# A Simple Ultraviolet Method for Discriminating between Polychlorobiphenyls and Organochloride Pesticides Coeluting Under Gas Chromatography with Electron-Capture Detection

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## Abstract

**Certain congeners of Aroclor 1260 coelute with *o,p'*- or *p,p'*-DDT under gas chromatography with electron-capture detection. We describe a simple ulraviolet irradiation method that allows qualitative and quantitative analyses of mixtures of these organochlorides in complex matrices. Detection limits are 0.20 and 0.22 µg/kg dry mass for Aroclor 1260 and the two DDTs, respectively. The method is applied to six replicate pork liver samples, for which recoveries ranged from 72 to 90%.**

## Introduction

Polychlorobiphenyls (PCBs) are fat-soluble and environmentally persistent and thus tend to accumulate in biological tissues. Similarly stable nonpolar contaminants such as organochloride pesticides and aliphatic hydrocarbons accumulate with PCBs and can hamper their analysis (1). In the case of aliphatic hydrocarbons, this is easily overcome because they are not detected by the technique of choice for PCB analysis: gas chromatography with electron-capture detection (GC–ECD). Pesticides, however, are detected by GC–ECD and, because they are rarely eliminated in standard extraction, cleanup, and quantitation methods, often give signals overlapping PCB peaks in the chromatogram (2). Existing solutions to this problem include chemically altering the analytes by alkaline dehydrogenation (3) or dechlorination followed by selective oxidation (4) or eliminating one of the interfering analytes by adsorption chromatography (5).

Alternatively, such problems can be avoided by selecting only reference contaminants that are not known to suffer from interference (6). In the analysis of Aroclor 1260 and the organochloride pesticides *o,p'*-DDT and *p,p'*-DDT by GC–ECD, the latter compounds interfere with the peaks due to two of the PCBs in the Aroclor mixture. In this work, we describe a cheap and simple method for discriminating between these PCB congeners and the DDT isomers. This method is based on irradiation of the sample with ultraviolet (UV) light and was applied here to the analysis of organochlorides in commercial pork liver.

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## Experimental

### Samples and reagents

Pork liver was purchased in local supermarkets. Aroclor 1260 was purchased from Monsanto Ibérica (Barcelona, Spain). Lindane, heptachlor, aldrin, isodrin, heptachlorepoxide, dieldrin, endrin, methoxychlor, *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT were from Alltech (Deerfield, IL). Residue analysis-grade *n*-hexane and dichloromethane were from Merck (Darmstadt, Germany), and Sep-Pak Silica Plus cartridges were from Waters (Milford, MA).

### Extraction procedure

The liver was lyophilized at a vacuum of 1 mm Hg and between –30 and 25°C for 72 h. Aliquots of the lyophilizate (0.5 g) were spiked with Aroclor 1260 (12 mg/kg) and DDT (2 mg/kg) and then extracted with *n*-hexane–dichloromethane (1:1) in a Soxhlet extraction tube (Afora, Barcelona, Spain). The extract was concentrated to 1 mL under a nitrogen stream and cleaned up on a Sep-Pak Silica Plus cartridge (Waters) with *n*-hexane (10 mL) as an eluant (7).

**Table I. Photodegraded Proportion (%) of Each Pesticide at the Three Concentration Levels***

| Pesticide | 1.0 mg/L | 0.8 mg/L | 0.6 mg/L |
|---|---|---|---|
| Lindane | 93.3 ± 0.83 | 94.5 ± 0.17 | 98.1 ± 0.13 |
| Heptachlor | 100 | 100 | 100 |
| Aldrin | 100 | 100 | 100 |
| Isodrin | 100 | 100 | 100 |
| Heptachlorepoxide | 94.6 ± 0.25 | 95.2 ± 1.05 | 96.6 ± 0.08 |
| *p,p'*-DDE | 98.6 ± 0.64 | 100 | 100 |
| Dieldrin | 99.3 ± 0.36 | 99.8 ± 0.09 | 99.9 ± 0.02 |
| Endrin | 98.5 ± 0.42 | 99.9 ± 0.00 | 99.9 ± 0.08 |
| *o,p'*-DDT | 95.7 ± 0.42 | 100 | 100 |
| *p,p'*-DDT | 90.1 ± 1.34 | 100 | 100 |
| Methoxychlor | 100 | 100 | 100 |

* Six replicates.

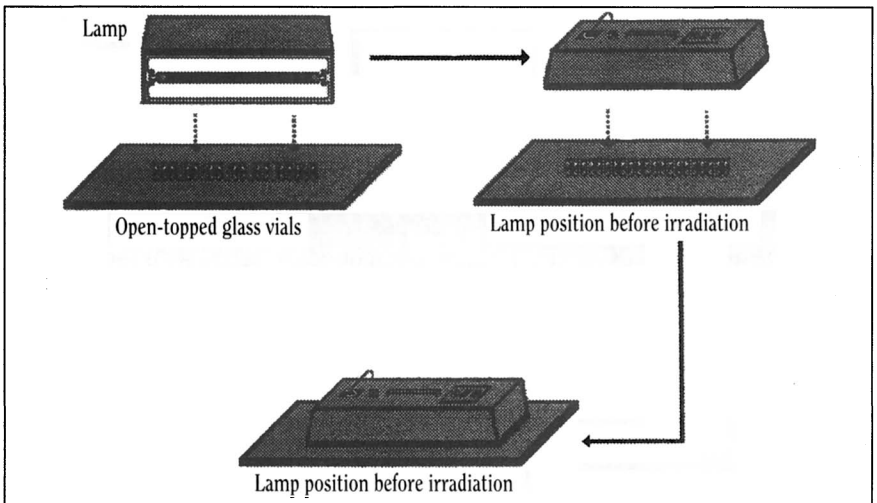


**Figure 1.** Details of lamp and glass vials before and during irradiation.

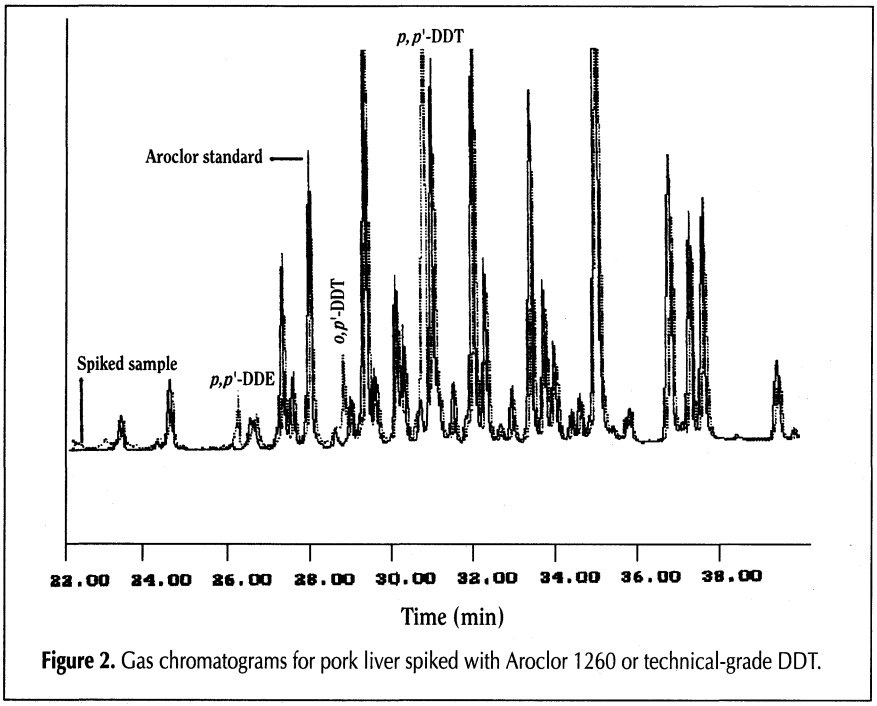


**Figure 2.** Gas chromatograms for pork liver spiked with Aroclor 1260 or technical-grade DDT.

### Chromatography

GC–ECD was performed on a Perkin-Elmer 8500 GC equipped with a Perkin-Elmer AS 8300 autosampler, a Sugelabor SGL-5 capillary column (25 m × 0.25-mm i.d.) containing 5% diphenylmethylsilicone (0.1 µm), and a $^{63}$Ni ECD. Nitrogen was the carrier gas (flow rate, 1 mL/min; measured at 50°C) and makeup gas (200 kPa). The injector and detector temperatures were 320 and 350°C, respectively. The flow rate of the splitter was 20 mL/min. The oven temperature was held at 50°C for 1 min, then increased at 20°C/min to 175°C, then increased at 3°C/min to 320°C, and held for 17 min. The total analysis time was 70 min.

### UV irradiation

The sample was irradiated at 254 nm (ATOM 70 lamp, 50 Hz, 8 watts) for 12 h, a time that had been demonstrated as sufficient to completely photodegrade the pesticides. The lamp distance and approximate depth of the solution were 1 mm and 30 mm, respectively. Initially, a standard solution containing the pesticides listed in Table I was made up in *n*-hexane at concentrations of 0.6, 0.8, and 1 mg/L. These were then analyzed by GC–ECD under the conditions described above. These same solutions were placed in open-topped glass vials and irradiated from above (i.e., through the solution) with UV light at 254 nm using an ATOM 70 lamp (Figure 1). After 12 h, these irradiated samples were analyzed again.

## Results and Discussion

Table I contains the proportions of each pesticide photodegraded in 12 h at each concentration level. At the highest concentration level (1 mg/L), photodegradation was greater than 90% for all the compounds and was complete (100%) for heptachlor, aldrin, isodrin, and methoxychlor. At lower concentations, complete degradation was observed for an increasing number of pesticides. At 0.8 mg/L, the DDT isomers (*p,p'*-DDE; *o,p'*-DDT; and *p,p'*-DDT) were also fully degraded after 8 h, and dieldrin and endrin were more than 99% degraded. Lindane and heptachlor epoxide showed the greatest resistance to degradation but were nonetheless more than 95% photodegraded at 0.8 mg/L and more than 96% photodegraded at 0.6 mg/L.

In preliminary experiments, the photodegradation data were poorly reproducible, which was attributed to hexane evaporation during irradiation. This was confirmed in a series of experiments in which all pesticide

solutions were evaporated to dryness, irradiated for 12 h, and redissolved in fresh *n*-hexane prior to GC–ECD. The photodegraded proportion of each pesticide under these conditions was in all cases much smaller than for the above experiments.

Figure 2 shows the chromatograms for the spiked pork liver samples. The peaks due to the congeners PCB 1 and PCB 2 of Aroclor 1260 coincide with those due to *o,p'*-DDT or *p,p'*-DDT, respectively, hampering identification and quantitation of these analytes. However, irradiation at 254 nm caused photodegradation of the pesticides, eliminating their signals from the chromatogram (Figure 3). By contrast, irradiation of mixtures containing PCBs modified their signals slightly but did not photodegrade the PCBs (Figure 4). These changes permited quantitation of the PCBs and pesticides by comparison of the peak areas for the irradiated ($A_i$) and non-irradiated samples ($A_n$), as follows.

Before irradiation: $A_n = A_{PCB} + A_{DDT}$

After irradiation: $A_i = A_{PCB}' + A_{DDT}'$

where $A_{DDT}'$ (the area due to the pesticides) can be assumed to be zero.

Three cases can occur for a given sample. For the first time, if the peaks were due solely to the pesticides *o,p'*-DDT and *p,p'*-DDT, $A_i$ would be zero and the pesticides could easily be quantitated by the external standard method. However, the peaks could be due solely to the PCBs, in which case a calibration line would need to be constructed, its general equation being as follows:

$$|A_i - A_n| = \Delta A_{PCB} = b + a \times A_{PCB}$$

In this work, the equations obtained for PCB 1 and PCB 2 (Aroclor 1260 concentrations in the range of 1–11 mg/L) were as follows (note that for PCB 2, $A_{PCB}'$ was less than $A_{PCB}$):

$$\Delta A_{PCB1} = A_{PCB1}' - A_{PCB1} = 6677.3 + 1.5268\,A_{PCB1} \quad (r = 0.9927) \qquad \text{(Fig. 5)}$$

$$\Delta A_{PCB2} = A_{PCB2} - A_{PCB2}' = -862.4 + 0.8891\,A_{PCB2} \quad (r = 0.9973) \qquad \text{(Fig. 6)}$$

Finally, peaks could be due to both PCBs and DDTs, in which case $A_{PCB1}$ and $A_{PCB2}$ could be estimated by substituting the corresponding $A_i$ for $A_{PCB}'$ in the calibration equations above because the pesticide gave no response for the irradiated sample. $A_{DDT}$ would then be calculated for the interfering pesticides by means of the following equation:

$$A_{DDT} = A_n - A_{PCB}$$

Table II lists the instrumental limits of detection and quantitation, which were calculated by the method proposed by Knoll (8). For the pork liver, Table III lists the recoveries obtained for six replicate samples spiked with Aroclor 1260

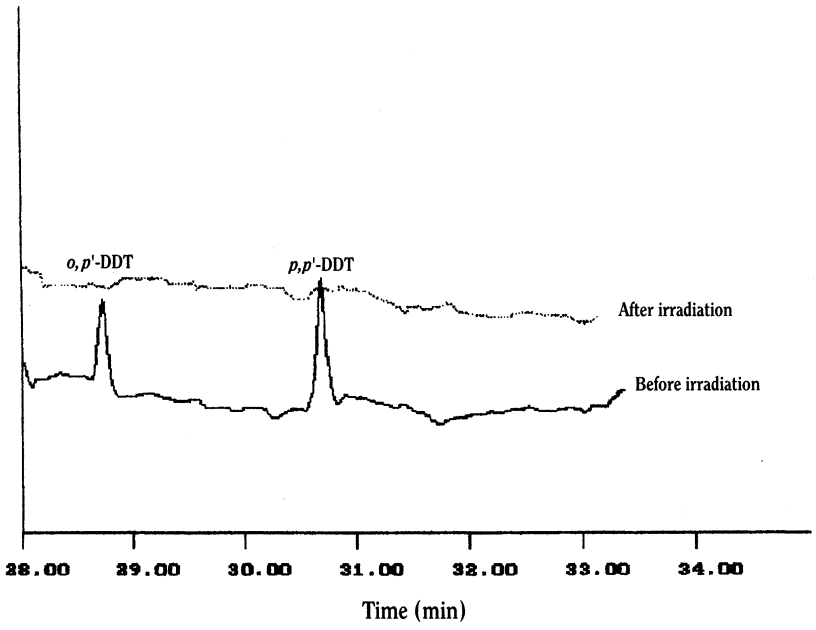


**Figure 3.** Gas chromatograms of a 1-mg/L standard solution of technical-grade DDT before and after irradiation with UV light at 254 nm.

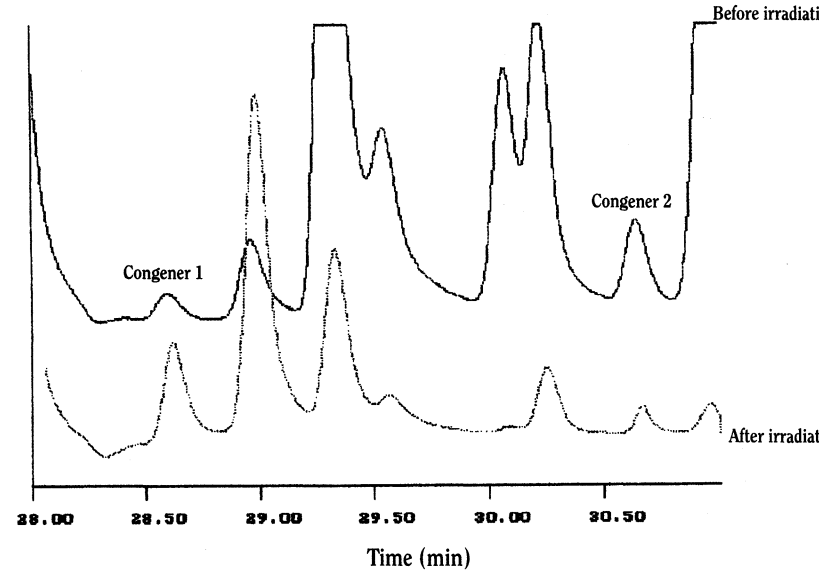


**Figure 4.** Gas chromatograms of a 1-mg/L standard solution of Aroclor 1260 before and after irradiation with UV light at 254 nm.

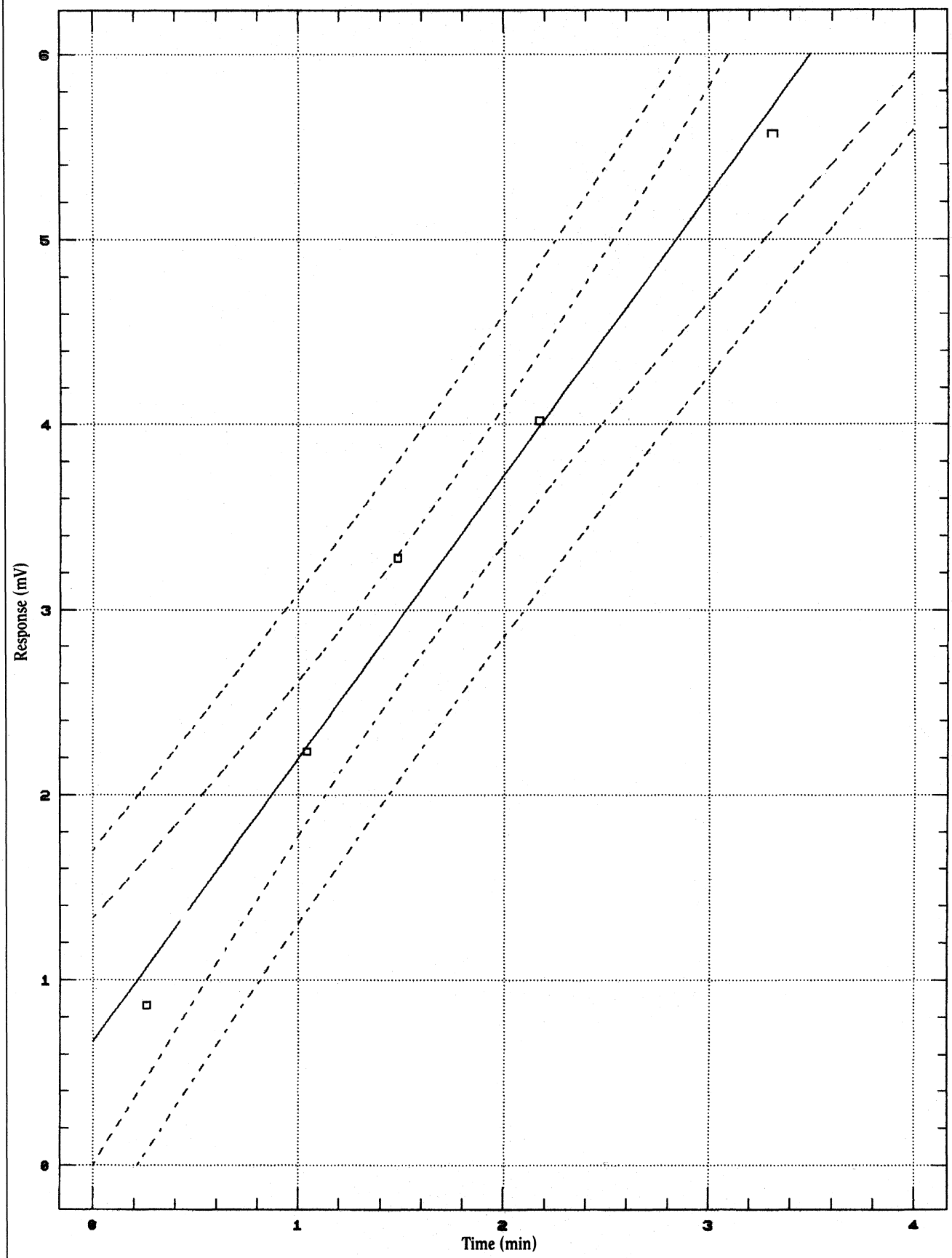


**Figure 5.** Calibration curve for PCB 1 ($\Delta A_{PCB1} = A_{PCB1}' - A_{PCB1} = 6677.3 + 1.5268\ A_{PCB1}[r = 0.9927]$).

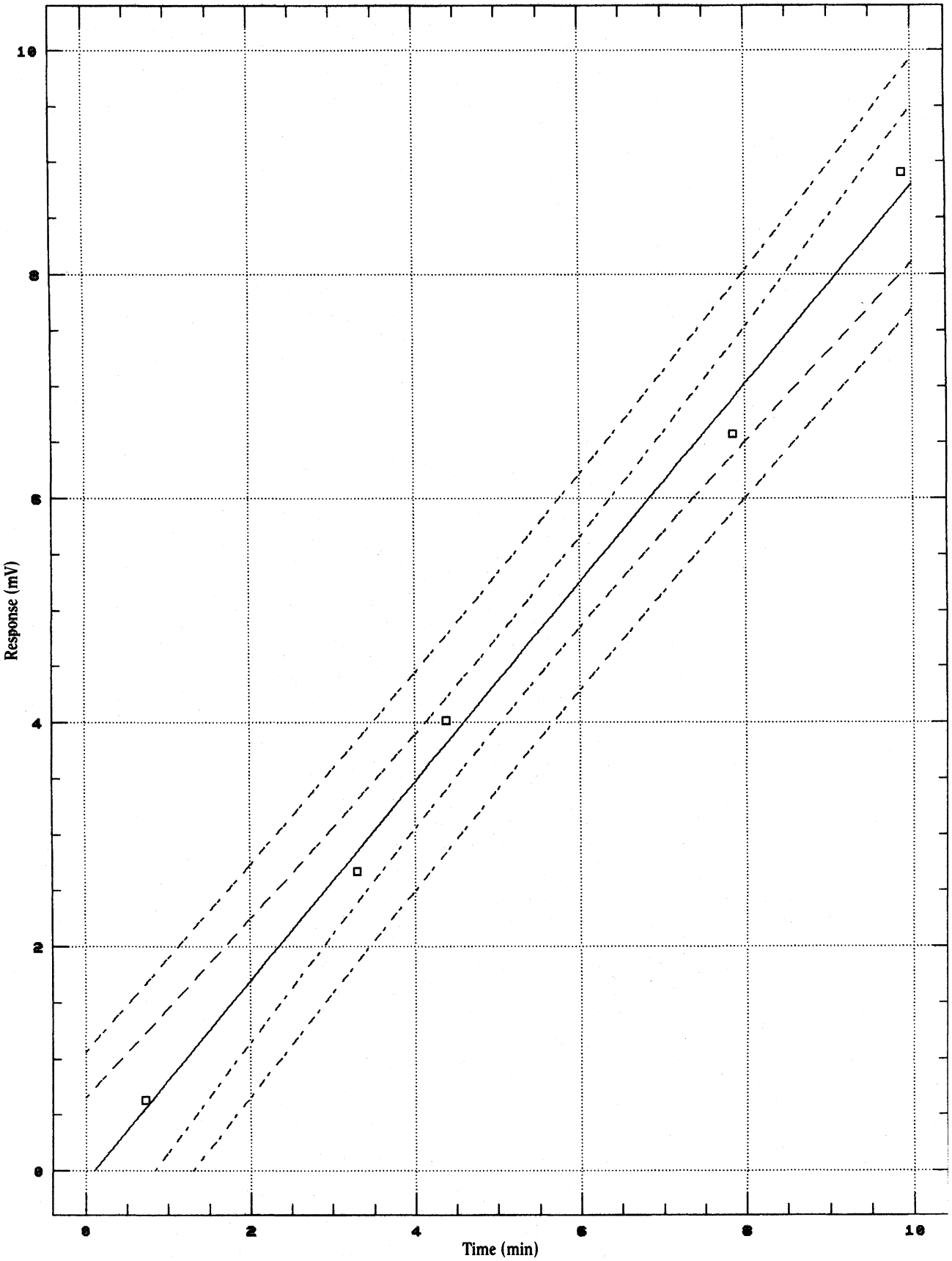


**Figure 6.** Calibration curve for PCB 2 ($\Delta A_{PCB2} = A_{PCB2} - A_{PCB2}' = -862.4 + 0.8891\ A_{PCB2}$ [$r = 0.9973$]).

**Table II. Detection and Quantitation Limits of the GC Instrument**

| | Aroclor 1260 | *o,p'*-DDT | *p,p'*-DDT |
|---|---|---|---|
| Detection limit (µg/kg dry mass) | 0.20 | 0.22 | 0.22 |
| Quantitation limit (µg/kg dry mass) | 0.59 | 0.64 | 0.64 |

**Table III: Proportion of Each Analyte Recovered***

| | Amount added (mg/L) | Recovery (%) ± standard deviation |
|---|---|---|
| Aroclor 1260 | 12 | 89 ± 0.75 |
| *o,p'*-DDT | 2 | 79 ± 2.76 |
| *p,p'*-DDT | 2 | 72 ± 1.54 |

* Six samples.

and DDT as described above. Recoveries ranged from 72 to 90%, which are acceptable values for these analytes (9,10).

## Conclusion

The UV irradiation method described should prove a useful adjunct to GC–ECD for the qualitative and quantitative analysis of PCB and pesticide contaminants in complex environmental matrices. It may thus be useful for discriminating between these pesticides and interfering contaminants with different photochemical properties.

## References


1. L. Marsili and S. Focardi. Organochlorine levels in subcutaneous blubber biopsies of fin whales *(Balaenoptera physalus)* and striped dolphins *(Stenella coeruleoalba)* from the Mediterranean Sea. *Environ. Pollut.* **91:** 1–9 (1996).
2. L.G. Hansen. Food chain modification of composition and toxicity of polychlorinated biphenyl (PCB) residues. *Rev. Environ.Toxicol.* **3:** 149–212 (1987).
3. G.R. Harvey, H.P. Miklas, V.T. Bowen, and W.G. Steinhaver. Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms. *J. Mar. Res.* **32:** 103–18 (1974).
4. J.K. Ludwicki and K. Góralczyk. Organochlorine pesticides and PCBs in human adipose tissues in Poland. *Bull. Environ. Contam. Toxicol.* **52:** 400–403 (1994).
5. M.E. Zabik, M.J. Zabik, A.M. Booren, M. Nettles, J. Song, R. Welch, and H. Humphrey. Pesticides and total polychlorinated biphenyls in Chinook salmon and carp harvested from the great lakes: Effects of skin-on and skin-off processing and selected cooking methods. *J. Agric. Food Chem.* **43:** 993–1001 (1995).
6. R. Frank, H.E. Braun, and B. Thorpe. Comparison of DDE and PCB residues in the general diet and in human blood—Ontario 1986–87. *Bull. Environ. Contam. Toxicol.* **51:** 146–52 (1993).
7. S.T. Carril González-Barros, M.E. Alvarez Piñeiro, J. Simal Lozano, and M.A. Lage Yusty. Simultaneous determination of aliphatic hydrocarbons, PCBs and PCTs in pork liver by gas chromatography. *Chromatographia* **43:** 398–400 (1996).
8. J.E. Knoll. Estimation of limit of detection in chromatography. *J. Chromatogr. Sci.* **23:** 422–25 (1985).
9. H.T. McCarthy and A.R. Sullivan. Comparison of recoveries of selected organochlorine pesticides related compounds, and polichlorinated biphenyls 1254 and 1260 from fat after Kuderna-Danish and Turbo-Vap concentration. *J. AOAC Int.* **78:** 1294–1302 (1995).
10. C. Nerín, A.R. Tornés, C. Domeño, and J. Cacho. Determination of organochlorine pesticides in animal diet: A comparative study of clean-up procedsures. *Fresenius' J. Anal. Chem.* **352:** 364–71 (1995).


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