

Analytical monitoring of the photodegradation of POPs pesticides using graphitized carbon black extraction and GC-MS

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The photo-induced degradation of chlordane, heptachlor and lindane (g-hexachlorocyclohexane) in aqueous ethanol was studied. The degradation was monitored and analyzed by solid-phase extraction using graphitized carbon black and GC-MS. Graphitized carbon black was efficient in extracting these pesticides in 30:70 ethanol-water solutions with recoveries ranging from 69% to 109% (SD of 0 to 5). The UV irradiation of chlordane and heptachlor resulted to photodegradation products that were also extracted by graphitized carbon black and detected by GC-MS.

Keywords: pesticides; photodegradation; graphitized carbon black; SPE; GC-MS

INTRODUCTION

The harmful effects of persistent organic pollutants (POPs) to human health and the environment have resulted in bans or restrictions of use, and the eventual stockpiling of these compounds in many countries. The 12 Stockholm Convention POPs are mostly agrochemicals that make up a large portion of these stockpiles. In Japan, for example, about 3,680 tons of POPs are being stored underground. Lindane, DDT, aldrin, dieldrin and endrin constitute some 78% of these stored chemicals. Strategies implemented to manage and reduce the risks of POPs in stockpiles include: (1) containment, (2) transport, disposal and destruction that abide international guidelines and standards, and (3) remediation of contaminated sites that follows environmentally sound procedures, among others. Of the 12 “Stockholm” POPs, polychlorinated biphenyls or PCBs have

been widely studied for non-incineration technologies such as plasma arc destruction and reduction processes (e.g., base-catalyzed dechlorination) [1–3].

A number of photodegradation studies of POPs pesticides using sunlight or lamps as radiation sources have been reported. The photocatalytic degradation of aldrin in water produced dieldrin, chlordane, and 12-hydroxy-dieldrin as transformation products [4]. Endrin that was irradiated in cyclohexane and hexane solutions produced a half-caged ketone as main product [5]. Chlordane, heptachlor, and other methanoindene compounds were irradiated in acetone using Hg vapor lamps, and as thin films using sunlight or germicidal lamps. Spectrometric analysis resulted to a complex mixture of photoproducts including half-caged and full-caged compounds [6–7].

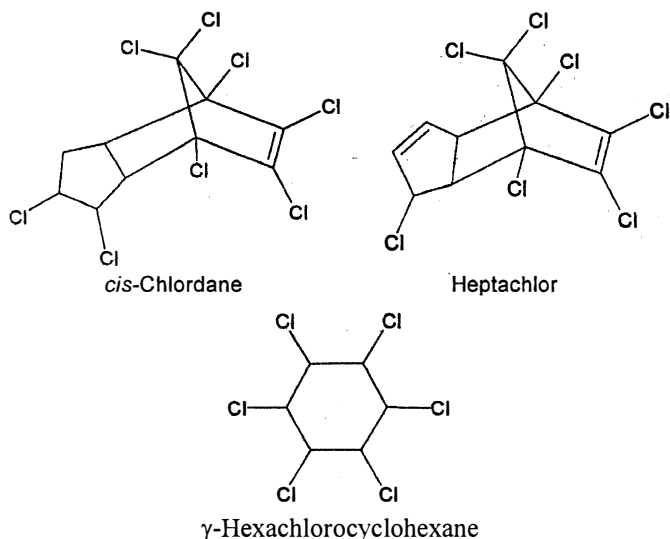


Fig. 1. Chemical structures of the pesticides studied.

A UV radiation treatment to degrade POPs pesticides in aqueous ethanol was investigated in the present work. The photodegradation of pesticides in a polar medium such as an ethanol-water solution was expected to result in a faster degradation rate. In this study, an analytical method for monitoring the degradation process was developed. Irradiated solutions of pesticides in 30:70 ethanol-water were extracted on a solid-phase before determination by GC-MS.

Solid-phase extraction (SPE) has paralleled the classical liquid-liquid extraction in many applications. Graphitized carbon black (GCB) has been used in SPE applications to monitor organic pollutants in environmental water samples [8–10] and to extract drugs and metabolites from physiological fluids [11]. Its uses include the preservation of pesticides in large volumes of water, offering advantages of on-site extraction and ease of storage and transport without compromising the integrity of the analytes [12]. GCB is produced by heating carbon blacks at elevated temperatures up to 3000°C. It is a non-porous material with high specific surface area that has found many chromatographic applications. Investigations on the chemical nature of GCB surface found hydroquinone, quinone, chromene, and benzpyrylium salt structures enabling it to act as anion-exchanger and as a non-specific sorbent [12–13]. Multiresidue extraction and trace level enrichment using GCB has been demonstrated for compounds of wide range polarities [13–18]. GCB has been used to extract ppt levels of pesticides including the POPs compounds aldrin, dieldrin, endrin, and heptachlor in water [19]. It has also been tested for the extraction of selected pesticide residues, including lindane, in fruits and vegetables [20].

We report an extraction procedure for the POPs pesticides chlordane and heptachlor, and a POPs candidate γ -hexachlorocyclohexane (γ -HCH). Figure 1 shows the chemical structures of the pesticides investigated. An SPE procedure

using graphitized carbon black and GC-MS were used to describe and monitor the degradation of chlordane, heptachlor, γ -HCH, and a technical formulation of lindane (mainly γ -HCH) in aqueous ethanol during UV irradiation.

EXPERIMENTAL

Chemicals. Heptachlor (98%) was purchased from Wako Pure Chemical Industries, Ltd., Japan. *cis*-Chlordane (99%) was purchased from Cambridge Isotope Laboratories, Inc., USA. γ -Hexachlorocyclohexane (97%) was purchased from Aldrich Chemical Co., Inc., USA. The technical formulation of lindane used in this study was reported to contain 8.92% impurities of: *cis*- and *trans*-chlordane (5.83%), oxychlordane (<0.05%), *trans*-nonachlor (2.25%), *cis*-nonachlor (0.84%). Pentachloronitrobenzene (99.9%) was purchased from Supelco, USA. L(+)-ascorbic acid (99.5%) was purchased from Cica-Reagent Kanto Chemical Co., Inc. The solvents used were products of Wako Pure Chemical Industries, Ltd. and Cica-Reagent Kanto Chemical Co., Inc., Japan: acetone, 99.8%; ethanol, 99.5%; methanol, 99.8%; hexane, 96%.

Pesticide solutions were prepared using Milli-Q water that was passed through a PF Filter Organo-Model III Apparatus and Millipore Simpli Lab UV Ultrapure System in series.

Ultraviolet spectra measurements. The UV absorption spectra of 10 mg/L chlordane, heptachlor, and γ -HCH in ethanol were obtained using a UV160 UV-Vis recording spectrophotometer (Shimadzu, Japan).

UV irradiation. The pesticide in 30:70 ethanol-water solution was irradiated in a cylindrical glass reactor (ca. 1.4 L) with an inner quartz tube encasing a low pressure Hg lamp (Germipak UV Cell GCL212, Light Sources Inc., USA). The lamp has 1.7 W UV output and 254 nm as main wavelength. The intensity of radiation was measured at 6.72 mW/cm² using a UVX radiometer (UVP, Inc., CA, USA). The solution was continuously mixed with a magnetic stirrer placed at the reaction vessel base. Replicate samples were drawn from the reactor at regular time intervals during UV irradiation.

Solid-phase extraction. A 12-port Visiprep SPE vacuum manifold (Supelco) was used for solid-phase extraction. Isolute Env+ (hypercrosslinked polystyrene sorbent, 200 mg/3mL) columns were obtained from International Sorbent Technology, UK. Supelclean EnviCarb (graphitized carbon black, 250 mg/3mL and 500 mg/6mL) columns were purchased from Supelco.

The Isolute Env+ solid-phase was conditioned as follows: 5 mL hexane, 5 mL 10:90 acetone-hexane, 5 mL methanol, and 5 mL 30:70 ethanol-water. The Supelclean EnviCarb sorbent was conditioned with: 5 mL hexane; 5 mL 10:90 acetone-hexane, 5 mL methanol; 10 mL ascorbic acid solution, 10 mg/L; 5 mL methanol; 5 mL 30:70 ethanol-water. A 20 mL (for γ -HCH) or 50 mL (for chlordane and heptachlor) pesticide in 30:70 ethanol-

water was allowed to pass through the solid-phase at 2.5 mL/min flow rate. The solid phase was then washed with 5 mL 30:70 ethanol-water solution and air dried for 10 min before elution with: 0.5 mL methanol, 6 mL 10:90 acetone-hexane, and 8 mL hexane. The eluate was concentrated to 1 mL using a gentle stream of nitrogen gas. A 20 μ L (for γ -HCH and heptachlor) or 50 μ L (for chlordane) of 5000 mg/L pentachloronitrobenzene (internal standard) was added prior to injection into the gas chromatograph.

Gas chromatography-mass spectrometry. The extracts were analyzed on a 30 m HP-5 MS column (0.25 mm i.d., 0.25 μ m film) using a HP6890 series GC system and HP5973 mass selective detector operated in the scan mode (30–800 μ mass range). Helium was used as carrier at 111 kPa pressure and 1.5 mL flow. The instrument operating conditions include: positive electron impact mode at 70 eV; 5 μ L injection volume in splitless mode; 250°C and 280°C injector and detector temperatures, respectively. The GC oven programme was as follows: 100°C, 2 min isothermal; raised to 280°C at 10°/min; and isothermally held for 2 min at 280°C.

Quantitative measurements of the pesticides were done using calibration standards and selected ion monitoring. Chlordane, heptachlor, γ -HCH, and pentachloronitrobenzene (IS) were monitored with m/z 373, m/z 100, m/z 181, and m/z 237, respectively.

DISCUSSION OF RESULTS

Development of extraction procedure. Chlordane, heptachlor and γ -HCH, like the rest of the POPs chemicals, are highly insoluble in water and preferentially dissolve in organic solvents. Table 1 summarizes the properties of the pesticides under investigation. A series of solubility tests using different concentrations of ethanol in water found that a 30:70 ratio of ethanol-water completely dissolves 5 to 10 mg/L of the POPs pesticides. Lowering the ethanol content decreases the solubility of the pesticides particularly for chlordane and heptachlor.

The study of the photodegradation of pesticides in aqueous organic medium requires an extraction procedure before quantitative measurements using GC-MS. Graphitized carbon black

Table 2. Extraction recoveries using graphitized carbon black and Isolute Env+

Pesticide	Pesticide concentration and matrix	% Recoveries ^a		
		GCB, 250 mg	GCB, 500 mg	Isolute Env+, 200 mg
Chlordane	10 mg/L in 50:50 ethanol-water		63 (1) ^b	65 (15) ^b
	5 mg/L in 30:70 ethanol-water	106 (0) ^c	98 (12) ^c	99 (5) ^c
Heptachlor	10 mg/L in 50:50 ethanol-water		24 (1) ^b	47 (15) ^b
	5 mg/L in 30:70 ethanol-water	69 (4) ^c	58 (5) ^c	63 (3) ^c
γ -HCH	10 mg/L in 50:50 ethanol-water		69 (1) ^b	61 (16) ^b
	5 mg/L in 30:70 ethanol-water	87 (0) ^c	77 (5) ^c	87 (3) ^c

and Isolute Env+ that were used for extraction have been demonstrated to be efficient in recovering analytes of wide range polarities in aqueous solutions. Initial experiments using different solvents and solvent combinations showed high recoveries for both sorbents when 10:90 acetone-hexane followed by 100% hexane were used as eluents.

The extraction recoveries of 10 mg/L pesticides in 50:50 ethanol-water using GCB and Isolute Env+ ranged from 24% to 69% (Table 2). Isolute Env+ showed better retention of chlordane and heptachlor during extraction. The lower recoveries using GCB suggest low retention when the pesticides were dissolved in a 50:50 ethanol-water solvent system. Decreasing the ethanol content required decreasing the amount of pesticide in solution. A 30:70 ethanol-water solvent improved the retention and recoveries of 5 mg/L pesticides in both Isolute Env+ and GCB extraction. A lower ethanol content in the solvent system particularly improved retention of the analytes during sample loading. Using 250 mg GCB columns, the extraction of 5 mg/L of the pesticides in 30:70 ethanol-water resulted in higher recoveries for chlordane, heptachlor and γ -HCH. Increasing the amount of GCB sorbent to 500 mg did not improve the recoveries. Isolute Env+ and GCB may be used for the extraction of POPs pesticides in 30:70 ethanol-water solutions.

GCB may prove to be efficient in the extraction of pesticides and degradation products that form during UV irradiation. In this study, POPs pesticides were retained in the GCB surface mainly by hydrophobic interactions. The degradation products may be retained by hydrophobic as well as electrostatic interactions.

UV irradiation of POPs pesticides. When chlordane, heptachlor, and γ -HCH in ethanol were exposed to UV radiation, an apparent decrease in concentration was observed with the corresponding decrease in their absorptive spectra. Figure 2 shows

Table 1. Physiochemical properties of POPs pesticides.

	γ -HCH	Heptachlor	Chlordane
Molecular Formula	C ₆ H ₆ Cl ₆	C ₁₀ H ₅ Cl ₇	C ₁₀ H ₆ Cl ₈
Molecular Weight	290.83	373.32	409.78
Solubility, μ g/L [23]	7000 (at 20°C)	180 (at 25°C)	56 (at 25°C)
log K _{ow} [24]	3.95	5.00	5.94

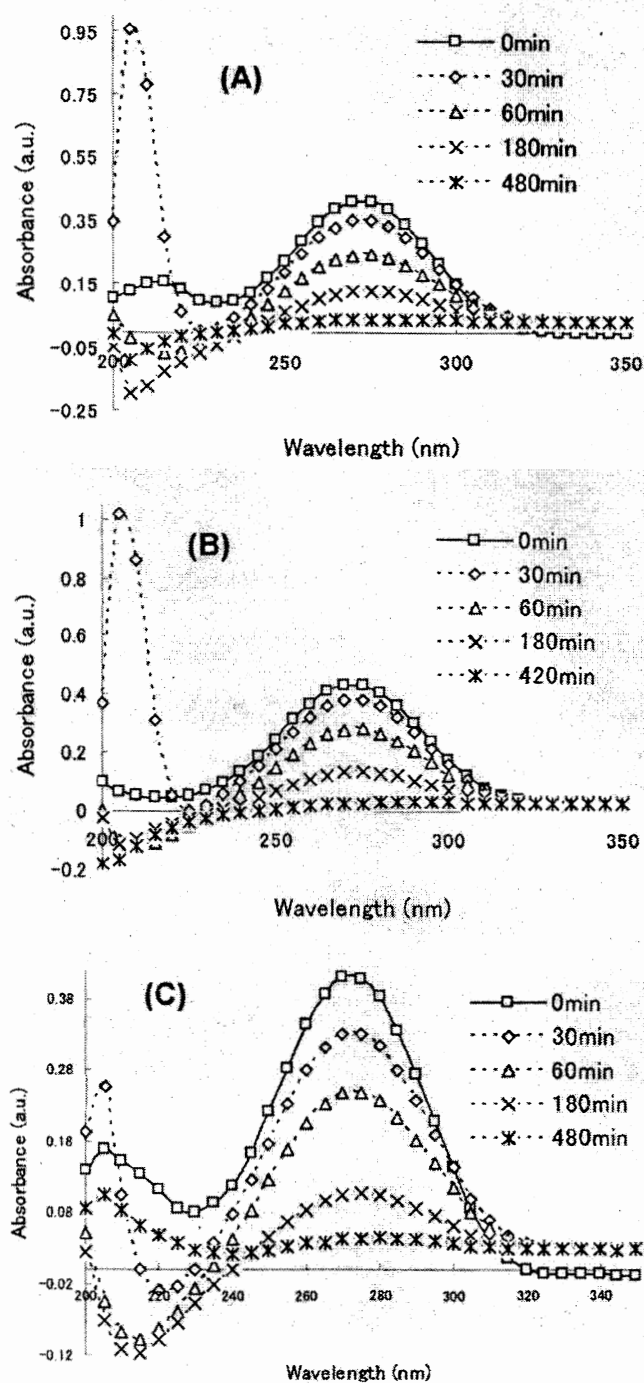


Fig. 2. UV absorption spectra of (A) chlordane, (B) γ -HCH, and (C) heptachlor in ethanol at varying irradiation times.

the decrease in the characteristic absorption spectra of chlordane, γ -HCH, and heptachlor upon exposure to UV radiation. It required 480 min of UV exposure for chlordane and 420 min for γ -HCH to completely cease to record an absorbance. Although heptachlor still showed residual absorption after 480 min of irradiation, a significant decrease in concentration was noted. These pesticides, therefore, degrade when exposed to UV light.

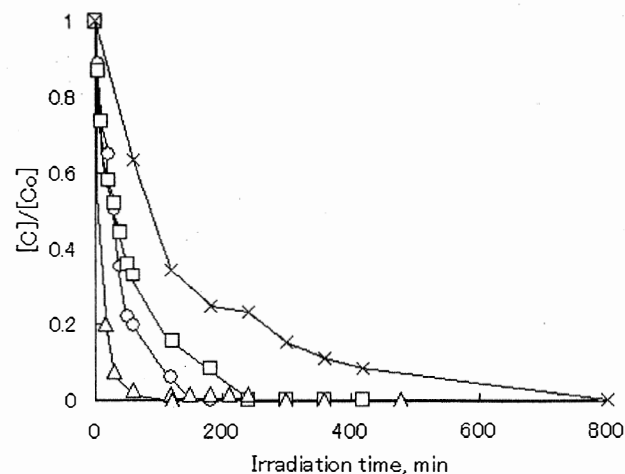


Fig. 3. Degradation of γ -HCH (○), technical lindane (□), heptachlor (△) and chlordane (×) in 30:70 ethanol-water by UV irradiation.

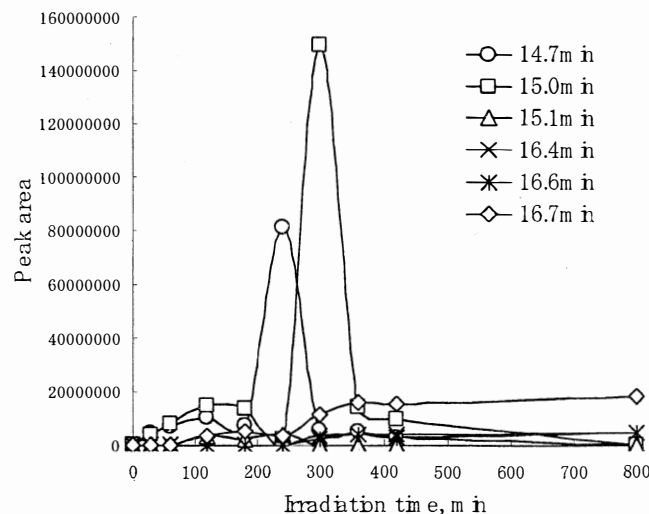


Fig. 4. Formation of chlordane photoproducts.

Maximum absorbances appeared between 205 and 215 nm in the absorption spectra of the three compounds after 30 min of irradiation. This suggests possible formation of diolefins, conjugated hydrocarbons or molecules with aldehydic or carbonyl functional groups that have electronic absorption bands in this range [21–22]. These absorbances also disappeared with prolonged UV irradiation times.

Degradation of POPs pesticides. Figure 3 shows the decrease in concentration of γ -HCH, technical lindane, heptachlor, and chlordane in 30:70 ethanol-water solutions when exposed to UV radiation. These concentrations were measured by GC-MS. The photodegradation of γ -HCH, technical lindane and chlordane followed a first-order kinetics with 0.024, 0.013 and 0.006 min^{-1} rate constants and 28.9, 52.2 and 121.6 min half-lives, respectively. Heptachlor that was no longer detected after 240

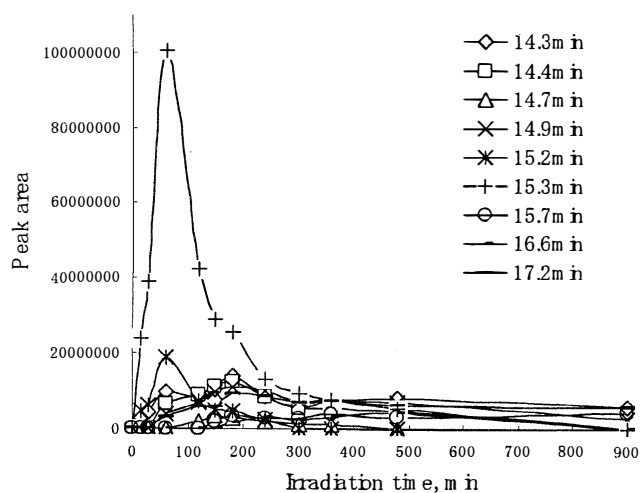
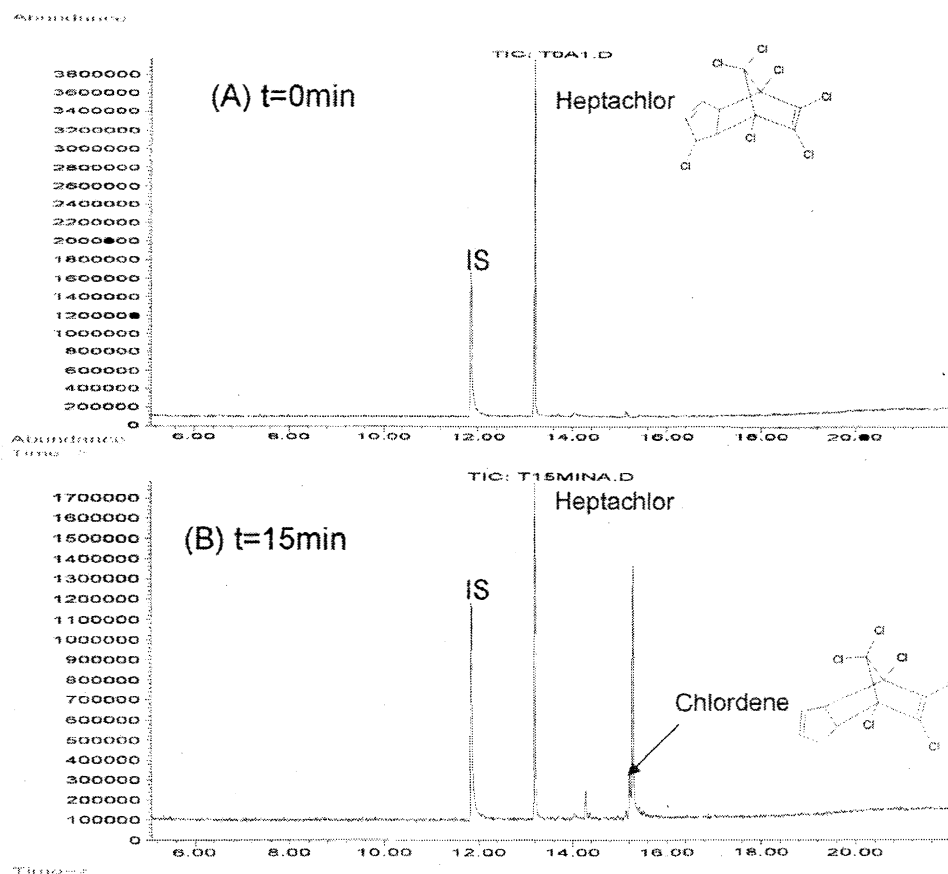


Fig.5. Formation of heptachlor photoproducts.

min appeared to follow a second-order reaction mechanism. However, further experiments and additional sampling data are required to confirm the exact reaction mechanism.

The photodegradation products of the pesticides were also extracted using GCB and analyzed by GC-MS. While the degradation of g-HCH did not result to any protoproducts that can be detected by GC-MS, chlordane and heptachlor produced a number of photodegradation products. Although this report does not attempt to elucidate the chemical structures of the degradation products, their formation in irradiated solutions of chlordane and heptachlor is of interest. Figures 4 and 5 show the appearance of degradation products in chlordane and heptachlor solutions during irradiation. Both pesticides produced at least two degradation products of relatively high amounts. These products were also degraded by UV light.

Fig. 6. Total ion chromatograms of heptachlor at (A) $t=0\text{min}$ and (B) $t=15\text{min}$ UV irradiation.

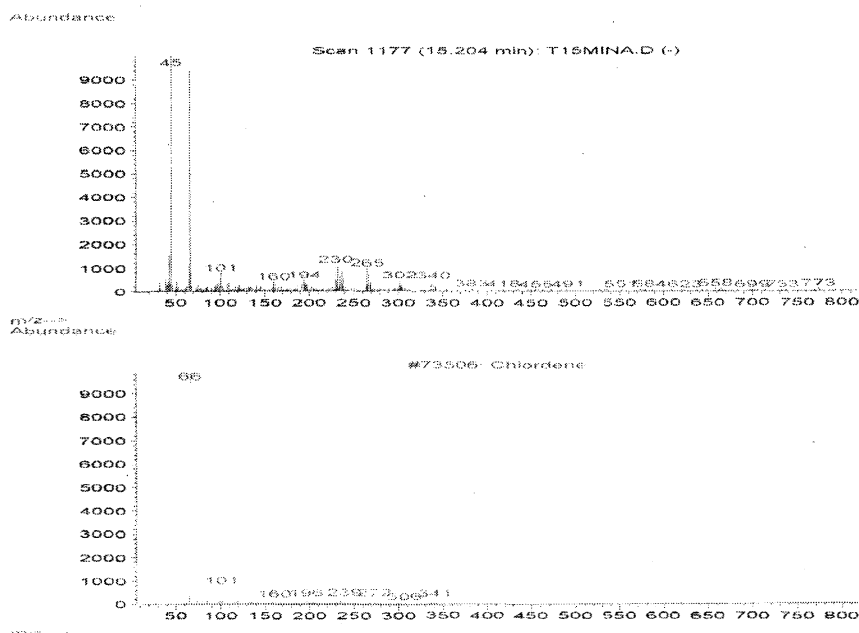


Fig. 7. Mass spectra of chlordene.

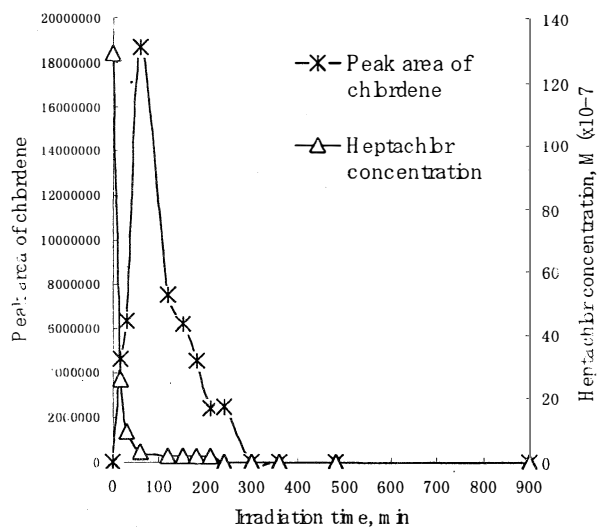


Fig. 8. Appearance of chlordene during heptachlor degradation.

In the absence of authentic standards for the photodegradation products, their identities can be elucidated by mass spectral analysis. Figure 6, for example, shows TICs of non-irradiated and irradiated heptachlor solutions. The photodegradation product at 15.2 min retention time was analyzed to be chlordene. Figure 7 shows the mass spectrum of this degradation product and a mass spectrum of chlordene from the mass spectral library. Heptachlor, therefore, produces chlordene as one of its photodegradation products during UV irradiation. Figure 8 shows the appearance of chlordene and the decrease in heptachlor concentration during UV irradiation. Chlordene that appeared after 15 min of irradiation persisted until heptachlor

was no longer detected in solution. The dechlorination of heptachlor at C-1 to form chlordene is one of the main routes of heptachlor degradation. The other photodegradation products of heptachlor and those of chlordanes require further study using isolated and purified materials for spectroscopic analyses. Authentic standards are also needed to allow for structure elucidation and identification.

The results of this study demonstrated the use of graphitized carbon black extraction in monitoring the UV radiation treatment of POPs pesticides in aqueous ethanol. A survey of published literature did not find any study on the GCB extraction of POPs pesticides in ethanol-water solutions. This extraction procedure is useful for future investigations on UV irradiation as a treatment technology for POPs in stockpiles.

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