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Application of a two-dimensional chromatography system for gas-phase photodegradation studies of polychlorinated dibenzo-*p*-dioxins

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Abstract

Gas-phase photodegradation of polychlorinated dibenzo-*p*-dioxins was studied with a two-dimensional gas chromatographic system consisting of two independently operated gas chromatographs interfaced to a photoreactor. Gas flow through the chromatographs and photoreactor were directed with two switching valves. This arrangement permitted isolation and irradiation of solute in the photoreactor for varied periods and under different atmospheres. The irradiation experiments revealed that different dioxin congeners degrade at different rates; e.g., a 20-min irradiation resulted in the degradation of approximately 80% of 2,3,7-trichlorodibenzo-*p*-dioxin, while only 30% of the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was found to degrade under the same conditions. As expected, photodegradation rates decreased with an increase in the number of chlorines. Degradation rates were also influenced by the position of chlorine substitutions. The results showed that, in contrast to solution-phase studies, congeners with peri chlorines photodegrade more rapidly than congeners with laterally substituted chlorines. These results indicate that, in the gas phase, more toxic (laterally substituted) congeners are more persistent than less toxic (peri substituted) analogues.

1. Introduction

Many sites in the USA and abroad are contaminated with polychlorinated dibenzo-*p*-dioxins (PCDDs) as a result of accidents or prolonged industrial activities. PCDDs, or dioxins (as these chemicals are generally known), are highly toxic unwanted byproducts of a number of chemical processes such as incineration and application of chlorine bleach in the pulp and paper industries [1–4]. The 75 PCDD homologues show varied physicochemical properties and toxicities depending on the degree and position of chlorine substitutions. Analogues with four or more chlorines are practically insoluble in water, resistant to biodegradation and exhibit a high degree of environmental persistence [5,6].

Photodegradation, i.e., destruction (transformation) achieved through exposure to the near-UV components of sunlight, is reported to be the most significant natural mechanism for removal of dioxins in the environment [7]. The degradation proceeds through a free radical

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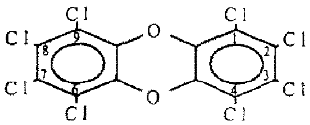
mechanism and, under suitable conditions, leads to the formation of analogues with fewer chlorines. Depending on the substitution, the elimination of chlorine can result in analogues with higher or lower toxicities [8]. A number of studies dealing with photodegradation of dioxins and related polychlorinated dibenzofurans (PCDFs) in the solution phase have been reported in literature [9–15]. However, the mechanism of photoreaction for these compounds has not been fully elucidated. It has been observed that both the rate of degradation and the nature of photoproducts are affected by the physical state of the matrix. Significant differences have been reported in the types of dechlorination products formed in solution phase and on solid particles [16,17]. A preferential loss of chlorines from the lateral positions (2,3,7,8) has been reported in a number of solution phase studies. However, Kieatiwong et al. [18] have observed that dechlorination of octachlorodibenzo-*p*-dioxin (OCDD) adsorbed on soil occurs preferentially at the peri positions (1,4,6,9). Similar results have been obtained by Tysklind et al. [19] with PCDD bearing fly ash samples. Surprisingly, dechlorination of PCDFs, in the same study [19], was shown to occur preferentially at the lateral position. Since the toxicity of PCDD is dependent on the chlorine substitution, the dechlorination route can have significant effect on toxicity. A review of literature revealed that one of the most overlooked areas has been photodegradation in the vapor phase.



Lateral positions: 2,3,7,8
Peri positions: 1,4,6,9

The primary reason for the lack of information in this area is related to the low ambient vapor pressure of these compounds. However, it is quite evident that despite their low vapor pressure, substantial portions of PCDDs in the troposphere exist in the vapor phase; e.g., according to one estimate, ca. 20–60% of TCDD is present in the vapor form [20]. Furthermore, one of the major sources of widespread distribution of dioxins in the environment is incineration which releases these contaminants into the atmosphere [21–23]. These facts, coupled with the observation that bioavailability of dioxins through pulmonary uptake is nearly 100% [24], make gas-phase photochemistry of dioxins an important and interesting area of research.

The objective of the study was to investigate the vapor-phase photodegradation of PCDDs in the gas phase. The emphasis was placed on degradation kinetics of variously substituted dioxins and characterization of photoproducts obtained under different atmospheric conditions. These objectives were met with the application of a dual-column chromatographic system interfaced to a photoreactor.

A number of studies on gas-phase reactions with dual-column gas chromatographic systems have been reported in literature [25–27]. A few of these studies have been dedicated to the gas-phase photolysis of organic compounds [28,29]. The advantages of such chromatographic arrangement for gas-phase photolysis have been discussed by Aue and Aigner-Held [28]. The system used in the present study permitted a convenient means of discerning the photodegradation rate for PCDDs and permitted characterization of hydrodehalogenation products.

2. Experimental

The chromatographic system was constructed around a thermostated aluminum block. The block served as the housing for the photoreactor, two switching valves, and an externally mounted cryogenically cooled trap consisting of a thin-wall 1/8-in. (1 in. = 2.54 cm) stainless-steel tube with a nichrome wire wound around it. The low mass cryogenic trap was rapidly cooled by passing liquid nitrogen through it and rapidly heated by passing an electrical current through the nichrome resitive wire. The gas chromatographs, photoreactor and the cryotrap were interconnected through the switching valves. A schematic of the system is shown in Fig. 1. The analytes of

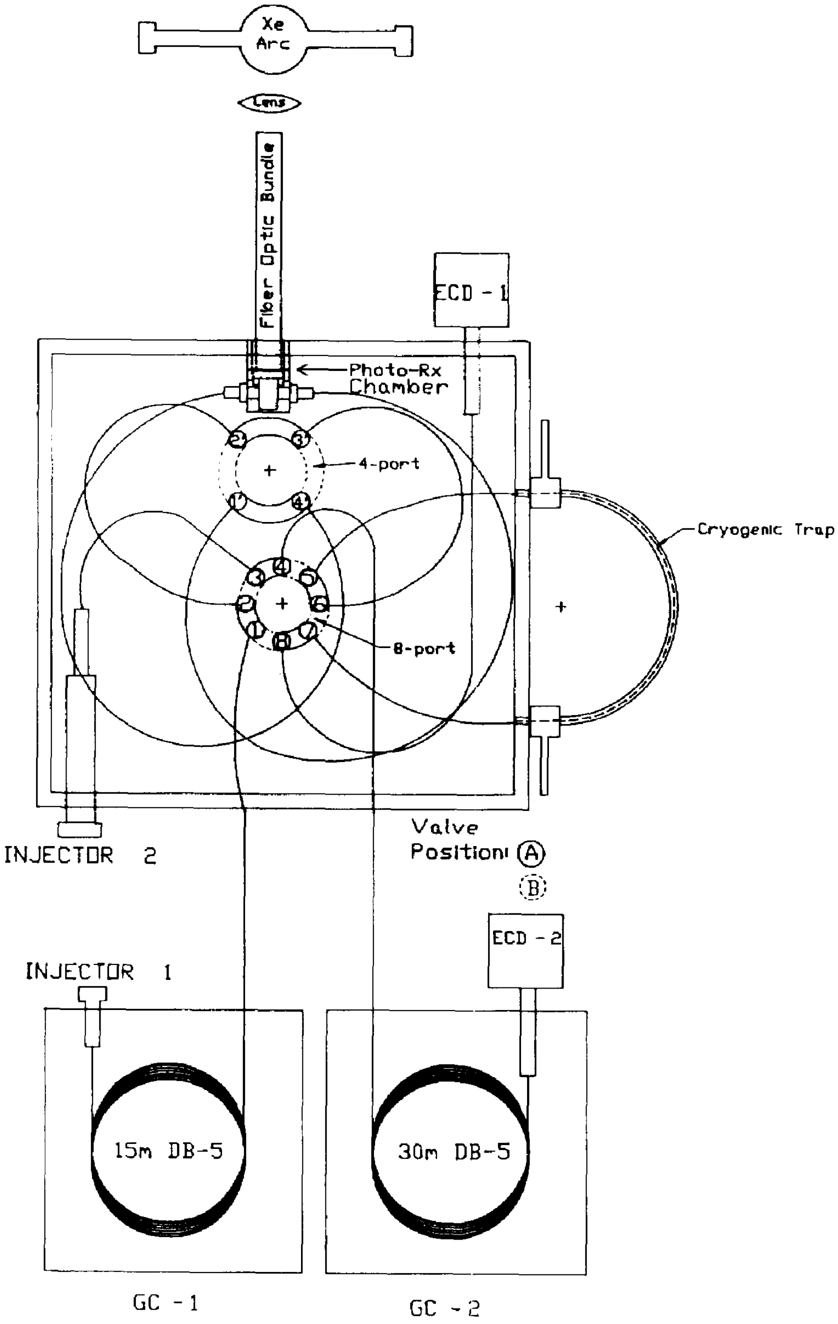


Fig. 1. Schematic diagram of two-dimensional reaction gas chromatography system. Broken lines denote valve positions B.

interest were introduced into the system via the first gas chromatograph (GC-1) equipped with an electron-capture detector (ECD-1). The detector served as a monitor for eluting components and facilitated in switching the appropriate component. The component transfers were accomplished with an eight-port valve (V1; VICI 4C8WT). A four-port valve (V2; VICI 4C4WT) was also incorporated into the system to permit transfer and entrapment of the selected analyte in the photoreactor. The low-dead-volume valves were obtained from Valco (VICI, Houston, TX, USA). This feature allowed variation of irradiation time over a wide range. After irradiation, the residual analytes and photoproducts were transferred to the cryotrap and standard analytes were added to the second injector to facilitate product peak confirmation through co-chromatography. All components of the system were interconnected with 0.25 mm I.D. aluminum clad fused-silica tubing.

The photoreactor consisted of a 500-μl quartz cell placed in gas-tight stainless casing. The broadband-UV excitation used for irradiation was obtained from a xenon arc lamp. The light from the xenon lamp was passed through a water filter (Oriel 61945) to absorb IR radiation. The filtered light was collected and focused with a fiber optic coupler (Oriel 77800) onto a high-grade fused-silica fiber optic bundle. The optic bundle was obtained from Fiberguide Industries (SFS320/385T). The bundle was designed to withstand temperatures up to 325°C for extended periods of time.

Initially, both valves were switched to position A. This permitted passage of effluent from GC-1 to ECD-1 while bypassing the photoreactor. All valve-switching operation timing began with the appearance of the solvent front at ECD-1. The change of V2 to position B allowed the sample band to pass into the photoreactor. After a set time interval, V2 was switched to position A, trapping the sample band in the photoreactor. The analyte in the reactor was irradiated with broadband radiation in the UV–visible region. After the desired exposure period, the reactor contents were transferred to the cryogenically cooled trap by switching V2 to position B. V1 was switched to position B, and the trapped residual analyte and photoproduct were flash vaporized and introduced into the second column. The separated components were monitored by the second electron-capture detector (ECD-2) or a quadrupole mass spectrometer. An example of the timing sequence for the photoanalysis of hexachlorobenzene is given in Fig. 2. The initial separation of the analyte was carried out with a 15 m × 0.25 mm fused-silica capillary column coated with 95% methyl-/5% phenylpolysiloxane. This column was installed in GC-1, a benchtop gas chromatograph (Tracor Model 560) equipped with a split/splitless injector. Separation of the residual and photoproducts was accomplished with a 30 m × 0.25 mm fused-silica capillary column coated with 95% methyl-/5% phenylpolysiloxane that was installed in GC-2 (Shimadzu MiniGC-3). The column oven parameters and chromatographic conditions were optimized for the analyte of interest.

3. Results and discussion

The overall objective of the present study was to investigate photoinduced disappearance (dechlorination) of PCDDs in the gas phase. The specific objectives of the study were to determine the correlation between rate of disappearance (degradation) and chlorine substitution and to characterize neutral photoproducts. A two-dimensional gas chromatography system with a photoreactor was selected as the apparatus of choice for the study. Although similar systems have been used for photochemical and analytical studies in the past [26–29], the present system provided better resolution, permitted a higher degree of flexibility in the irradiation time and allowed for condition modification in the photoreaction chamber.

Prior to its use in PCDD studies, the performance of the system was evaluated with hexachlorobenzene (HCB). This polychlorinated compound was selected because of its high response with both ECD and MS as well as its good chromatographic properties. Chromatographic profiles of HCB obtained through peak transfer to GC-2 are shown in Fig. 3. The peak in profile A shows HCB transferred without irradiation whereas profile B depicts two peaks obtained after 5 min irradiation. One of the peaks in profile B eluted with the same retention time as HCB while the other eluted 2.94 min earlier than HCB. The retention time of the early peak matched that of pentachlorobenzene.

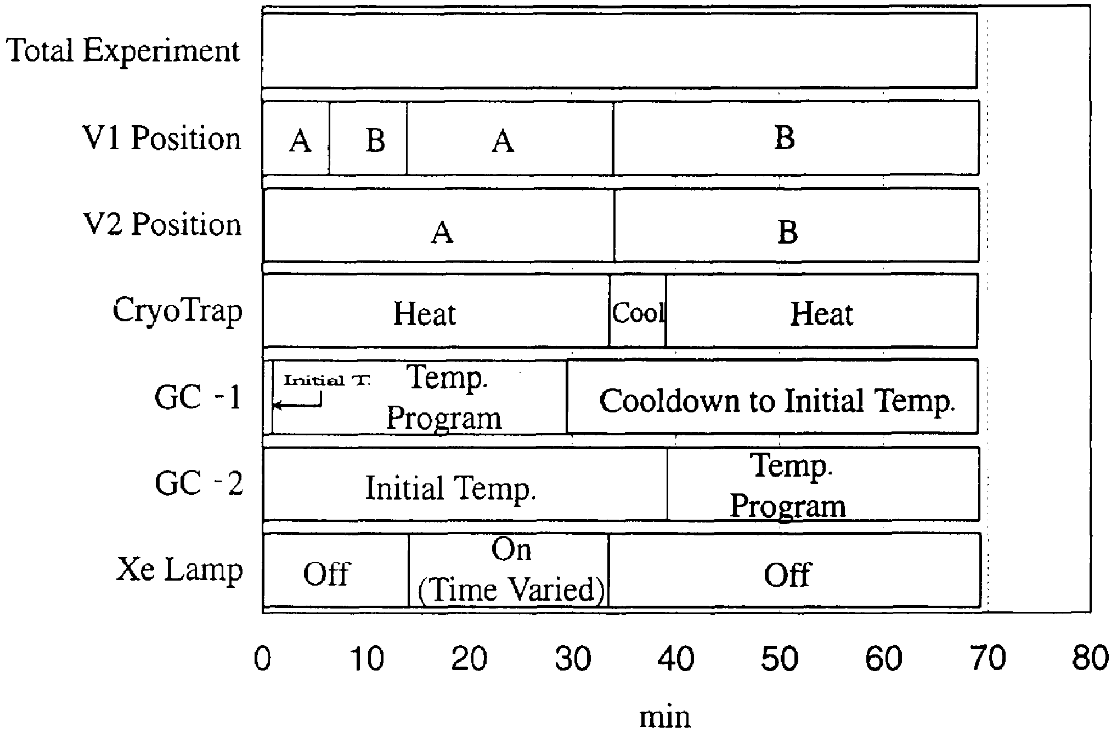


Fig. 2. An example of a timing sequence used for the gas-phase photodegradation of a typical analyte. Initial injection was at $T = 0$.

This observation was confirmed by co-chromatography. For this purpose, a standard solution of pentachlorobenzene was injected into the second injector and pentachlorobenzene was trapped in the cryotrap. The residual HCB and photoproduct obtained after irradiation was also trapped in this same trap. The contents of the trap were heat desorbed and chromatographed on the second column. The photoproduct and standard pentachlorobenzene were found to co-elute, thus establishing the identity of the photoproduct. A quantitative assessment of the photoreaction revealed that, under the experimental condition, approximately 5% of HCB was converted to pentachlorobenzene. Similar replacement of chlorine with hydrogen upon irradiation of chlorinated benzenes has been reported by Aue and Aigner-Held [29]. The photoproduct yields in the mercury sensitized system used by Aue appears to be appreciably higher than the pentachlorobenzene yields obtained with the present system with "pure" He. However, an increased yield of photoproducts was obtained when a hydrogen donor such as hexane was added to the gas stream. The products obtained with the carrier gas doped with hexane are shown in Fig. 4. The degradation kinetics of HCB degradation was studied in a limited set of experiments by irradiating a known amount (500 pg) of HCB for varied time periods. The results yielded first-order degradation kinetics (Fig. 5). The successful evaluation of the system with HCB led us to its use with the PCDDs. The system can be used to study vapor-phase phototransformation of other environmental pollutants such as polychlorinated biphenyls.

In order to delineate a correlation between dioxin structure and photodegradation, a number of trichloro- through pentachloro- dioxins were subjected to photoirradiation. The congeners selected for the study included 2,3,7-trichlorodibenzo-*p*-dioxin (TriCDD); 1,2,3,4-

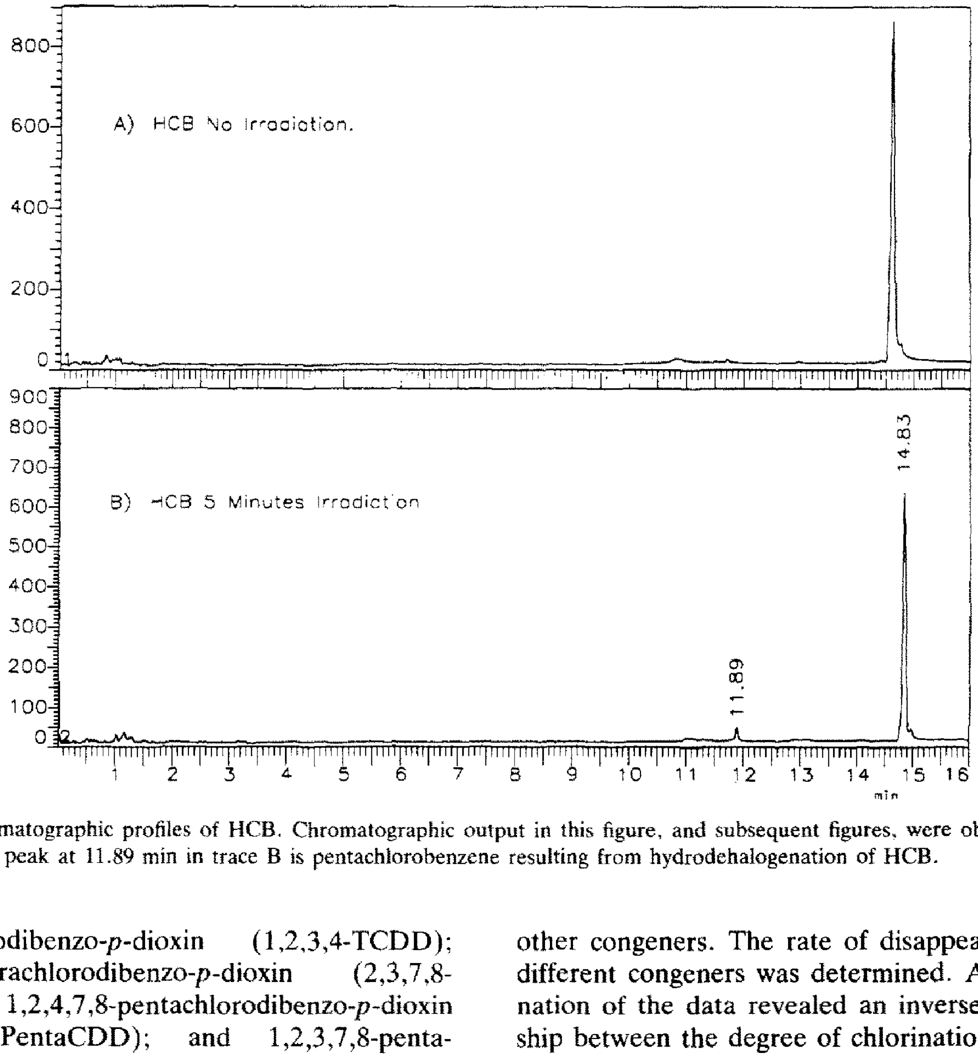


Fig. 3. Chromatographic profiles of HCB. Chromatographic output in this figure, and subsequent figures, were obtained with ECD-2. The peak at 11.89 min in trace B is pentachlorobenzene resulting from hydrodehalogenation of HCB.

tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD); 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD); 1,2,4,7,8-pentachlorodibenzo-*p*-dioxin (1,2,4,7,8-PentaCDD); and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PentaCDD).

The irradiation experiments revealed that different dioxin congeners degrade at different rates; e.g., a 20-min irradiation resulted in degradation of as much as 80% of TriCDD while only 30% of the 2,3,7,8-TCDD was found to degrade under the same conditions. The results also showed that, in contrast to HCB, none of the dioxin congeners yielded a hydrodehalogenation photoproduct. The chromatographic output for 1,2,3,4-TCDD is shown in Fig. 6. The upper trace represents non-irradiated analyte and the bottom trace depicts the residual analyte after 20 min of irradiation. These chromatographic results are typical of the profiles obtained with the other congeners. The rate of disappearance for different congeners was determined. An examination of the data revealed an inverse relationship between the degree of chlorination and the rate of disappearance. The results are shown in Fig. 7. The data also shows that the trichloro congener degraded at a faster rate than the tetrachloro which, in turn, degraded faster than the pentachloro congeners. The data also showed that degradation followed first-order kinetics.

As discussed earlier, the differences in the stability of laterally and peri substituted congeners is an important toxicity criterion. Significant differences have been shown to exist in photo-induced dechlorination of PCDD in the solution phase and on solid surfaces. Preferential loss of lateral chlorines in solution-phase photolysis has been reported by a number of researchers. The

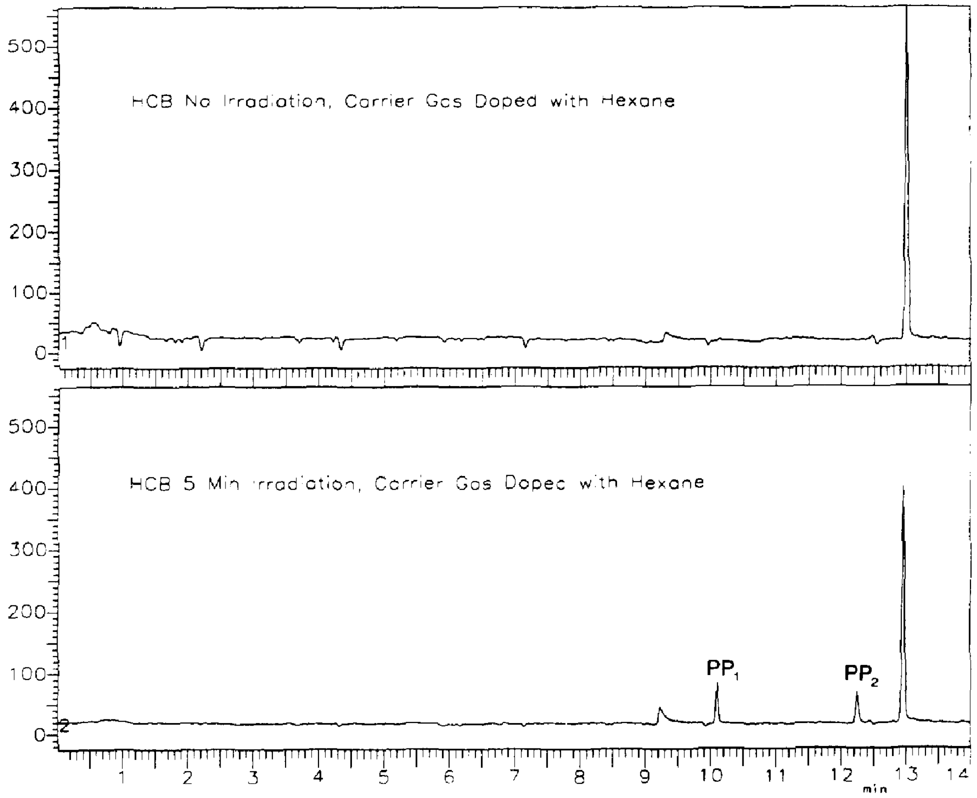


Fig. 4. Chromatographic profiles of residual HCB and photoproduct obtained in the presence of hexane (dopant) in the carrier gas. PP = Photoproduct.

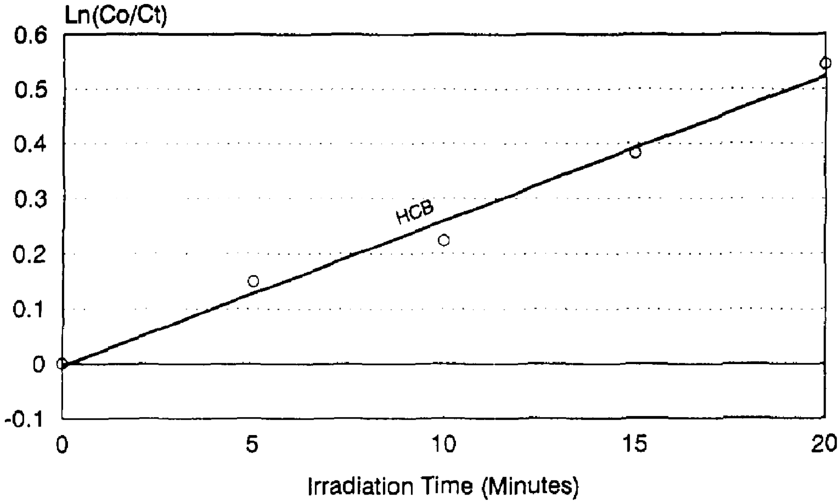


Fig. 5. Plot of HCB photodegradation vs. irradiation time. Co = Initial concentration; Ct = concentration at time *t*.

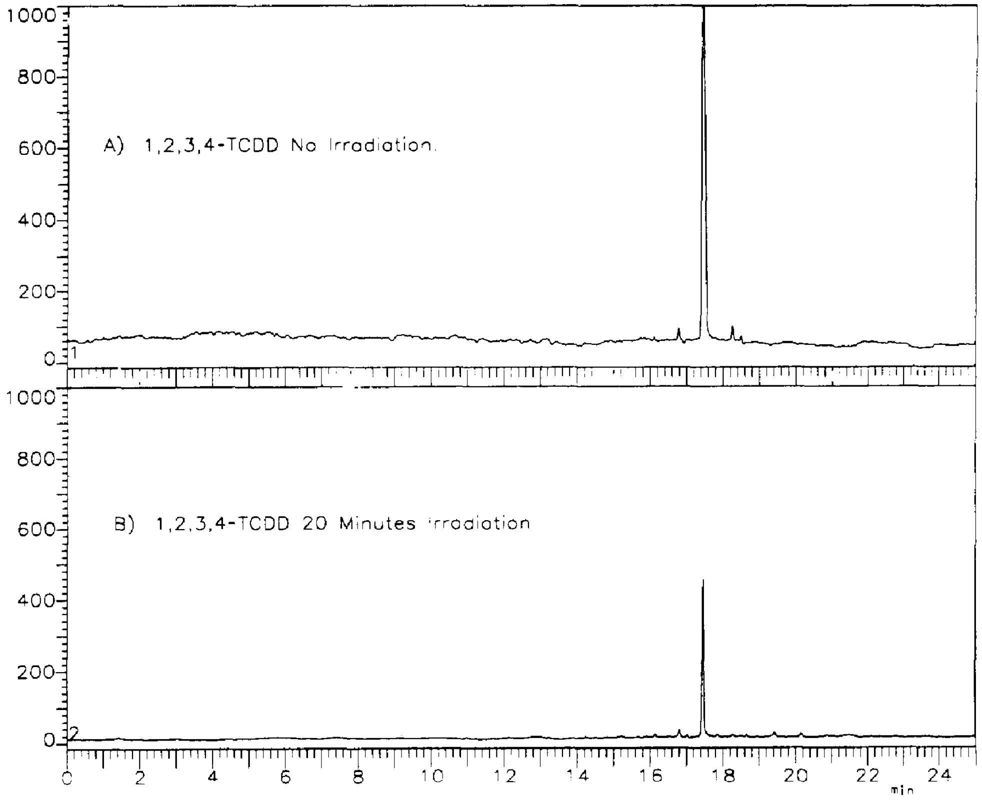


Fig. 6. Chromatographic profile of 1,2,3,4-TCDD.

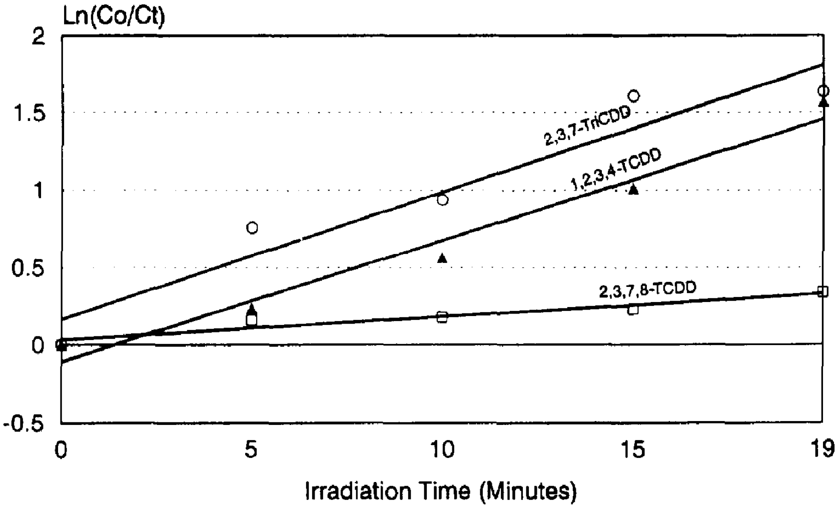


Fig. 7. Plot of PCDD degradation vs. irradiation time.

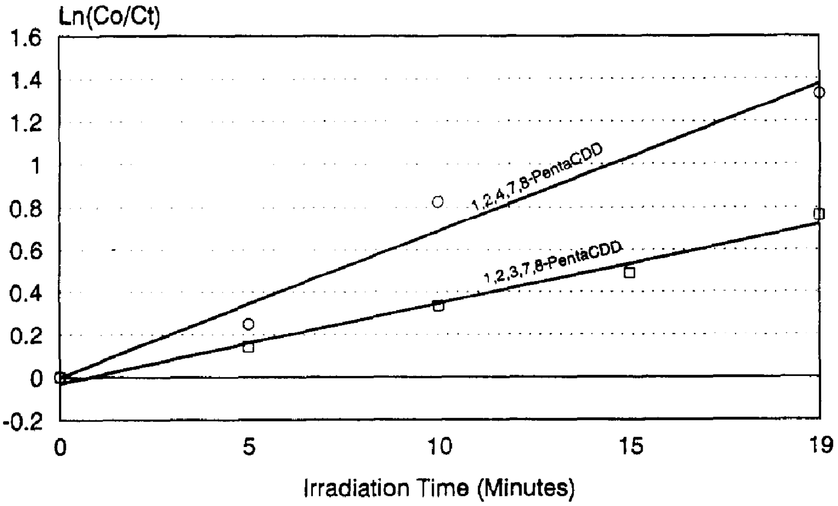


Fig. 8. Plot of PentaCDD degradation vs. irradiation time.

loss of chlorine has been shown to occur from the peri positions on adsorbent surfaces. The data obtained from the present studies indicated that photodechlorination occurred preferentially from the peri position, and the lack of photoproducts prevented an independent confirmation of the preferential loss mechanism. Therefore, this conclusion was drawn only on the basis of the relative rates of disappearance of the analyte peak. The degradation rate for 2,3,7,8-TCDD (which possesses no peri chlorines) was measurably slower than all trichloro through pentachloro congeners. Clear differences were also obtained between the two pentachloro isomers. 1,2,4,7,8-PentaCDD with two peri (1 and 4) chlorines degraded faster than 1,2,3,7,8-PentaCDD which contains only one peri chlorine. These results are summarized in Fig. 8. The data seem to indicate that the more toxic laterally substituted congeners degrade at a slower rate than the peri-substituted congeners.

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