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ANALYSIS FOR POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL SAMPLES

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## ABSTRACT

Polychlorinated biphenyls (PCB's) have been found to be widely distributed and very persistent in the environment. This paper describes the various techniques used by the Y-12 Plant<sup>(a)</sup> Laboratory for the analysis of PCB's.

(a) Operated for the Department of Energy by Union Carbide Corporation-Nuclear Division.

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## SUMMARY

The Y-12 Plant Laboratory has the capability to monitor almost any form of PCB pollution and maintains a continuous monitoring program for water leaving the plant.

## INTRODUCTION

Polychlorinated biphenyls (PCB's) have been used in a wide variety of industrial products because of their thermal and chemical stability. They have been used in the production of paper, adhesives, and textiles and as fire retardant, heat transfer, machining, hydraulic, and transformer fluids. These properties which make PCB's desirable for industrial usage also make them an undesirable industrial pollutant. This family of compounds is highly resistant to chemical, metabolic, and photochemical breakdown, and is easily taken up by living organisms and thus accumulated in the higher levels of the food chain. (1), (2), (3), (4)

The primary usage in the Y-12 Plant for Aroclor 1260 (60% chlorine) has been in transformer fluids. Aroclor 1248 (48% chlorine) has in the past been used extensively as a machining coolant when mixed with oil. When monitoring environmental samples for PCB's all techniques have been aimed at the analysis of Aroclors 1248, 1254, and 1260.

## APPARATUS

Two different gas chromatographs have been used in these studies. Preliminary investigations were made using a Perkin-Elmer 900 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector. Secondary investigations and routine analyses were made using a Varian 1400 gas chromatograph equipped with a  $\text{Sc}^3\text{H}$  electron capture detector. Both instruments performed satisfactorily; however, the Varian had a more linear response and was more stable for day-to-day operation. The instrumental conditions listed in Table 1 are those used on the Varian instrument and all the figures found in this report.

Table 1  
Instrumental Operating Conditions

Column - - - - -	6' x 1/4" x 2 mm glass column packed with 3% OV-101 on Chromosorb WHP
Column Temperature - -	Isothermal at 200 °C
Injector Temperature -	200 °C
Detector Temperature -	260 °C
Carrier Gas - - - - -	Nitrogen
Flow - - - - -	30 cc/min.
Injector Volume - - -	2 $\mu\text{l}$

All glassware used for extraction and evaporation was cleaned by baking at 400 °C for one hour. Separatory funnels were equipped with Teflon stopcocks which were cleaned in hexane.

## STANDARDS

Standards of purified mixtures were obtained from Analabs and are available from a number of other suppliers. All standards were prepared using "pesticide-grade" hexanes. The usable range of standards for chromatographic standardization was limited to 0.05 mg/l to 1.0 mg/l Aroclor 1248, 1254, and 1260. Figures 1, 2, and 3 show chromatograms of the standard Aroclor mixtures at the 0.66 mg/l levels. The numbers above each peak serve as peak identifiers and are actually relative retention times with respect to p,p'-1,1-dichloro-2,2-chlorophenylethylene (p,p'-DDE).

## PROCEDURES

## DETERMINATION OF PCB IN WATERS

One liter of the sample is transferred to a 2-liter separatory funnel and extracted with 60 ml of hexanes. After phase separation, the hexanes extract is passed through a drying column and collected in a Kuderna-Danish evaporative concentrator fitted with a 10-ml receiving flask. The sample is extracted twice more with hexanes and the extracts combined in the concentrator. The extracts are evaporated on a boiling water bath to a volume of 10 ml. The concentrate is cooled and mixed and is ready for analysis. Figure 4 shows the chromatogram of an extracted water sample that contains PCB. Note the large interfering peak. Nonetheless, it is clear that the sample contains 1248 and 1254. With the normal 100-fold concentration given water samples, a lower reporting limit of 0.0005 mg/l is easily achieved.

## DETERMINATION OF PCB IN SOILS AND SEDIMENTS

Samples are dried in a forced air convection oven at 50 °C overnight. They are then ground, passed through a 10-mesh screen to remove extraneous material, and blended to insure homogeneity. A 50-g aliquant is transferred to a coarse extraction thimble and Soxhlet extracted with hexanes at a rate of 12 cycles per hour for 2 hours. The hexanes are evaporated under a stream of warm nitrogen until the leachate can be transferred to a 100-ml volumetric flask and diluted to volume with hexanes. The sample is now ready for analysis with a lower reporting limit of 0.1 µg/g.

## DETERMINATION OF PCB IN FISH AND ANIMAL TISSUE (5)

Approximately 10 g of tissue is weighed into a stoppered Erlenmeyer flask and dissolved with 30 ml of 20% methanolic potassium hydroxide (5% methanol by volume) for two or three hours or until dissolution is complete. The resulting solution is chilled and extracted with three 20-ml portions of diethyl ether. The combined extracts are evaporated under a flow of warm nitrogen and the residue dissolved with 5 ml of hexanes. The sample is now ready for analysis with a lower reporting limit of 0.025 µg/g. Figure 5 is a chromatogram of a fish which contains a mixture of 1254 and 1260.

## DETERMINATION OF PCB IN OILS

One gram of the sample is dissolved in hexanes, transferred to a 100-ml volumetric flask, and diluted to volume with hexanes. The sample is ready for analysis with a lower reporting limit of 5 µg/g. Figure 6 is a chromatogram of an oil sample which contains a mixture of 1248 and 1254.

## DISCUSSION

Quite often samples prepared according to these procedures do not yield chromatograms as "nice" as the ones in the figures. Sometimes many interfering peaks can be seen among the PCB "fingerprint". Often the chromatographic pattern is completely unrecognizable. A technique that has proved to be very useful in removing interfering peaks and high background levels from the PCB "fingerprint" is the Florisil column cleanup. The extracted water chromatogram in Figure 4 was obtained after such a cleanup. Figure 7 shows the chromatogram of the same water sample without cleanup. Without the column cleanup, this sample could not have been identified as containing PCB or the actual level calculated. Another sample that benefited from a Florisil column cleanup is shown in Figures 8 and 9. The chromatogram of this oil sample before cleanup shows a pattern not matching any of the standard mixtures. The chromatogram of the sample after cleanup shows a near perfect 1260 pattern.

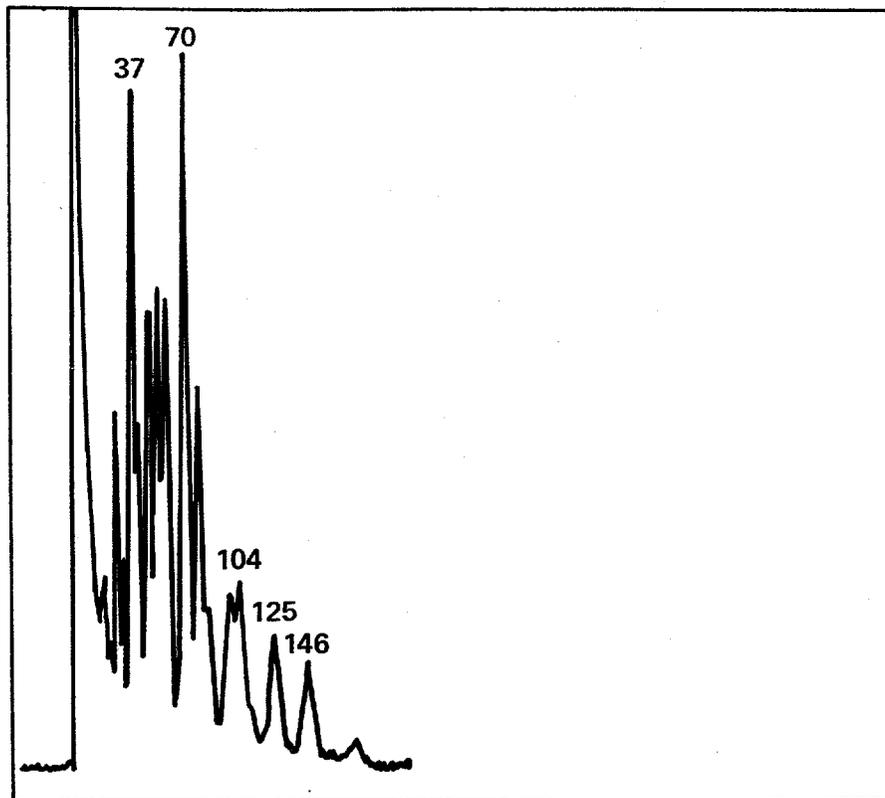


Figure 1. Aroclor 1248.

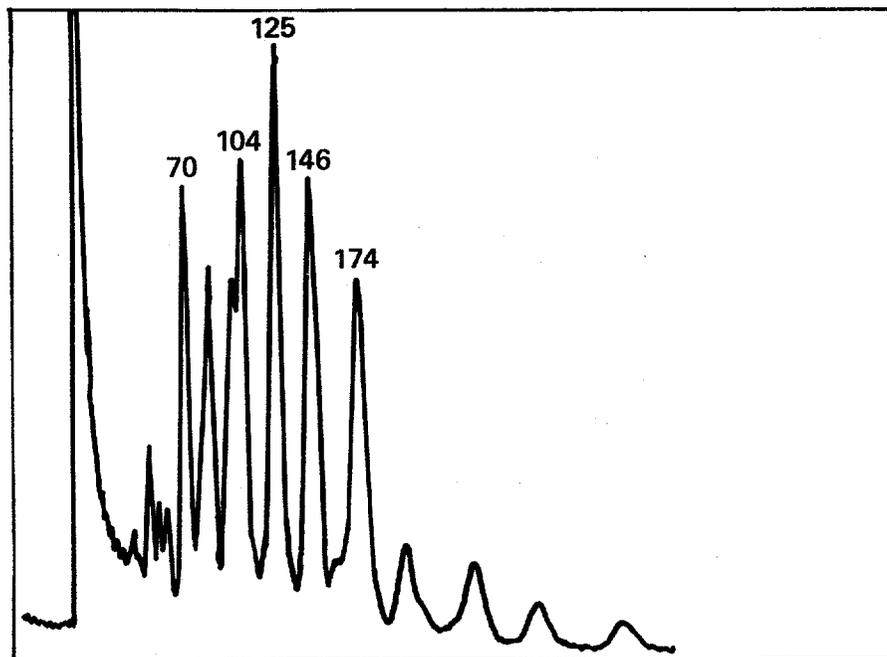


Figure 2. Aroclor 1254.

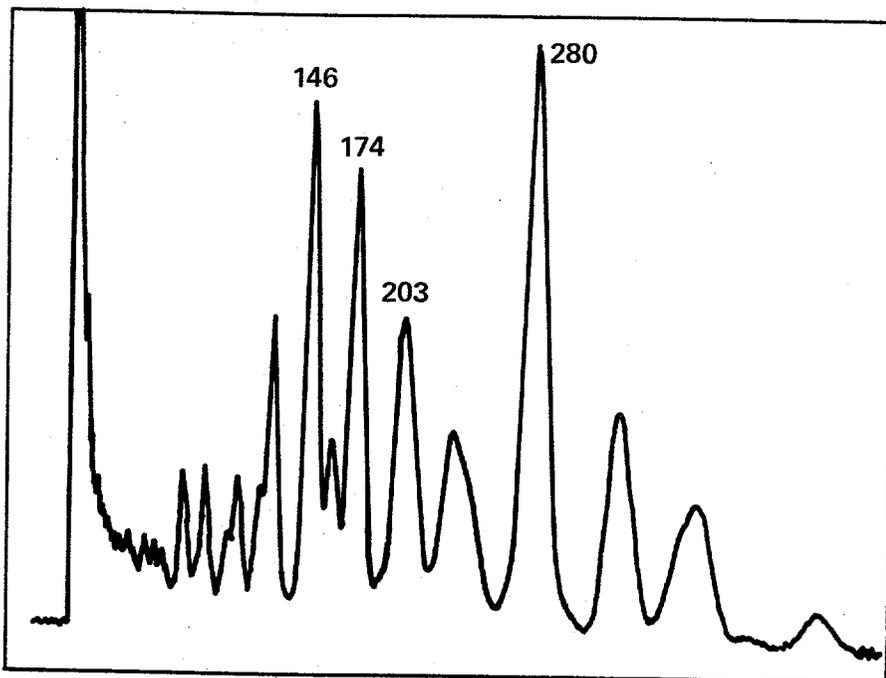


Figure 3. Aroclor 1260.

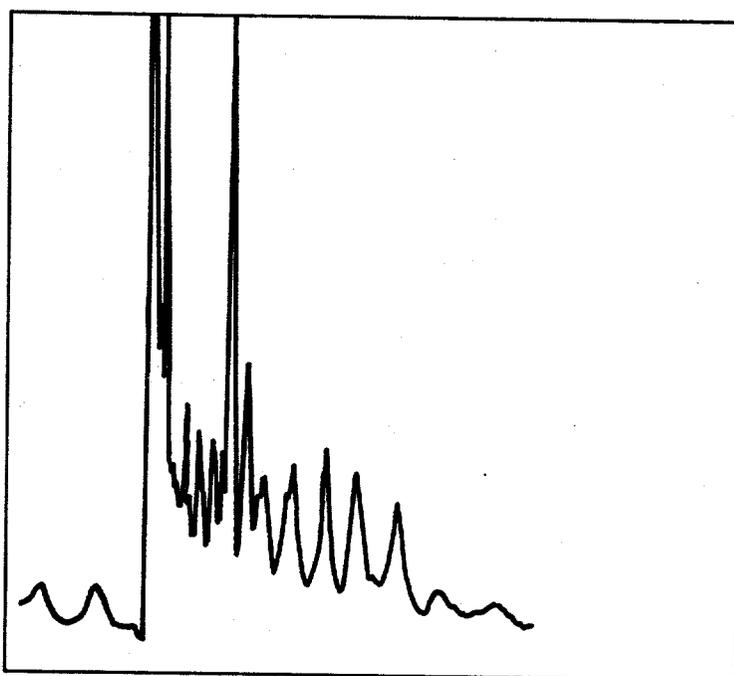


Figure 4. Extracted Water Sample.

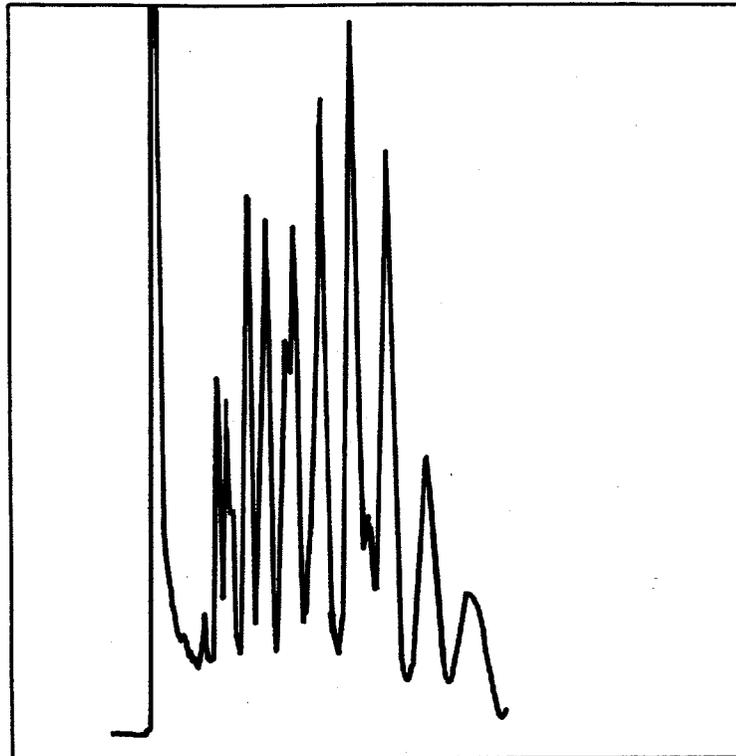


Figure 5. PCB in Fish.

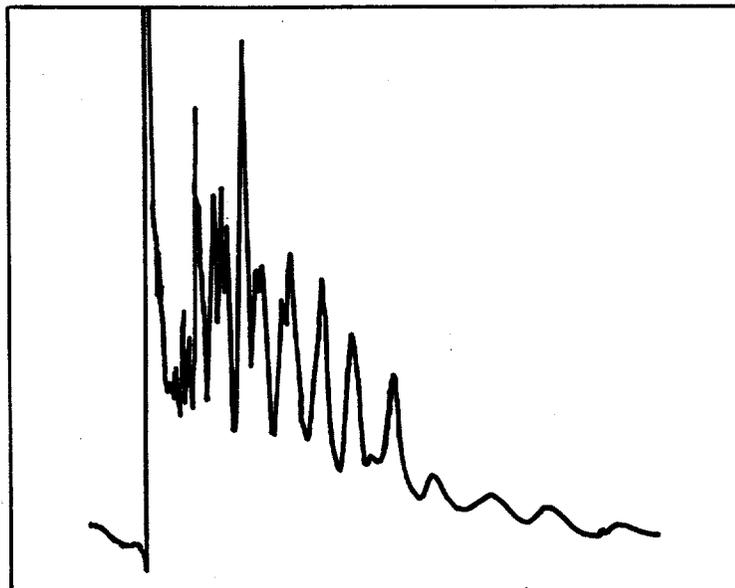


Figure 6. PCB in Oil.

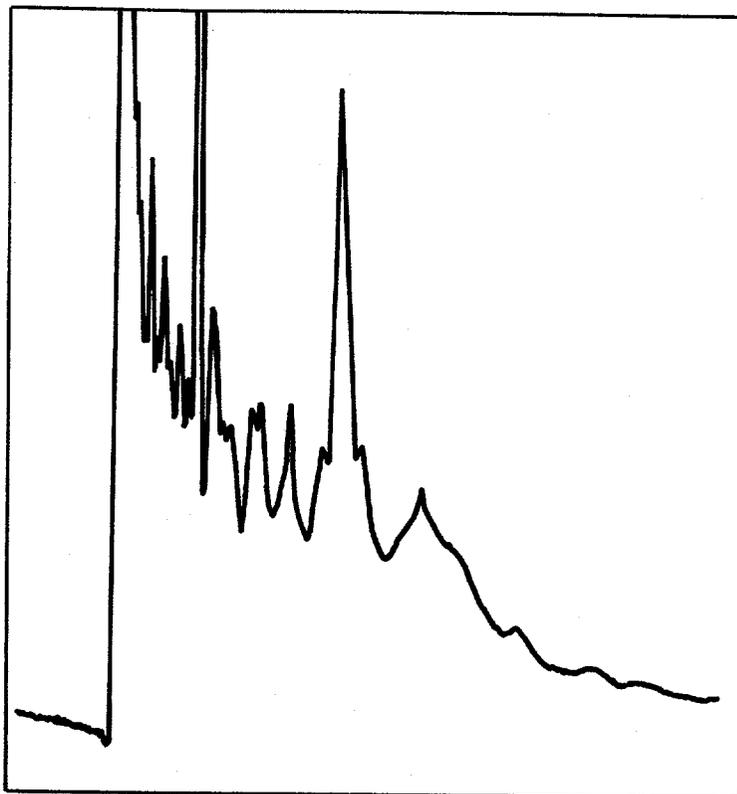


Figure 7. Extracted Water, No Cleanup.

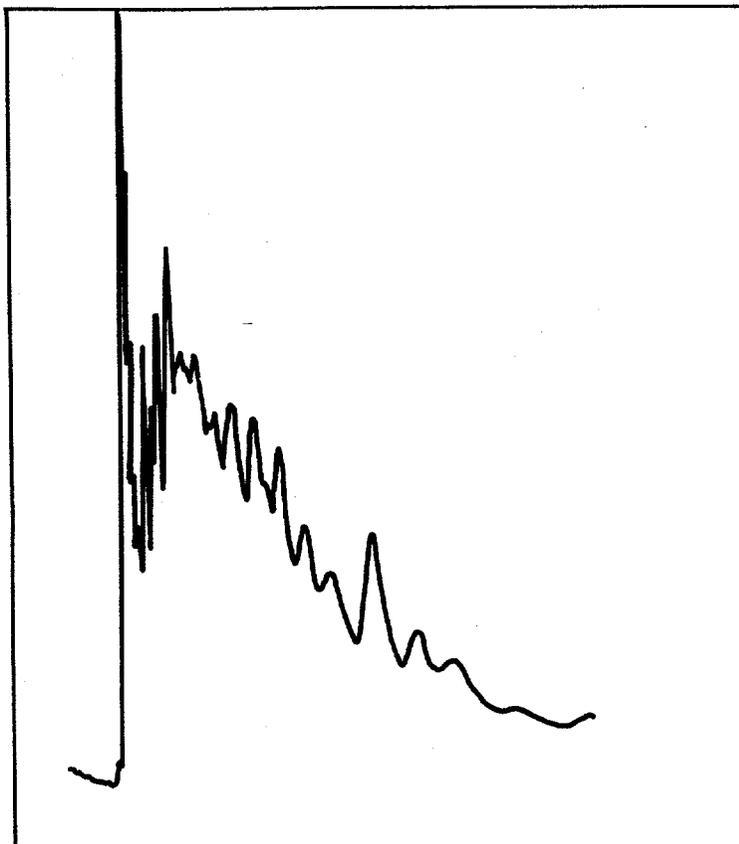


Figure 8. Oil, Before Cleanup.

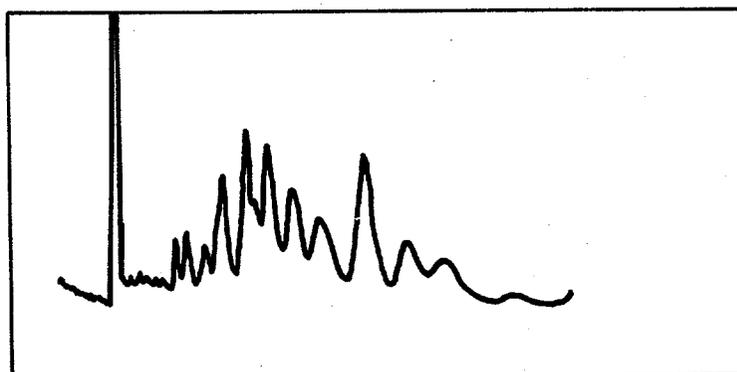


Figure 9. Oil, After Cleanup.

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