allowing the aqueous phase to pass through. For example, refractory pollutants might be collected on activated carbon or metal oxide surfaces positioned within a suitable radiation field. The efficiency of radiation utilization would be increased, as the target material would receive larger exposure times and energy expended on the water would be minimized.

SECTION III

INTRODUCTION

Within recent years environmentalists have become aware of widespread contamination of the environment by inorganic and persistent organic compounds. The general cause for this is attributable to urbanization, industrialization, and highly developed agricultural practices. More specifically, inappropriate disposal procedures and accidental releases account for a large portion of the present contaminant levels. Agricultural activities also contribute significantly, mainly persistent pesticides. Pesticides must be dispersed over large areas to be useful, and their subsequent control becomes impossible.

Most persistent pesticides are organochlorine compounds and for the purposes of this discussion may be grouped with a large number of herbicides, plasticizers, flame retardants, and other chlorinated hydrocarbons that find their way into the environment. The problem cannot be solved by prohibiting the manufacture and use of these compounds, as many are not particularly harmful and they are all very useful (if indeed not indispensable) to our present level of technology. Chlorinated organic compounds, for instance, which are used as pesticides have been exceedingly beneficial by controlling the vectors of serious human disease which have claimed millions of lives and by greatly increasing the yields of many crops. The need for food will increase as the population grows, and thus it appears likely that the need for pesticides will also increase.

The problem therefore becomes one of control in the production, use, and disposal of potentially harmful compounds. It may eventually prove necessary to ban some materials, but careful use and disposal techniques would greatly reduce the present rate of environmental contamination. This would reduce human contact with chlorinated hydrocarbons which is at present unavoidably high because chlorinated hydrocarbons are resistant to degradation and they accumulate in the food chain.

Chlorinated hydrocarbons are, in general, soluble in fat and insoluble in water, which causes them to accumulate in the lipid tissue of organisms with which they come in contact; thus, their concentration increases to many times that in the water. This effect is repeated as the material moves up the food chain, producing damaging and/or lethal concentrations in higher organisms. These insidious properties of chlorinated hydrocarbons are shared by many of the starting materials and reaction by-products (they themselves being chlorinated hydrocarbons) involved in their manufacture.

Because of the biomagnification phenomenon, dilution of this type of waste as a means of disposal is not acceptable, and other disposal procedures are needed. Pollution of both fresh and salt water by chlorinated hydrocarbons, including persistent pesticides and herbicides, polychlorinated biphenyls (PCB's), and polychlorinated naphthalenes, originates in two ways: (1) as residues in trace amounts from the use of these materials in agriculture and industry and (2) in much higher concentration as waste effluents from chemical companies manufacturing these compounds. It does not appear feasible to process all the water in a large river to remove those chlorinated hydrocarbon residues present in concentrations of a few parts per million or less; however, it may be feasible to process the highly concentrated effluent of a chemical company manufacturing chlorinated hydrocarbon products.

In many chemical processes, the initial result of a reaction is a complex mixture of compounds which include, in addition to the desired end product, such things as unreacted starting material, products of competing or side reactions (of both the initial reactants and their impurities), condensation products, and decomposition products. Various purification processes such as crystallization, filtration, distillation, and extraction may be utilized to separate out the desired product, leaving all the remainder for disposal.

From the waste treatment view, it would be highly desirable to recycle and/or recover some usable by-product from the residual mixture, even if the economics were not particularly attractive. In the usual case, however, it is cheaper simply to discard the unwanted residues.

Conventional methods of waste treatment such as sedimentation and bacteriological degradation have little if any effect on these wastes. Even when a resistant compound disappears from the water, it may only be adsorbed but not metabolized and therefore may reappear in the food chain often in a more concentrated form. Sometimes when compounds are altered, the primary degradation product is as stable and as toxic as the initial compound. Adsorption on activated carbon may be possible, but this does not completely solve the problem because the saturated adsorbent remains for disposal.

Bacteria can be acclimated to decompose many organic compounds including some that are ordinarily quite resistant. With highly resistant compounds, acclimation is very difficult, and for many compounds has so far proven impossible. Even when acclimation is possible, deacclimation occurs rapidly if an alternate source of carbon becomes available. No suitable cultures have yet been reported for chlorinated hydrocarbons, some of which are very toxic to bacteria and may even be used as disinfectants. A need therefore exists for an effective, economic procedure for the destruction of unwanted

chlorinated hydrocarbons or for their degradation to a form that is amenable to treatment by conventional procedures.

Ionizing radiation profoundly affects organic molecules through rupture of chemical bonds, and it is possible that radiation could effectively degrade biorefractory compounds. Radiolytic decomposition may proceed via direct interaction between a photon and the organic molecule, or the effect may be brought about indirectly by radicals or ions created by interaction of photons with the solvent. It seems likely that both actually occur, although the direct action is perhaps less important in aqueous solution where radiation is known to produce a number of active ions and free radicals including hydrogen, hydroxyl, peroxy, plus a large number of more complex entities.

It has been observed in this laboratory that the effects of radiation may be increased by the presence of an oxidant or other chemical agent. Experiments have demonstrated that dye solutions can be decolorized by a combined treatment of gamma radiation plus hypochlorite. The combination is much more effective than the two applied individually. Megarad radiation doses alone are required to achieve the same result that can be obtained with 25-50 kilorads of gamma radiation in the presence of hypochlorite.

There was no a priori reason to believe that similar results could not be achieved with chlorinated hydrocarbons, or, for that matter, any other type of organic compound, although operating conditions would not necessarily be the same. Radiolytic reactions involving chlorinated hydrocarbons in water include oxidation, hydroxylation, and dechlorination, all of which appear beneficial. These and other degradative reactions are greatly increased in the presence of a chemical oxidant. In general, each of these reactions would be expected to result in increased susceptibility to further chemical or biological degradation, decreased toxicity, and increased solubility in water and, therefore, less accumulation in the food chain. Radiolytic condensation and polymerization reactions would also be encountered. The products of these reactions would be less soluble and hence more susceptible to removal by sedimentation.

The ultimate usefulness of any treatment process depends largely on economic factors. Neither radiation nor chemical treatment alone seem likely to be economically attractive under most circumstances. However, costs may be greatly reduced by a suitable combination treatment, particularly in the presence of an efficient catalyst.

In the work here described, the effect of ionizing radiation, alone and in combination with chemical agents, on chlorinated hydrocarbons and mixtures of chlorinated hydrocarbons typical of those in waste effluents from chemical companies making these compounds was studied. Included in this program was a study of the rate of

destruction of various chlorinated compounds as a function of their concentration in the effluent, a study of the dose rate dependence of the destruction, a study of the effects of various chemical and physical agents on the rate of destruction of the chlorinated compounds, and finally, a study of the radiation products produced in these various experiments.

SECTION IV

EXPERIMENTAL DETAILS

RADIATION SOURCES

Two irradiation facilities were employed in the experimental work and preliminary plans were made to provide a capability for performing dynamic flow tests.

Cesium-137 Source

A 12,000 curie cesium-137 source is available at Georgia Tech for static irradiation tests. This source is housed in a 20-foot deep, sub-surface well and is arranged to provide uniform irradiation in an annular, coaxial configuration to as many as 12 vial specimens at a time. The dose rate in aqueous samples in the standard geometry is fixed at 1.0 Mrad per hour and total doses are varied by varying the exposure time. Sample insertion takes less than one second from a negligible field region.

Cobalt-60 Source

To provide greater variability in total dose and dose rate, an irradiation arrangement was devised, using encapsulated cobalt-60 strips totaling approximately 100,000 curies. The cobalt-60 was stored in a stainless steel bucket 15 feet below the surface of the storage pool at the Frank H. Neely Nuclear Research Center at Georgia Tech. Samples were irradiated in an aluminum pipe, the bottom of which was fastened inside a circular aluminum container. The radiation field inside the pipe was then governed by the number of individual cobalt-60 strips placed in the container. Thermoluminescent dosimeters were used to calibrate the field strength.

PROCEDURES

Maximum effects are obtained when the compound under study is in solution, and suitable solvent systems were sought in all cases. Hydrocarbons, alcohols, and base solutions were utilized at different times. Some samples which could not be easily solubilized were deposited on glass wool and immersed in water. The results were not significantly different from those obtained by irradiating non-dispersed solid covered with water.

A portion of the prepared sample was then irradiated by inserting it into the cesium-137 or cobalt-60 irradiator for the selected period of time. Following the irradiation period, the chlorinated

hydrocarbon was extracted from solution and its gas chromatogram was obtained. This was compared with the gas chromatogram obtained from the remaining (non-irradiated) portion of the sample.

The gas chromatograph used was a Microtek Model 220 fitted with a flame ionization detector and an Ni-63 electron capture detector. A 6-foot long, 1/4 inch diameter stainless steel column containing 5% SE-30 on Chromport, 80/90 mesh was used with the flame ionization detector. A glass column of the same dimensions containing 3% OV-1 on Chromosorb W, 80/100 mesh was used with the electron capture detector. The carrier gas utilized was a "prepurified" grade marketed by Matheson Gas Products. Optimum column temperatures for the various materials studied were in the range of 140-210 $\frac{1}{2}$ °C. Injected samples ranged in size from two to eight microliters.

Careful attention was given to the extraction technique in order to assure quantitative recovery of the chlorinated hydrocarbon. In some cases it was found necessary to methylate the compound prior to determination of the gas chromatogram. This was accomplished using diazomethane to convert the hydroxy to a methoxy form and was applied to pentachlorophenol, 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. Any phenol resulting from cleavage of an oxygen-carbon bond during irradiation of the acids would have been readily methylated while the acid was undergoing esterification. Non-methylated samples of these materials were found to pass through the gas chromatograph column very slowly and yield strong "tailing" of the peak. Such data were extremely difficult to analyze.

The quantity of the compound of interest present in any sample was determined by measuring the area under its main peak on the gas chromatograph. Area measurements were made with a polar planimeter, and were reproducible within one percent.

Other procedures were followed as the need arose. Some gross carbon content determinations were made using a Beckman Model 915 Total Organic Carbon Analyzer according to standard operating procedures. A Beckman Model DBG-T Spectrophotometer was used to obtain ultraviolet and visible spectra.

SECTION V

TEST RESULTS

POLYCHLORINATED BIPHENYLS

Arochlor 1254, a mixture of polychlorinated biphenyls containing 54% chlorine by weight was used to represent this type of compound. Typical PCB's are water soluble only to the extent of a few milligrams per liter, so for practical laboratory studies, other solvents or means of dispersion were required. Arochlor 1254 is quite soluble in ethanol and benzene, and it was found that slightly more than 400 mg/l would dissolve in 15% ethanol-85% water mixture. This solvent system was used for some studies, although commercial waste effluent streams would not likely contain any auxiliary solvent. To eliminate any effects caused by the alcohol, Arochlor 1254 was also deposited on glass wool and on fine copper turnings for irradiation. This was accomplished by placing the glass wool or copper turnings in an alcohol solution of the Arochlor and evaporating the solvent under reduced pressure. The container was then filled with distilled water. Air was bubbled through the liquid during most irradiations, and attempts were made to maintain an emulsion without any solubilizing or suspending agent. The bubbling action was not satisfactory for this purpose, and it was found that the Arochlor 1254 became rapidly attached to the walls of the container and to the air inlet.

Benzene was used for the extraction of Arochlor 1254 from the various solvent and dispersion systems, and gas chromatograms were obtained from the benzene solutions. Recovery by benzene extraction was essentially quantitative as shown by the results obtained with a 400 mg/l solution of Arochlor 1254 in a 15% ethanol-85% water mixture:

<u>Extraction</u>	<u>Total % Recovered</u>
1	83.9
2	92.3
3	98.6
4	99.9

Extraction from glass wool was slightly easier:

<u>Extraction</u>	<u>Total % Recovered</u>
1	85.0
2	98.2
3	100.1

The experimental data concerning Arochlor 1254 is summarized in Table 1. Some of the preliminary work showed destructions of more than 20%, but these results were subject to a rather large experimental error, and are therefore of doubtful validity. The major source of error lies in the analysis of the gas chromatograms, where the position of the base line cannot be determined unequivocally, and at times must be assumed rather arbitrarily. The problem in essence is that of measuring small differences between rather large quantities. Overlapping of solvent tailings also presented difficulties. Two methods of determining the area under peaks of the gas chromatograms were evaluated. Some peaks were scissored from the recorder chart and weighed, but this proved less satisfactory than measurement of area with a polar planimeter. The planimeter technique, reproducible to within about 1%, was therefore utilized during the remainder of the work.

One experiment resulted in the rather interesting situation illustrated by Figure 1. The total destruction of Arochlor 1254 was essentially zero, but there was apparently a change in composition during irradiation as indicated by an increase in the peaks shown by the dotted line. This suggests an increase in two of the more volatile, lower molecular weight components of the mixture, and may have been caused by loss of chlorine from one of the heavier components.

The variability of results obtained even under supposedly constant conditions makes interpretation of the data difficult, particularly when it is noted that a 6% "destruction" was noted when air was bubbled through the solution for two hours without irradiation. It is concluded however, that some Arochlor 1254 was destroyed under the experimental conditions employed, and the use of copper turnings as a support medium had little, if any, effect on the results obtained.

PENTACHLOROPHENOL

The gas chromatograms obtained from pentachlorophenol are much simpler than those obtained from the mixture of PCB's identified as Arochlor 1254. There was a considerable initial problem with tailing of the pentachlorophenol, and all samples were subsequently methylated before injection into the gas chromatograph. Diazomethane was the methylating agent used, and was prepared from N-methyl-N-nitroso-p-toluenesulfonamide. In each methylation, approximately 2 1/2 - 3 times the stoichiometric amount of diazomethane was added. Because of the hazardous and not entirely predictable behavior of diazomethane, all methylations were carried out behind the safety glass of a fume hood, and no problems were encountered.

The results of all the pentachlorophenol experiments are summarized in Table 2. One experiment involving deposition on glass

Table 1. SUMMARY OF AROCHLOR 1254 EXPERIMENTS

Concentration Mg/l	Solvent or support	Radiation megarads	Arochlor 1254 % destroyed	Comments
400	Ethanol	1	0	No air bubbled
400	Benzene	1	0	No air bubbled
400	15% Ethanol	2	9	
420	15% Ethanol	19.5	21	See text
440	15% Ethanol	20.5	0	See figure 1
420	15% Ethanol	20.6	4	
400	15% Ethanol	20.6	23	See text
410	15% Ethanol	20.75	9	
27 mg on support	Glass wool	16	<3	
"	Cu turnings	0.0	6	Air bubbled
"	Cu turnings	0.5	1	
"	Cu turnings	0.5	5	
"	Cu turnings	4.0	4	
"	Cu turnings	4.0	11	
"	Cu turnings	15.0	10	
"	Cu turnings	39.0	11	

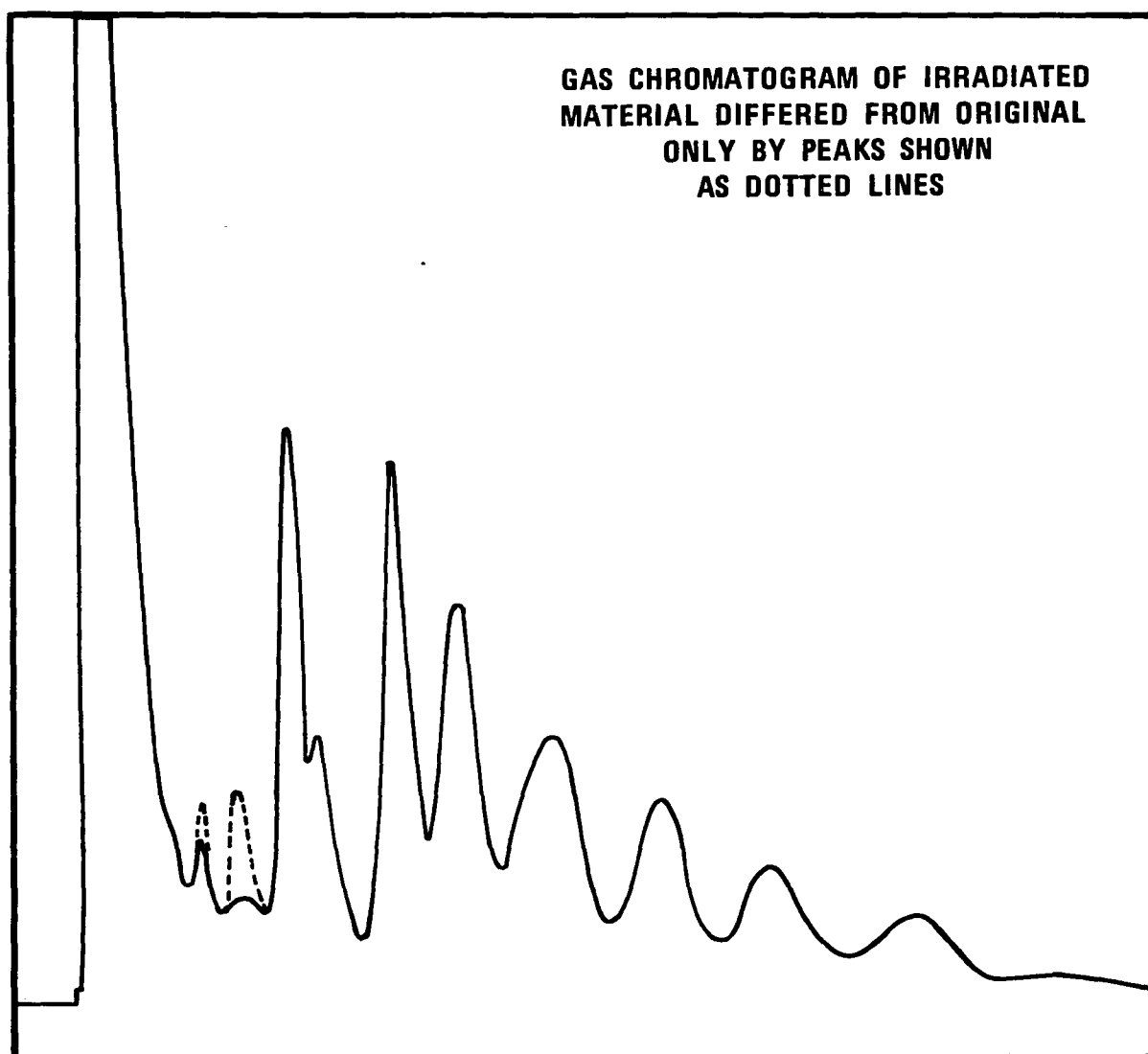


Figure 1. Effect of radiation on Arochlor 1254.

Table 2. SUMMARY OF PENTACHLOROPHENOL EXPERIMENTS

Concentration mg/l	Air bubbling ^a	Radiation megarads	% PCP destroyed	Comments
10 mg + water	Yes	18	>95	On glass wool
10 mg + water	No	18	3.7	On glass wool
900	Yes	0	26	19 hrs. air
900	1 b	0	0	25.5 hrs. air
900	3 b	0	10	26 hrs. air
900	Rapid	0	15	9.5 hrs. air
900	5-10 b	1	76.1	
900	Yes	17.5	95.6	
2860	10 b	0	0	17 hrs. air
2860	10 b	0.25	12.9	
2860	Rapid	0.25	12.1	Copper foil present
2860	10 b	1.0	41.5	
2860	No	1.0	41.7	
2860	10 b	4.0	90.2	
2860	10 b	17.5	97.3	
28,600	Rapid	1	8.6	
28,600	No	8	47.0	
28,600	No	16	68.6	
400	No	1	95.7	
900	No	0.5	47.6	
900	No	1.6	98.0	
6000	No	1.0	21.0	
15,000	No	1.0	15.2	

^aBubbles per second = b

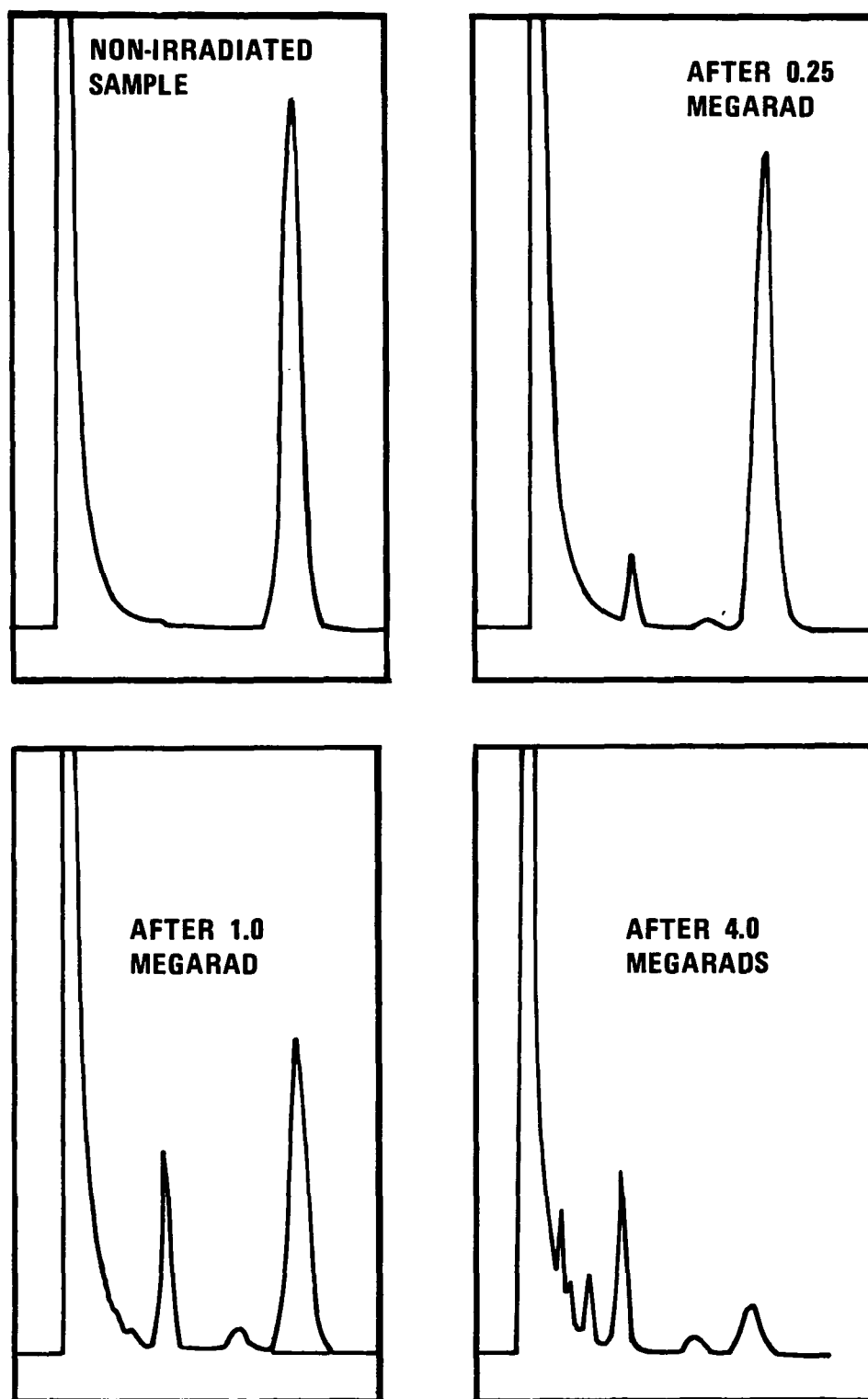


Figure 2. Gas chromatograms of Pentachlorophenol after various radiation doses.

wool was performed, and destruction greater than 95% was observed. It is believed, however, that most of this "destruction" is probably due to volatilization of the pentachlorophenol during the long aeration period. A repetition of the experiment without air bubbling showed only a very small reduction of pentachlorophenol. All other experiments were performed on solutions obtained by dissolving pentachlorophenol in 1% sodium carbonate. Benzene was the extraction solvent and was used directly to recover the sample deposited on glass wool. The aqueous solutions were acidified prior to benzene extraction.

It is clear that pentachlorophenol is destroyed by radiation under the various conditions utilized. Figure 2 shows a series of gas chromatograms of samples following various periods of irradiation of a 2860 mg/l solution. The strong pentachlorophenol peak diminished as the radiation dose was increased, and at the same time other peaks corresponding to more volatile species grew. The effect of irradiation on this particular concentration of pentachlorophenol can be summarized as follows:

<u>Dose delivered</u> <u>Megarads</u>	<u>PCP remaining</u> <u>Per cent</u>
0.0	100
0.25	87.1
1.0	58.5
4.0	9.8

These data, along with similar data for other concentrations have been plotted and appear as Figure 3. It therefore appears that destruction is proportional to the period of irradiation when the sample is exposed at a constant dose rate.

A determination of pentachlorophenol destruction as a function of concentration was made through a series of 1 megarad irradiations. Various concentrations from 0.04% to 2.86% were tested, and the residual pentachlorophenol determined. The number of molecules destroyed was calculated and the information plotted as Figure 4. These data indicate that the number of pentachlorophenol molecules destroyed by a given dose increases with concentration up to approximately three percent, but the fraction of the material destroyed drops quite rapidly with increased concentration.

When pentachlorophenol was dissolved in 1% sodium carbonate, the resulting solution typically had a pH of 10-11. It was observed that in all cases the pH was reduced by irradiation to about 8-9 for short irradiations and to 4-4.5 for a 24 hour irradiation. Appreciable chloride ion also appeared in the irradiated mixtures, indicating that, in effect, hydrochloric acid had been formed through removal of

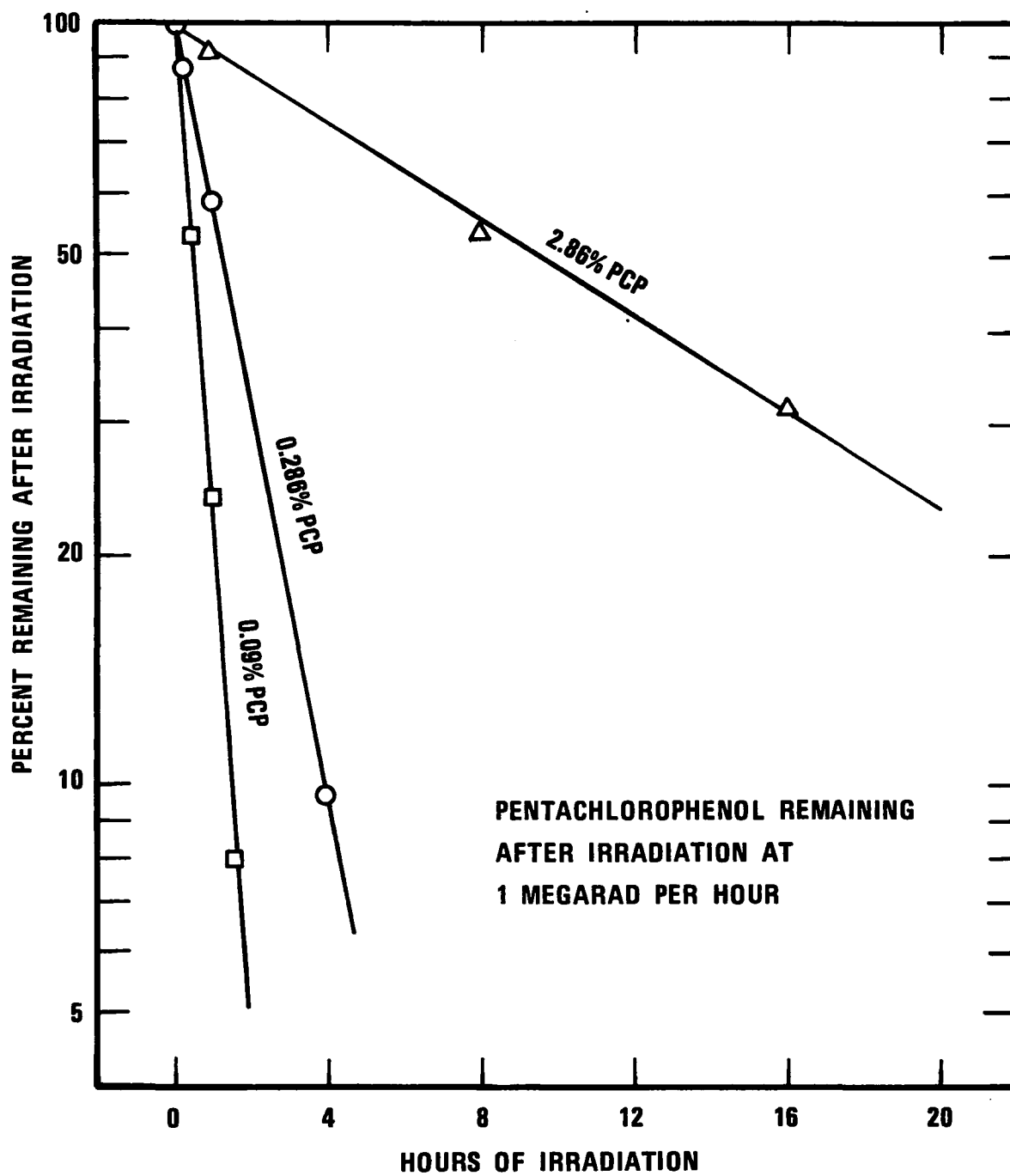


Figure 3. Destruction of Pentachlorophenol by irradiation.

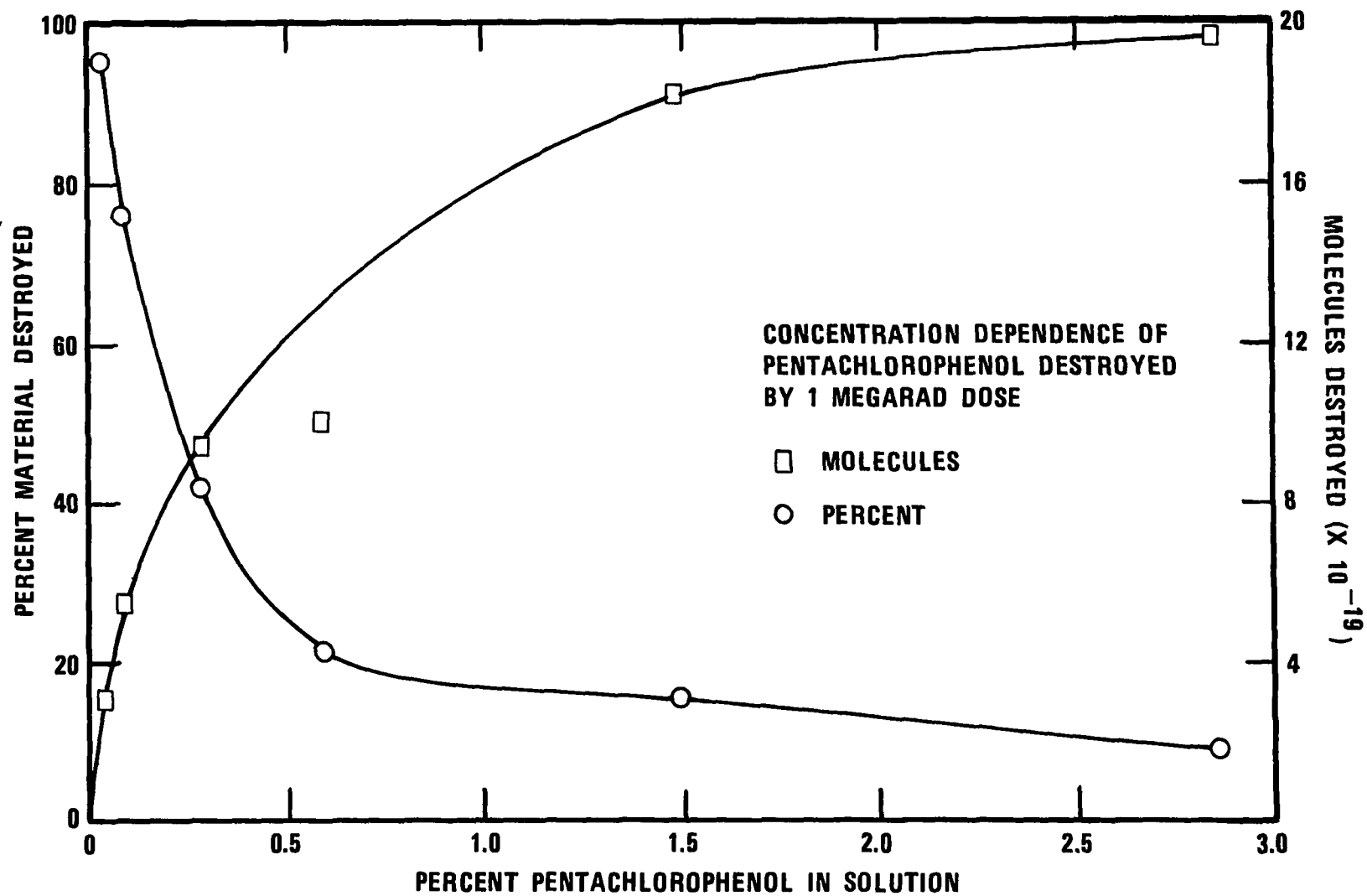


Figure 4. Molecules and percent of Pentachlorophenol destroyed by irradiation.

chlorine from the organic molecule. This is consistent with similar observations recorded in the literature.

A precipitate was present in the mixture subjected to 24 hours of irradiation, and when nitric acid was added to lower the pH from 4 to 1, additional solid was formed. This solid material was found to be insoluble in water and in hexane, but slightly soluble in chloroform and benzene. It melted in the 150-160° range. It was subjected to elemental analysis with these results: carbon 31.6%, hydrogen 0.83%, chlorine 51.3%, oxygen (by difference) 14.1%, inorganic residue 2.2%. A 1.15 gram sample of pentachlorophenol yielded 0.78 grams of precipitate. A gravimetric determination of chloride in the supernatant showed the presence of 0.3 gram. The total accounts fairly well for all the starting material. A Rast determination showed the molecular weight of the precipitate to be 650-750.

The infrared spectra indicated hydroxyl and aromatic groups. The color of the dry solid was tan-gray; however, the material in solution was dark brown. Chromatography of a chloroform solution on neutral alumina showed a slight color in the eluent, but very little material. Most of the material stayed at the top of the alumina column and did not move.

The above properties indicate that the precipitated solid is a low molecular weight "polymer" of probable formula $[C_6Cl_3(OH)_2]_x$ which is in agreement with similar results recorded in the literature¹. It was reported that radiolysis of a six carbon aromatic compound gave "a C_{12} fraction, a C_{18} fraction, and higher molecular weight material. The average molecular weight of the mixture increased with the increasing absorbed dose." Perhaps the property of the irradiation product that is most significant in this work is the greatly reduced solubility of the product compared to the starting material, pentachlorophenol.

2,4,5-TRICHLOROPHENOXYACETIC ACID

This material, commonly known as 2,4,5-T, is widely used in the ester or salt form as a herbicide for species of plants that are resistant to 2,4-dichlorophenoxyacetic acid derivatives (2,4-D). 2,4,5-T falls in the class of chlorinated compounds that persist in the environment, and its dispersion should be subjected to the same scrutiny accorded other similar materials. However, it is frequently accompanied by an accidental impurity, 2,3,7,8-tetrachlorodibenzo-p-dioxin that is formed during manufacture. This by-product, commonly known as TCDD or simply dioxin, is significant because of its persistence in the environment and its exceptionally toxic properties. Experiments on the destruction of dioxin were performed, and are discussed below.

All of the experiments involving 2,4,5-T were carried out with the organic material dissolved in a 1% sodium carbonate solution. Gas chromatograms were obtained from benzene extracts of acidified samples. Experiments with other compounds led to the conclusion that the continuous bubbling of air through a sample during irradiation was of little or no effect. Consequently no air injection was made during the studies of 2,4,5-T.

Table 3 summarizes the observed effects of radiation on 2,4,5-T solutions of several different concentrations. A number of replicated runs are included and illustrate the degree of reproducibility of the results. It was noted that the pH of the samples was lowered by irradiation in the same manner as pentachlorophenol solutions. These experiments show that 2,4,5-T can be destroyed quite effectively by moderate doses of gamma rays from cesium-137. The dose required to destroy a given percentage of a sample was found to depend strongly on the initial concentration of the material as shown in Figure 5.

Visible and ultraviolet spectra were obtained from a 0.1% 2,4,5-T solution before and after irradiation for 55 minutes (0.92 megarad). A small peak was noted at 281 nm prior to irradiation, but was absent in the spectrum of the irradiated sample. Gas chromatographic analysis of the same sample indicated destruction of 81.5% of the 2,4,5-T present. Spectra of other materials were also obtained, but the information available from gas chromatograms was considered more reliable and was therefore utilized.

Possible temperature effects were evaluated in an experiment where destruction at room temperature was compared with destruction obtained at 90-95° C. A sample of 0.1% 2,4,5-T was heated by wrapping the irradiation vessel with a heating tape that could be lowered into the cesium-137 source. The temperature ranged during irradiation from 90° to 95° C as measured with a thermocouple. The heated sample showed a destruction of 67.9% as compared to 69.1% for an unheated control. These values are well within the limits of experimental error, and it was concluded that the increased temperature had no effect on the results obtained.

The effect of the solvent was clearly shown in a series of 1 megarad irradiations. Solutions of 2,4,5-T (0.1%) in diethyl ether, benzene, and hexane revealed no destruction. This is in contradistinction to the 84% destruction obtained under the same conditions when the 2,4,5-T is dissolved in 1% sodium carbonate.

In addition to irradiations carried out in the cesium-137 irradiator at 1 megarad per hour, other tests were made in a cobalt-60 facility where the dose rate was approximately 5.5 megarads per hour. The higher dose rate is quite effective in the destruction of

Table 3. SUMMARY OF 2,4,5-TRICHLOROPHENOXYACETIC ACID EXPERIMENTS

Concentration per cent	Radiation megarads	Area under G. C. peak (in ²)	Average area (in ²)	% 2,4,5-T destroyed
0.02	0	1.43		
		1.33		
		1.34		
		1.22		
		1.32	1.33	0
0.02	0.25	0.40		
		0.36	0.38	31.4
0.02	0.53	0.07		
		0.05	0.06	95.5
0.02	1.0	~0	~0	~100
0.02	4.0	~0	~0	~100
0.1	0	2.07		
		1.96		
		2.01	2.01	0
0.1	0.25	1.38		
		1.45		
		1.35	1.39	30.9
0.1	1.0	0.30		
		0.32		
		0.34	0.32	84.1
0.1	4.0	~0		
		~0		
		~0	~0	~100
0.5	0	2.35		0
0.5	0.25	2.11		10.2
0.5	0.5	1.98		15.7
0.5	1.0	1.57		33.2
0.5	4.1	0.26		88.9

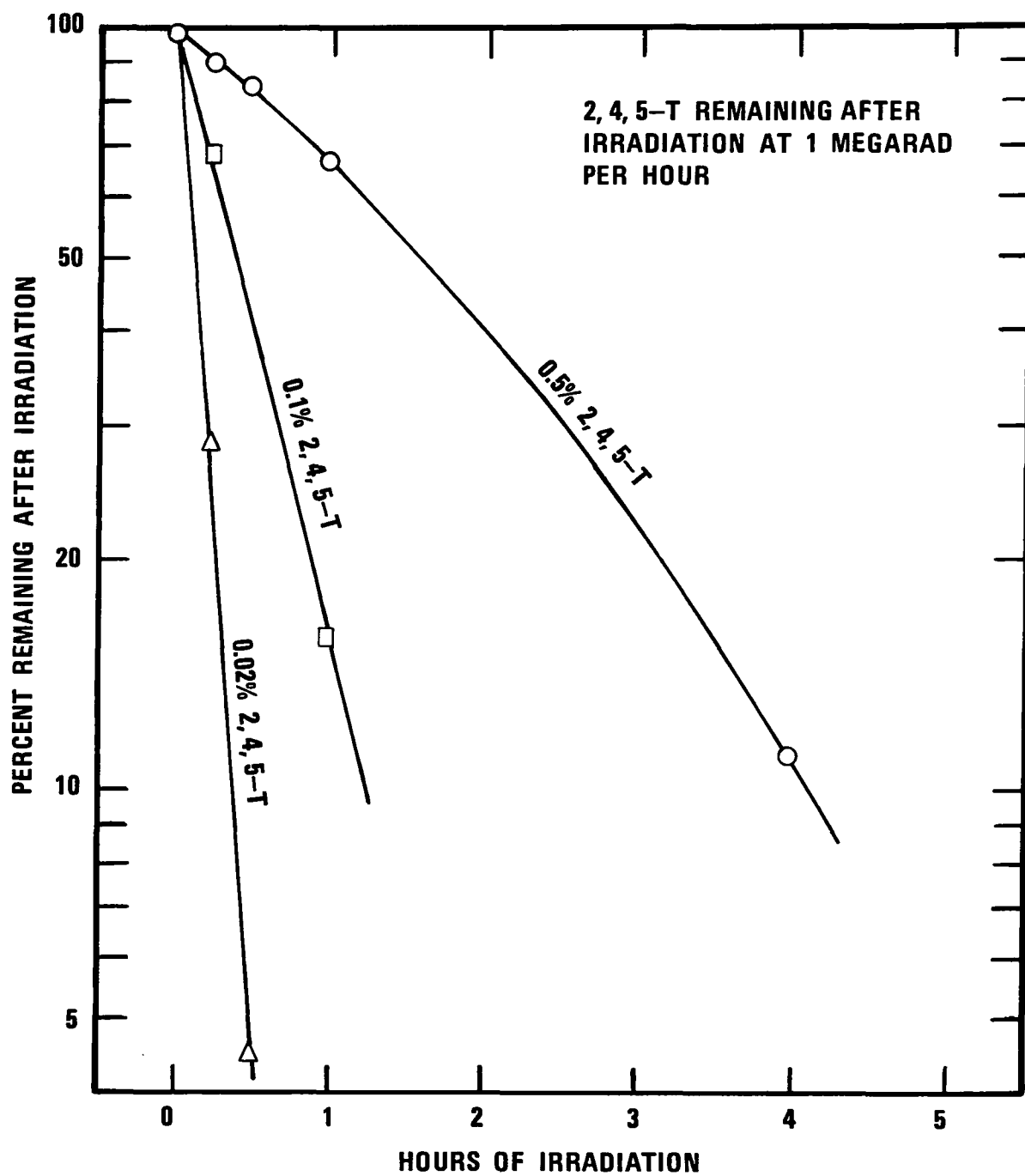


Figure 5. Destruction of 2,4,5-Trichlorophenoxyacetic Acid by irradiation.

2,4,5-T, but is less efficient. The cobalt-60 experiments are summarized in Table 4.

2,4 DICHLOROPHENOXYACETIC ACID

The irradiation studies of 2,4-D produced results similar to those for 2,4,5-T; i.e., dilute aqueous solutions of 2,4-D can be destroyed quite effectively by moderate doses of gamma rays from cesium-137. As was found with 2,4,5-T and pentachlorophenol the dose required to destroy a given percentage of a sample depends strongly on the concentration of the material. Aqueous solutions of 0.02 to 2.5 per cent 2,4-D in one percent sodium carbonate were irradiated. The doses ranged from 0.25 to 16.8 megarads. The results of these studies are given in Table 5 and plotted in Figure 6.

The product formed by longer irradiation of 2,4-D was found to be a low molecular weight polymer. The material resisted all attempts of crystallization, gave an elementary analysis indicating appreciable dechlorination, and gave an average molecule weight of 635, as determined by the Rast method. These results indicate something between a trimer and a tetramer which had lost some chlorine.

MIXTURES OF COMPOUNDS

Samples of a waste stream resulting from the manufacture of toxaphene were obtained and examined. The manufacturer reported the toxaphene level in this effluent to be very low, and our laboratory results concurred. The gas chromatograms of toxaphene are complex, and at the parts per billion range are difficult to interpret quantitatively. When effluent samples were irradiated at doses up to one megarad, little or no effect was discernable.

Herbicide orange, a mixture of esters of 2,4-D and 2,4,5-T was also the subject of investigation. This product contains a large number of different impurities and by-products, the most significant of which is 2,3,7,8-tetrachlorodibenzo-p-dioxin, commonly called dioxin. There is at present a large supply of the herbicide mixture in existence that could be used in many locations if the very toxic dioxin could be removed or destroyed.

Dioxin is present in the herbicide mixture at levels up to about 30 parts per million, and is difficult to detect in the presence of massive amounts of other organic compounds. Column chromatography offers one technique for the separation of dioxin from complex mixtures². The success of this procedure appears to depend strongly on the experience of the analyst, but was found to give acceptable results after some preliminary experimentation. It was found that within experimental uncertainties, no change in the dioxin content of

Table 4. IRRADIATION OF 0.1% 2,4,5-T IN 1% SODIUM CARBONATE
(cobalt-60 irradiator at 5.5 megarads/hour)

Time (Minutes)	Area (in ²)	Average (in ²)	% Destroyed
0	1.86	1.88	0
	1.90		
5	1.14	1.15	38.8
	1.15		
10	0.64	0.65	63.5
	0.66		
15	-	-	82.3
30	-	-	~100
60	~0	~0	~100
	~0		

Table 5. SUMMARY OF 2,4-DICHLOROPHENOXYACETIC ACID EXPERIMENTS

Concentration per cent	Radiation dose megarads	Area under G.C. peak (in ²)	Average area in ²	% 2,4,-D destroyed
.02	0	0.66		
		0.65		
		0.70	0.67	0
.02	0.25	0.38		
		0.41		
		0.38	0.39	41.7
.02	0.5	0.10		
		0.10		
		0.11	0.103	84.6
.02	1.0	0.005		
		0.0075		
		0.005	0.0058	99.1
.02	2.0	0	0	100
0.1	0	0.98		
		1.02		
		1.02	1.01	0
0.1	0.25	0.69		
		0.79		
		0.72	0.73	27.7
0.1	0.5	0.54		
		0.57		
		0.56	0.56	44.5
0.1	1.0	0.26		
		0.27		
		0.29	0.27	73.3
0.1	2.0	0.05		
		0.03		
		0.04	0.04	96.04

Table 5 (continued). SUMMARY OF 2,4-DICHLOROPHENOXYACETIC
ACID EXPERIMENTS

Concentration per cent	Radiation dose megarads	Area under G.C. peak (in ²)	Average area in ²	% 2,4,-D destroyed
0.5	0	1.06		
		0.90		
		0.82		
		0.94	0.93	0
0.5	0.25	0.77		
		0.80		
		0.84	0.80	14.0
0.5	0.5	0.74		
		0.85		
		0.87		
		0.83	0.82	9.0
0.5	1.0	0.77		
		0.63		
		0.60	0.67	25.5
0.5	4.0	0.21		
		0.20	0.205	77.2
0.5	16.8	~0	~0	~100
2.5	0	1.33		
		1.36	1.34	0
2.5	0.53	1.25		
		1.30	1.28	4.5
2.5	1.0	1.21		
		1.31	1.26	6.0
2.5	2.0	1.08		
		1.16	1.12	15.4
2.5	4.2	0.92		
		0.94	0.93	30.6
2.5	8.0	0.70		
		0.70	0.70	47.8

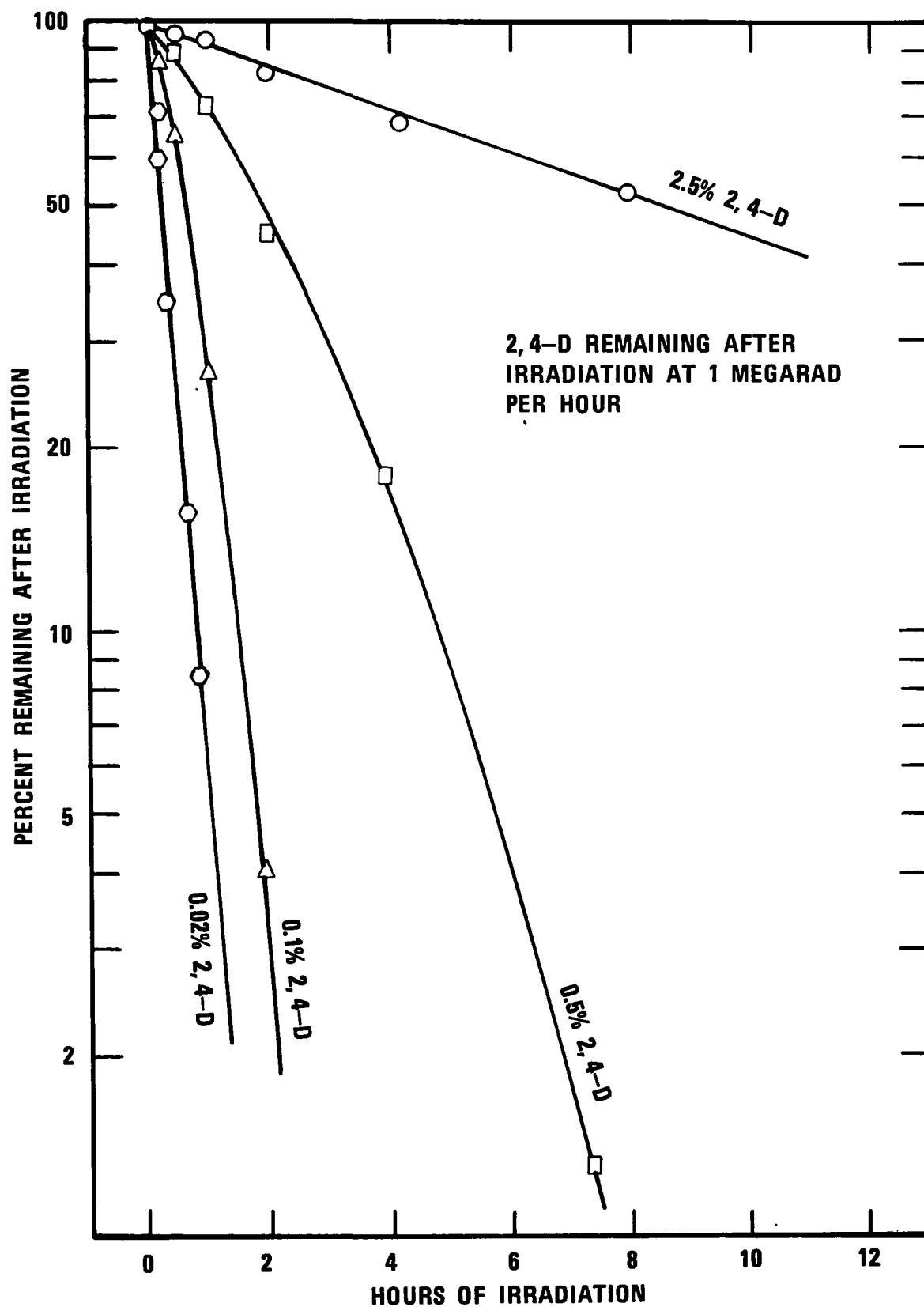


Figure 6. Destruction of 2,4-Dichlorophenoxyacetic Acid by irradiation.

herbicide orange was brought about by radiation doses up to one megarad.

Other means for the destruction of dioxin were attempted. Solutions of dioxin in hexane, benzene, and alcohol were refluxed in the presence of stainless steel for periods up to 48 hours. The resulting gas chromatograms gave well-defined peaks, but indicated no change in dioxin concentration due to the refluxing. The experiments were repeated with the refluxing carried out under ultraviolet light. Again the gas chromatograms were very good, but the ultraviolet radiation had no detectable effect.

G-VALUES

In radiation chemistry studies, it is important to measure the efficiency of radiation utilization. When dealing with liquids or solutions, the term G-value is frequently used and denotes the number of molecules changed for each 100 electron volts of energy absorbed. Thus G(X) refers to the number of molecules of product X formed on irradiation per 100 eV of energy absorbed and G(-Y) refers in the same way to the loss of material Y that is destroyed on irradiation.

A number of G-values were calculated for some of the compounds studied, and they indicate the relative efficiency (and therefore cost) of radiation destruction of the compound in question. For this work the G-value is defined as:

$$\frac{\text{Number of Chlorinated Molecules Destroyed}}{\text{Energy Absorbed by Sample (in units of 100 eV)}}$$

The calculated values are given in Table 6. As might be expected, the G-value for each compound depends on the concentration. In the more concentrated solutions, the target density is greater, and more interactions result. However, the order of magnitude of these values is too low to offer much hope for economic feasibility at the present cost levels of radiation processes.

ENHANCEMENT OF RADIATION UTILIZATION

Two approaches were evaluated in attempts to increase the efficiency of the gamma irradiations. The first method involved the use of a material of high atomic number to act as a secondary irradiator to increase the dose delivered to an aqueous solution. The objective was to increase the number of gamma ray interactions occurring in the sample and, in so doing, increase the number of energetic electrons depositing energy in the aqueous solution. An increase in the number of gamma ray interactions should result when a sample is loaded with a high Z element such as barium. If the barium compound is finely divided and maintained in dispersion, a

Table 6. CALCULATED G-VALUES

Compound	Concentration (percent)	G-Value
Pentachlorophenol	0.09	2.49
"	0.286	5.35
"	2.86	8.92
2,4,5-Trichlorophenoxyacetic acid	0.02	3.3
"	0.10	5.1
"	0.50	7.4
2,4-Dichlorophenoxyacetic acid	0.02	2.1
"	0.10	4.8
"	0.50	5.6
"	2.50	9.0

significant fraction of the electrons released in the barium compound should find their way into the aqueous solution where much of their energy might be deposited. The result would be an enhancement of the dose delivered to the aqueous sample.

A series of experiments was performed in which varying amounts of powdered barium sulfate were added to 20 ml portions of 0.1% 2,4,5-T in 1% sodium carbonate solution. Each sample was stirred during irradiation to maintain a uniform suspension of the barium sulfate. All samples were irradiated for 0.4 hr (at 1 megarad/hr). The presence of barium resulted in increased destruction in all cases. However, there is seemingly a saturation effect, as additions beyond 40 grams did not increase the destruction. The results of these experiments are plotted in Figure 7.

A second approach to enhancement of radiation efficiency involved evaluation of a number of potential catalysts. It has been reported³ that lanthanum phosphate catalyzes the conversion of aromatic chloro compounds to phenols at high temperatures (400° C). Attempts to repeat this work resulted in some dechlorination, but the percent conversion was quite low. Nevertheless, lanathanum phosphate was used in a series of experiments involving irradiation at ambient temperatures. A 0.1% suspension in water containing 0.5% finely divided lanthanum phosphate was irradiated while being stirred. Systems of Arochlor 1254 in water and 2,4,5-T in base were also irradiated under similar conditions. The results of these experiments indicate that lanthanum phosphate plays no significant role in the destruction of these chlorinated hydrocarbons.

The catalytic effects of ferric sulfate, sodium nitrate, sodium nitrite and sodium hypochlorite on dilute solutions and suspensions of various chlorinated hydrocarbons have been studied. One-tenth percent solutions or suspensions of DDT in water and 2,4,5-T in base were irradiated while in the presence of each of the above potential catalysts. No significant destruction of DDT occurred for doses to one megarad. The effect of these additives on the radiation destruction of 2,4,5-T is shown below for a dose of one megarad. For purposes of comparison the percent destruction is also shown for the case of no additive.

In each case 0.5 percent of the potential catalyst was added to the solution.

<u>Additive</u>	<u>Percent 2,4,5-T Destroyed</u>
No additive	84.1
Sodium Nitrate	32.6
Sodium Nitrite	10.0
Sodium Hypochlorite	67.2
Ferric Sulfate	84.0

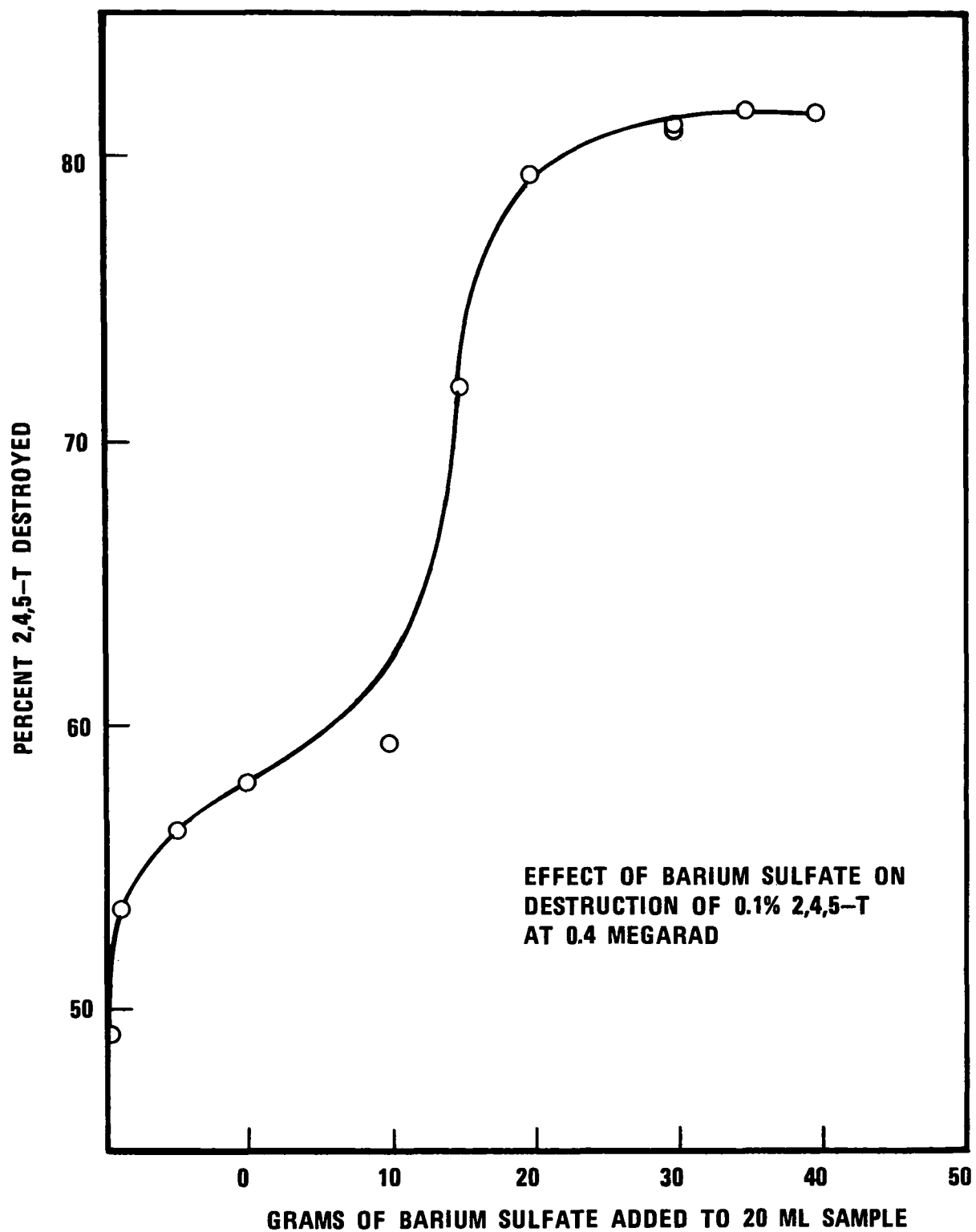


Figure 7. Barium Sulfate enhancement of radiation effects.

Ferric sulfate was apparently without effect, but all other materials decreased the amount of destruction. These findings suggest that the irradiation of manufacturing waste effluents is likely to be very inefficient due to the diversity of materials present, many of which would interfere with utilization of the radiation.

SECTION VI

REFERENCES

1. Spinks, J. W. T. and R. J. Woods. An Introduction to Radiation Chemistry. New York, John Wiley and Sons, Inc., 1964. p. 294.
2. Elridge, D. A. The Gas-chromatographic Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in 2,4,5-Trichlorophenoxyacetic Acid ("2,4,5-T"), 2,4,5-T Ethylhexyl Ester, Formulation of 2,4,5-T Esters and 2,4,5-Trichlorophenol. Analyst (London). 96:721-27, 1971.
3. Rennard, R. J., Jr. and W. L. Kehl. The Hydrolysis of Aryl-chlorides Over Rare Earth Phosphate Catalysts. (Presented at ACS Division of Petroleum Chemistry. New York. August, 1972.)

ADDITIONAL REFERENCES

- Blair, E. H. Chlorodioxins - Origin and Fate. Washington, D. C., American Chemical Society, 1973.
- Craft, T. F. and G. G. Eichholz. Dyestuff Color Removal by Ionizing Radiation and Chemical Oxidation. U. S. Environmental Protection Agency. Washington, D. C. Report EPA-R2-73-048. 1973.
- Craft, T. F. and G. G. Eichholz. Decoloration of Textile Dye Waste Solutions by Combined Irradiation and Chemical Oxidation. Nuclear Technology. 18:46-54, 1973.
- Edwards, C. A. Persistent Pesticides in the Environment. Cleveland, CRC Press, 1970.
- Friedlander, G., J. W. Kennedy, and J. Miller. Nuclear and Radiochemistry. New York, John Wiley and Sons, Inc., 1964.
- Garrison, A. W., F. N. Case, D. E. Smiley, and D. L. Kau. The Effect of High Pressure Radiolysis on Textile Wastes, Including Dyes and Dieldrin. (Presented at 5th International Conference on Water Pollution Research. San Francisco. July, 1970.)
- Kimbrough, R. D. Gamma Irradiation of DDT: Radiation Products and Their Toxicity. Journal of Agricultural and Food Chemistry. 19:1037-1038, 1971.

Lenz, B. L., E. S. Robbins, F. N. Case, D. E. Smiley, and D. L. Kau. The Effect of Gamma Irradiation on Draft and Neutral Sulphite Pulp and Paper Mill Aqueous Effluents. Pulp and Paper Magazine of Canada. 72:75-80, 1971.

Matsumura, F., G. M. Baush, and T. Misato (Editors). Environmental Toxicology of Pesticides. New York, Academic Press, Inc., 1972.

Morris, R. D. and T. F. Craft. Degradation of Acid Dyes by Irradiation Plus Oxidation. International Journal of Applied Radiation and Isotopes. 24:245-52, 1973.

Sherman, W. V., R. Evans, E. Nesyto, and C. Radlowski. Dechlorination of DDT in Solution by Ionizing Radiation. Nature. 232:118, 1971.

Swallow, A. J. Radiation Chemistry of Organic Compounds. New York, Pergamon Press, Inc., 1960.

Whittemore, W. L. Ionizing Radiation for the Treatment of Municipal Waste Waters. Gulf General Atomic Final Report GA-9924, Contract AT(04-3)-167. Atomic Energy Commission, Division of Technical Information. 1970.

Zabik, M. J., R. D. Schuetz, W. L. Burton, and B. E. Pape. Photochemistry of Bioactive Compounds: Major Photolytic Produce of Endrin. Journal of Agricultural and Food Chemistry. 19:308, 1971.

TECHNICAL REPORT DATA

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1. REPORT NO. EPA-660/2-75-017		2.	3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Radiation Treatment of High Strength Chlorinated Hydrocarbon Wastes			5. REPORT DATE	
			6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) T. F. Craft, R. D. Kimbrough, C. T. Brown			8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Engineering Experiment Station Georgia Institute of Technology Atlanta, Georgia 30332			10. PROGRAM ELEMENT NO. 1BB036	
			11. CONTRACT/GRANT NO. R800312	
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency National Environmental Research Center-Corvallis Southeast Environmental Research Laboratory College Station Road, Athens, Georgia 30601			13. TYPE OF REPORT AND PERIOD COVERED Final	
			14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES				
16. ABSTRACT <p>The possible use of gamma radiation for the treatment of waste effluents containing chlorinated hydrocarbons, particularly pesticides, has been investigated. Significant destruction was obtained of representative compounds such as pentachlorophenol, 2,4,5-trichlorophenoxyacetic acid, and 2,4-dichlorophenoxyacetic acid. Radiation treatment had little effect on polychlorinated biphenyls or mixtures of compounds, including actual manufacturing effluents.</p> <p>It was found that the addition of a material of high atomic weight, such as barium, increased the efficiency of radiation utilization. No other materials were found which increased the desired destruction. G-values were calculated for pentachlorophenol, 2,4,5-trichlorophenoxyacetic acid, and 2,4-dichlorophenoxyacetic acid.</p> <p>It is concluded from the magnitude of these values that radiation treatment of chlorinated hydrocarbons is not economically feasible at the present level of radiation costs.</p>				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Pesticides, Water Pollution Treatment, Gamma Radiation, Polychlorinated Biphenyls, 2,4,5-T, 2,4-D, Pesticides Control, Chlorinated Hydrocarbons, Tertiary Treatment		Pesticide Manufacturing Industry		06/06
18. DISTRIBUTION STATEMENT Release Unlimited		19. SECURITY CLASS (This Report) Unclassified		21. NO. OF PAGES 39
		20. SECURITY CLASS (This page) Unclassified		22. PRICE