

THE DETERMINATION OF THE LEVELS OF POLYCHLORINATED BIPHENYLS (PCBs) IN SOME URBAN AND RURAL AREAS OF JAMAICA

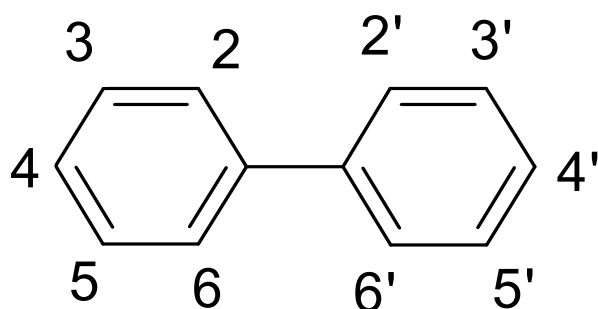
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ABSTRACT Studies were done to ascertain the levels of PCBs in soil, water and sediments in some urban and rural areas of Jamaica. All the soil samples collected contained less than 10 ppm PCB and PCB was found only in soil samples which were collected from sites where transformers were stored or are in use. The mean concentrations of PCBs in the urban and rural soil samples were 0.7 and 0.2 mg/kg respectively with over 80% of the samples containing less than 2.0 mg/kg. The median concentration for the urban soil samples was 1.4 mg/kg while that for the rural was less than 0.1 mg/kg. The concentration of PCBs was measured either by using a gas chromatograph attached to an electron capture detector or a mass spectrophotometric detector.

INTRODUCTION

Polychlorinated biphenyls, popularly known as PCBs, is a class of nonpolar chlorinated hydrocarbons with a biphenyl nucleus on which one to ten of the hydrogens have been replaced by chlorine. This class of chemical compounds consists of 209 congeners having similar physical properties and similar chemical structure. The general molecular formula is $C_{12}H_{10-n}Cl_n$ where $n = 1 - 10$; i.e., monochlorobiphenyl through decachlorobiphenyl, with the general structure:



Polychlorinated biphenyls are widely versatile, synthetic, chlorinated compounds whose manufacture was banned in 1977. The most dramatic decline appeared to occur in the late 1970s and mid-1980s time frame, which corresponds to the period following the regulatory controls imposed in the United States by the Toxic Substance Control Act¹. Of over 800 toxic and hazardous chemicals regulated under the US federal laws, PCBs top the list of chemi-

cals released in accidents, with 3600 accidents reported² from 1988 to 1992.

As with other species, PCBs tend to accumulate in fatty tissues in humans because of their nonpolar, lipophilic physical properties and their resistance to biochemical degradation. PCBs have entered the environment through legal and illegal use and disposal. Since PCBs do not readily degrade in the environment after disposal or dissemination, they tend to bioaccumulate.

Closed and controlled uses of PCBs such as dielectrics within electrical equipment have resulted in environmental releases because of spills, improper handling or improper disposal. Most of such releases tend to be localized near the use site, in landfills or elsewhere and can often result in relatively high, localized concentrations. Gradual advection of the PCBs from initial contamination sites contribute to the widespread background contamination at much lower concentrations. PCBs have low volatility and as a result, more than 99% of the environmental PCB mass is found in the soil³.

Volatilization of PCBs from spills, landfills, road oils and other sources resulted in measurable atmospheric emissions. Atmospheric transport is the primary mode of global distribution of PCBs. Environmental levels of PCBs increase near the source of the PCBs. Similarly, indoor levels are roughly one order of magnitude higher than outdoor levels, a trend in-line with many other air pollutants⁴. Human exposure to PCBs occurs primarily via low-level food contamination.

PCBs have been found in nearly all marine

plant and animal specimens, fish, mammals, birds, (especially fish-eating birds), birds' eggs and humans⁵. Animal studies with both commercial mixtures and individual congeners have shown a variety of chronic toxic effects.

While PCB regulations and disposal requirements differ from country to country, there is a common analytical interest in determining their presence in the environment and in potential sources to the environment. Regardless of the laws and rules, the analytical needs are similar: reliable, practical, sensitive methods which can determine PCBs in a variety of matrices.

Although the physical and chemical properties vary widely across the class, PCBs have low water solubilities and low vapour pressures⁷. They are soluble in most organic solvents, oils and fats. PCBs are very stable compounds and do not degrade easily. However, under certain conditions, they may be destroyed by chemical, thermal and biochemical processes. Because of their high thermodynamic stability, all degradation mechanisms are quite complex⁸. Incineration, chemical dechlorination and biodegradation are the destruction technologies which are most frequently practiced.

The present study has been undertaken to ascertain the levels of PCBs in soil, water and sediments in some urban and rural areas of Jamaica since little data is available on the distribution of PCBs in the Jamaican environment. Data of this nature are becoming increasingly important because most environmental organizations both locally and internationally, include PCBs as major environmental pollutants and as such, the levels have to be determined.

The widespread use of PCB as additives in transformer oil at our local power stations has raised concerns about possible spillage and its impact on the environment. As a result, an assessment of the distribution of PCBs in the environment was necessary. Even though the Jamaica Public Service has removed most of the contaminated soil from the known spillage areas and shipped to France for high temperature incineration, there are still indications of the presence of PCBs in soil samples collected from some of these power stations.

EXPERIMENTAL

Materials

Neat Aroclor 1232, Aroclor 1248 and Aroclor 1260 were obtained from SUPELCO, Bellefonte, PA 16823, USA. The other reagents used were either general purpose reagents (GPR) or analytical grade reagents (AR) obtained from British Drug House Chemicals Limited (BDH, Merck House, Poole, Dorset, BH15 1TD England) and Sigma-Aldrich Chemical Company (P.O. Box 14508, St. Louis, Missouri 63178, U.S.A.). Solvents for pesticide residue analysis were used and these were obtained from Sigma-Aldrich. Distilled and deionized water were generated from a LABCONCO^R WATER PRO^{T.M.} PS and FIS-TREEN^{T.M.} CYCLON^{T.M.} deionization unit.

High purity nitrogen gas (99.9999%) was supplied either locally by Jamaica Oxygen and Acetylene Limited or overseas by Air Products and Chemicals, Inc. Allentown, PA 18195, USA. Samples were collected from designated sites as indicated in the tables provided (see results).

Instrumentation

Gas chromatographic analyses were performed using the following.

- 1) Hewlett Packard 5890 gas chromatograph equipped with a ⁶³Ni electron capture detector and a Hewlett Packard 3396A integrator.
- 2) Hewlett Packard 5890 Series II gas chromatograph equipped with a ⁶³Ni electron capture detector, a Hewlett Packard Vectra VL2 4/50 computer and a Hewlett Packard Laser Jet 4 Plus printer.
- 3) Hewlett Packard 6890 Series gas chromatograph with a Hewlett Packard 5973 Mass Selective Detector, a Hewlett Packard Vectra Xm Series 4 5/166 computer and a Hewlett Packard Laser Jet 5 printer.

A fused silica column of dimensions 10 m x 0.53 mm x 2.65 mm film thickness (HP-1, methyl silicone gum) was used. The operating conditions were 150°C, 300°C and 200°C for oven, de-

tector and injector temperatures respectively. The flowrate of the carrier gas was 30 mL/min. A METTLER TOLEDO AB104 analytical balance and a SARTORIUS top loading balance were used for weight determination.

Extraction of PCBs

Water Extraction:

One litre of the water sample was placed in a two litre separatory funnel after which 100 mL of 15% methylene chloride/hexane mixture were added. The funnel was then stoppered and the mixture was shaken manually for 2 minutes and the two layers were allowed to separate. The lower aqueous layer was removed and kept for two more extractions. The upper organic layer from the three extractions were collected and pooled. This was then dried by passing it through 5 cm of anhydrous granular sodium sulfate which was placed in a glass column of dimension 30 cm x 2.5 cm I.D. and plugged with glass wool. The column was rinsed with three 10 mL portions of hexane and the dried extract was concentrated to 5 mL using a Kuderna-Danish (K-D) concentrator fitted with a graduated concentrator tube containing about 0.5 g of copper filings and five boiling chips. A steam bath was used as the heat source. The extract was then treated with concentrated sulfuric acid in a 1:2 acid:extract ratio.

In the second stage of the clean-up, the sample was chromatographed on a Florisil microcolumn containing approximately 1 g of activated Florisil (60-100 mesh) topped with a 5 mm layer of anhydrous sodium sulfate. The columns were activated at 130°C for 16 hours and prewashed with hexane prior to use. The extract was eluted with 10 mL of hexane and the eluate was concentrated to 1 mL. Analytical method blanks were prepared using the same procedure. The extracts were analysed using the GC-ECD and the GC/MS.

Soil Extraction by Soxhlet Method:

A thin layer of soil was spread on aluminium foil. The moisture in the soil was allowed to come to equilibrium with the moisture in the air. The soil was weighed (about 25 g) into the extraction thimble. To this an equal amount of an-

hydrous sodium sulfate (Na_2SO_4) was added and blended using a stirring rod. The resulting sample should be free flowing and not lumpy. If the sample was still moist, more sodium sulfate was added with stirring until it was free flowing.

A round bottom flask was half filled with 70:30 hexane/acetone mixture. Enough solvent was added so that when the extraction tube was filled to the siphon point, there was enough solvent left in the flask to prevent cracking due to heating. The extraction apparatus was assembled, the round bottom flask positioned in the heating mantle and the water flow started through the condenser. The apparatus was supported using a clamp and stand. The heat was adjusted for at least six cycles per hour. (The cycle is the filling of the extraction tube with solvent which evaporates from the flask and then condenses into the tube, followed by siphoning of solvent back into the flask). The sample was extracted for six (6) hours. The extract was concentrated using a Kuderna-Danish (K-D) concentrator fitted with a graduated concentrator tube containing about 0.5 g of copper filings and five boiling chips. A steam bath was used as the heat source. The extract was then treated with concentrated sulfuric acid in a 1:2 acid:extract ratio. The second stage of the clean-up procedure is similar to that for water extraction. The extracts were analysed by GC-ECD and GC/MS.

Extraction of soil and sediments for PCBs Using Mechanical Shaker Method

Soils were sampled to a depth of 3 cm and stored in hexane washed aluminium foil at -15°C prior to analysis. The samples were dried at 25°C to constant weight, ground and sieved to yield a particle size of less than 2 mm. 25 g portions of soil were extracted with 3 x 35 mL of 70:30 hexane:acetone mixture using a mechanical shaker and a shaking period of 30 minutes. The combined extract was washed with 2 x 100 mL water (to partition the acetone into the aqueous phase), then the organic layer was filtered through a column (30 cm x 2.5 cm I.D.) of anhydrous granular sodium sulfate and concentrated to 1 mL using a Kuderna-Danish (K-D) concentrator fitted with a graduated concentrator tube containing about 0.5g of copper filings and five boiling chips. A

steam bath was used as the heat source. The extract was then treated with concentrated sulfuric acid in a 1:2 acid:extract ratio. The second stage of the clean-up procedure was similar to that for water extraction. The concentrated sample was analysed using a Hewlett-Packard 5890 series gas chromatograph fitted with an electron capture detector and a HP1 or HP5 column. High purity nitrogen (99.9999%) was used as the carrier gas with a column flow rate of 30 mL/min. The injector and detector temperatures were 200°C and 300°C respectively and the oven temperature was maintained isothermally at 150°C.

Analysis of PCBs in transformer oil

Transformer oil (1.0 g) was accurately weighed in a 10 mL volumetric flask using a Mohr pipette and diluted to the mark with distilled hexane. The flask was then stoppered and mixed. This solution was transferred to a screw-cap glass bottle (~40-50 mL capacity) and 5 mL of concentrated sulfuric acid were added (using a measuring cylinder) and the solution was shaken vigorously and allowed to settle. The syringe was rinsed several times with distilled hexane before 1 mL of distilled hexane was withdrawn, then 1 mL of the sample (top layer) which was well above the sample-acid interface was withdrawn. The total volume in the syringe before injection was 2 mL. The hexane mixture was then injected into the gas chromatograph.

Gas chromatograph operating condition

Type of column:	HP1 or HP5 capillary
Length of column:	10 or 30 m
Oven temperature:	150°C (isothermal)
Type of detector:	electron Capture Detector (ECD)
Temperature of detector:	300°C
Temperature of injector:	200-220°C
Column flow rate:	30 mL/min

Analysis of Data:

Data obtained from the gas chromatograph were analysed by using an external standard of analytical grade and plotting a calibration curve of concentration versus peak area. Analysis of these data (including error analysis) were done

using Microsoft Excel 97.

RESULTS AND DISCUSSION

The data presented in Table 1 show that there is no significant difference in the efficiency between the method of Soxhlet extraction and that of the mechanical shaker. The average percentage recoveries were 80% and 85% for the Soxhlet extraction and the mechanical shaking, respectively. The limit of detection for PCBs was 0.1 mg/kg using a HP 3396 integrator and the coefficient of variation was 6.6%. A mass spectrometric detector was acquired in the latter stage of the project and the detection limit was 10 parts per billion (ppb). The extractions were carried out by using a mechanical shaker because it was less labour intensive, and in the event that there was a water lock-off, the solvent used would not be lost by evaporation as in the case of the Soxhlet extraction method.

TABLE 1 Data for Recovery Studies of PCBs using Soil, Water and Sediments

	<i>Mechanical Shaker</i>	<i>Soxhlet Method</i>
<i>% recovery for soil</i>	84, 79	80, 79
<i>% recovery for water</i>	87, 89 (manually shaken)	This was not done
<i>% recovery for sediment</i>	84, 86	80, 83

PCBs adsorb onto the soil particles. Some molecules are not easily removed due to strong chemisorption. Adsorption is dependent on the varying properties of the soil. Clay and organic matter are colloidal. They have high cation exchange capacities and high surface areas. These properties will enhance adsorption rates and lower percentage recovery. The percentage recovery of PCBs in water was not 100% due to the adsorption of the PCBs to the sodium sulfate, florisil and the glassware used in the extraction and the clean-up procedures.

Different methods for concentrating samples were used in order to verify the percentage recoveries. The steam bath was the preferred method because the recovery was just as good as the other methods and four times as many samples could be concentrated simultaneously due to the size of the steam bath employed (Table 2).

TABLE 2 Percentage Recoveries Using Different Methods for Concentrating Samples

[PCB]/ ppm	<i>Steam Bath</i>	<i>Hot Plate</i>	<i>Rotory Evaporator</i>
50	98, 99	97, 98	99, 99
500	99, 99	99, 99	98, 99

The steam bath was the preferred method because four times as many samples could be concentrated simultaneously due to the size of the steam bath employed.

The levels of PCBs in some urban and rural areas of Jamaica were determined (Tables 3 - 4 and Figures 1 and 2). All the soil samples collected contained less than 10 mg/kg PCB and PCB was found only in soil samples collected from sites where transformers were stored or in use. There was also evidence that there was spillage of transformer oil in these areas. These areas include a transformer storage area at Washington Boulevard, the Hunts Bay Power Station and the Old Harbour Bay Power Station. No PCB was found in the soil samples collected at the Rockfort Power Station. Seawater and sediment samples were also collected in the vicinity of the Rockfort and Hunts Bay Power Stations and no PCB was found. The mean concentrations of PCBs in the urban and rural soil samples were 0.7 and 0.2 mg/kg respectively with over 80% of the samples containing less than 2.0 mg/kg. The median concentration for the urban soil samples was 1.4 mg/kg while that for the rural was less than 0.1 mg/kg. The total numbers for urban and rural sample sites were 43 and 80 respectively. The highest concentration of PCBs detected in the urban and rural soil samples were 8.7 and 8.6 mg/

kg respectively. It should be noted that spillage of transformer oil occurred at these sites and as a result, these levels do not reflect the background levels for PCBs. That is, the very high levels of PCBs found at the sites with spillage will have unfair weighting on the average PCB concentration. The proximity to PCB sources, land use, wind direction, soil type and its organic content are expected to play a major part in determining the levels of PCBs at these sampling sites. The sampling sites were selected based on the principle of random selections and random tables (ANNOVA)^{9,10}.

No PCB was found in the soil, water and sediment samples collected in the Blue Mountain area. This was because of the fact that apart from transformers, there was probably no other source for PCB contamination and there was no report of contamination due to leakage or spillage of transformer oil in these areas.

Some transformer oil sampling sites such as Nain, Ewarton, Lydford and Washington Boulevard had PCB concentrations in the order of 7×10^5 mg/kg. However, transformer oils with concentration greater than 50 mg/kg are now being shipped to France for incineration or they are in the process of shipping. The percentage of transformer oil samples which did not contain PCBs was 40.1%. The duration of sampling was from March, 1996 to April, 1999 and the total number of transformer oil samples and soil samples analysed were 155 and 140 respectively.

In 1988, Jamaica was affected by Hurricane Gilbert and in that same year, PCB was found in a rural soil sample. This finding prompted further research even though this could have been due to spillage when a few transformers exploded during Hurricane Gilbert. It should be noted that the grid region in Figure 2 indicates that no sampling was done in that section of the island because there is no bauxite plant or electricity generating plant. These are the major users of transformer oil which contain PCBs.

In order to compare the concentration of PCBs obtained from areas that were contaminated with transformer oil, an area which had no reports of PCB contamination was chosen. This area constituted the sampling sites in Figure 1.

TABLE 3 The Location of the Transformer Oil Sampling Sites, the Total Number of Transformer Oil Samples Collected and the Average Detected Concentration of PCBs

Sampling Sites	Total Number of Samples Collected	Average [PCB]/(mg/kg)
Nain, St. Elizabeth	65	5.25×10^3
Lydford, St. Ann	34	2.00×10^4
New Kingston	4	4.38
Washington Boulevard, Kingston	2	28.6
Ewarton, St. Catherine	50	2.52×10^3

TABLE 4 The Location of the Soil Sampling Sites, the Total Number of Soil Samples Collected and the Average Detected Concentration of PCBs

Sampling Sites	Total Number of Samples Collected	Average [PCB]/(mg/kg)
Blue Mountain, St. Andrew	80	nd
Rockfort, Kingston	30	nd
New Kingston	2	nd
Hunts Bay, Kingston	7	0.68
Washington Boulevard, Kingston	10	1.56
Old Harbour Bay, St. Catherine	11	0.32

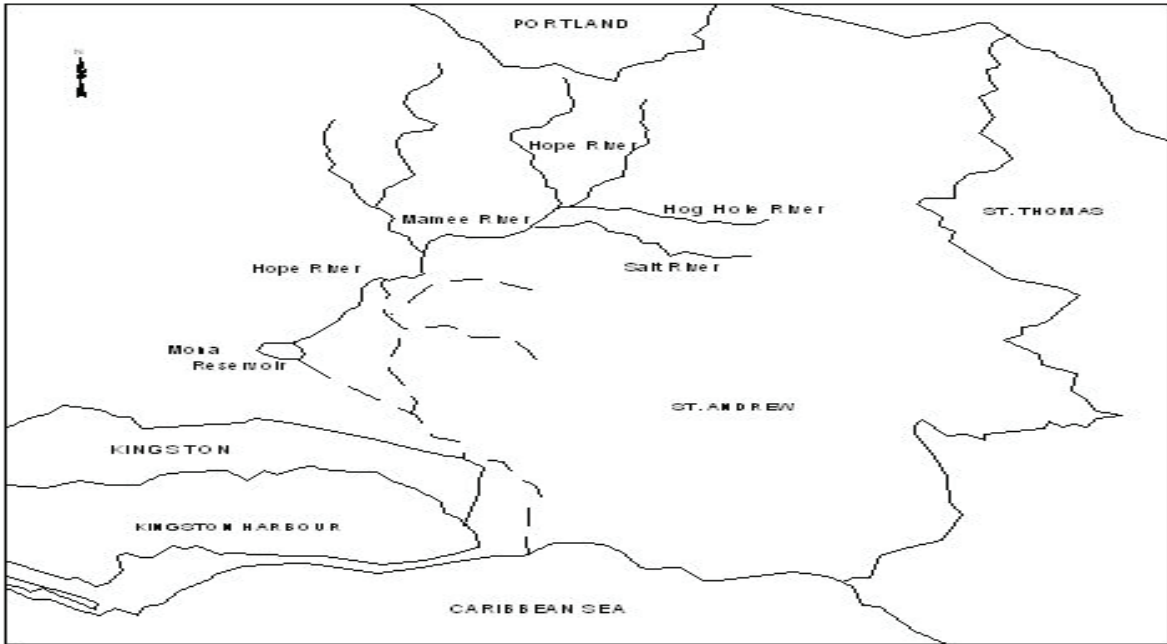


FIGURE 1 Major Sampling Sites of the Hope River Watershed

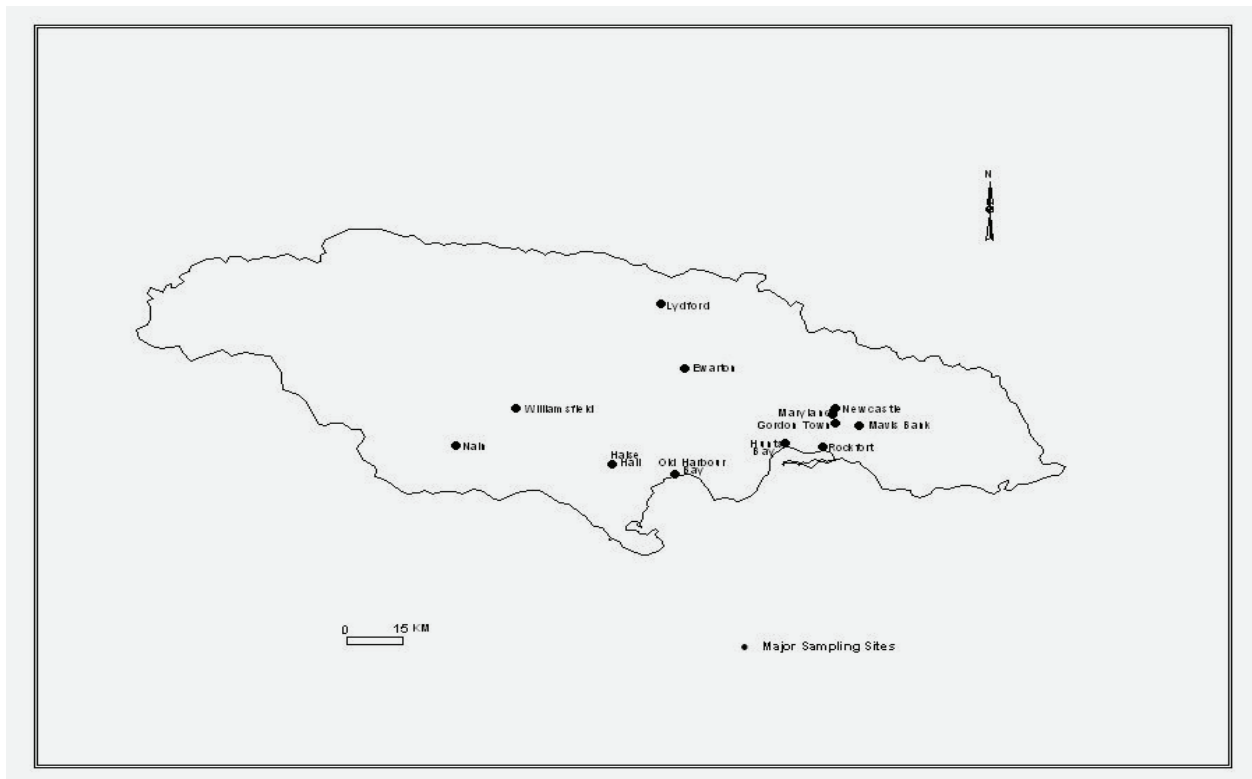


FIGURE 2 Major PCB Sampling Sites in Jamaica

CONCLUSIONS AND RECOMMENDATIONS

All the soil samples collected contained less than 10 mg/kg PCB. PCB was found only in soil samples collected from sites where transformers were stored or in use. No PCB was found in the soil, water and sediment samples collected in the Blue Mountain area (rural). It can be concluded from the data collected, that the presence of PCBs in Jamaican soil, water and sediments are restricted to PCB storage

areas and areas where PCBs are in use. An all island study should be embarked on so that a 'data bank' on the distribution of PCBs in Jamaica can be established.

In order to curtail the movement of spilled transformer oil which contains PCBs, the floor of the storage areas should be built with concrete and at a slight angle with collection areas. The collected transformer oil and any contaminated soil can then be degraded by an approved method such as chemical degradation or high temperature incineration.

APPENDIX

Calculation of [PCB]/(mg/kg) in transformer oil

$$[PCB]/(mg/kg) = \frac{B \times V_t}{A \times W} \quad \dots 1$$

where $A = \frac{\text{sum of std peak heights or areas}}{\text{mg of std injected}} = \text{mm/ng}$

and $B = \frac{\text{sum of sample peak or areas}}{\mu\text{L injected}} = \text{mm}/\mu\text{L}$

V_t = dilution volume of sample in mL

W = weight of sample in grams

Since the amount of sample injected = 1 μL ,

Equation 1 is reduced to equation 2 below.

$$[PCB]/(mg/kg) = \frac{\text{Total area of sample} \times V_t}{(\text{Total area of std} / 5) \times W} \quad \dots 2$$

$[\text{Aroclor 1260}]_{\text{std}} = 5 \text{ ppm} = 5 \text{ mg/L} = 5 \times 10^6 \text{ ng/L}$

1 L of std contains $5 \times 10^6 \text{ ng}$ of Aroclor 1260

$10^6 \mu\text{L}$ of std contain $5 \times 10^6 \text{ ng}$ of Aroclor 1260

Therefore, 1 μL of std contains $(5 \times 10^6 / 10^6) \text{ ng}$ of Aroclor 1260 = 5 ng

Hence, amount of std injected = 5 ng

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THE CATALYTIC DEGRADATION OF POLYCHLORINATED BIPHENYLS (PCBs)

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ABSTRACT Extensive investigation of the catalytic degradation of polychlorinated biphenyls (PCBs) was carried out in solution using some peroxy complexes of chromium (IV) and iron complexes in conjunction with hydrogen peroxide. The change in concentration of PCBs was measured by using a gas chromatograph attached to an electron capture detector. A mass spectrometric detector was also used. The results obtained are discussed.

INTRODUCTION

Polychlorinated biphenyls are probably the most widely distributed chlorinated organic pollutants which were commercially produced in vast quantities. A detailed study was carried out recently¹ on the level of contamination in soil at various regions of Jamaica.

There are many methods of PCB disposal which have been studied,²⁻⁶ and some of these include thermal destruction such as high temperature incineration (HTI); infrared thermal treatment or circulating bed combustor; physical separation such as thermal treatment (rotary thermal desorber and fluidized bed) and solvent extraction (soil washing and liquefied gas); solidification/stabilization such as chemical fixation (encapsulation, in-situ inorganic polymer and silicates); in-situ vitrification; biological treatment; and chemical dechlorination. However, the most effective method known in terms of percentage decomposition is high temperature incineration (HTI). In recent years, the HTI procedure has been challenged by the environmentalist. It has been claimed that during incineration, PCBs vaporize and toxic gases such as dioxins and dibenzofurans are released. During the last decade, attempts were made by various scientists to find a suitable method of degradation of PCBs in aqueous solution. However, these methods are not commercially viable.

The use of peroxy chromium(IV) complexes such as diperoxaqua(ethylenediamine) chromium(IV), $\text{Cr}(\text{O}_2)_2(\text{en})(\text{H}_2\text{O})$, diperoxo

(diethylenetriamine) chromium(IV), $\text{Cr}(\text{O}_2)_2$ (dien) and iron complexes were found⁷ to catalyse many oxidation reactions and as a result $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, $[\text{Fe}_2\text{O}(\text{phen})_4(\text{CrO}_4^{2-})](\text{ClO}_4)_2$ and $\text{Cr}_2\text{FeO}(\text{OOC}-\text{C}_4\text{H}_9)_6(\text{C}_5\text{H}_5\text{N})_3\text{ClO}_4$ were employed as catalysts. Vassell and Espenson⁸ got excellent results from their investigations of the catalytic ability of methylrhenium trioxide using hydrogen peroxide.

The compound methylrhenium trioxide, CH_3ReO_3 , sometimes referred to as MTO, is prepared easily from dirhenium heptoxide and tetramethyltin and is a highly effective catalyst. It is stable far above its melting point (106°C), soluble and stable in water and organic solvents and stable also to air and acid. Methylrhenium trioxide has been reported in the literature to be a good catalyst for olefin metathesis⁹, olefin oxidation¹⁰ and aldehyde olefination¹¹. This compound also has the advantage of being able to be used as a homogeneous or, with a support, heterogeneous catalyst.

It is quite evident from the published work on the degradation of PCBs that there is a need for continuing investigation on catalytic degradation of PCBs. In this paper, some transition metal complexes were selected which have potential to be good catalysts and hence, the investigation of their efficacies in the degradation of PCBs has been presented. The structures of these complexes are shown in Figures 1 to 5. Since hydrogen peroxide and methylrhenium trioxide together form a good catalytic system, methylrhenium and other similar synthetic catalysts were included in this research.

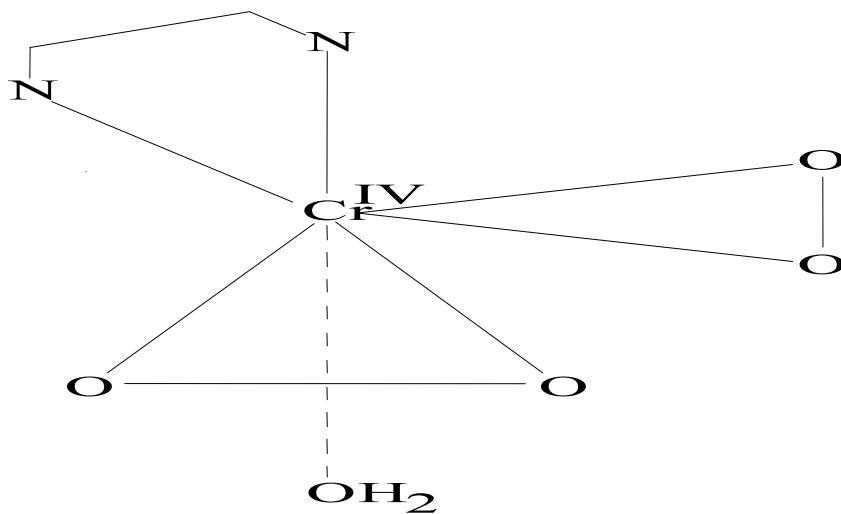


FIGURE 1 Diperoxaqua(ethylenediamine)chromium(IV)

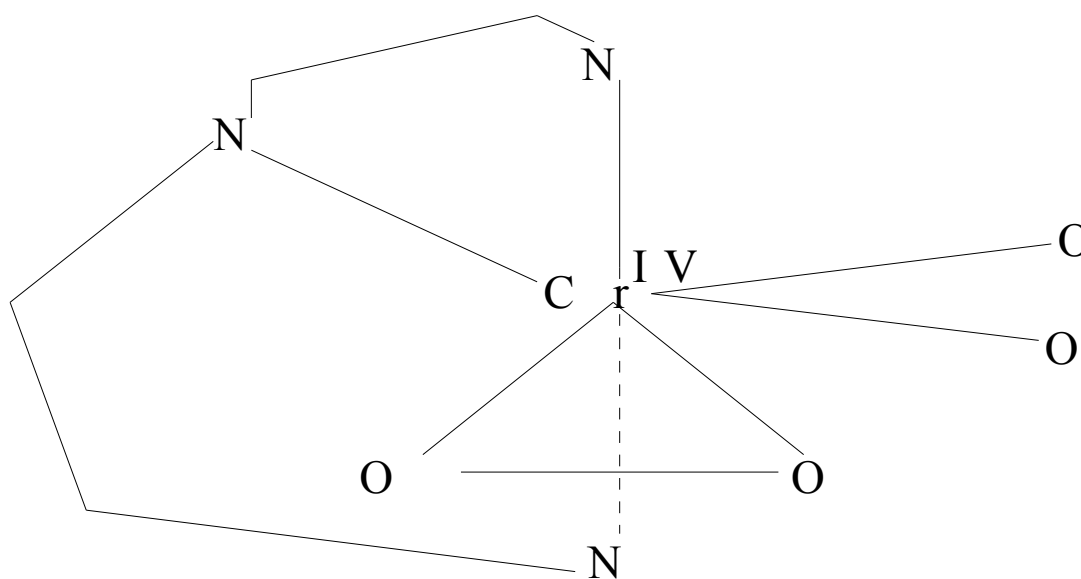
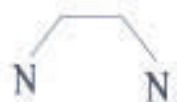
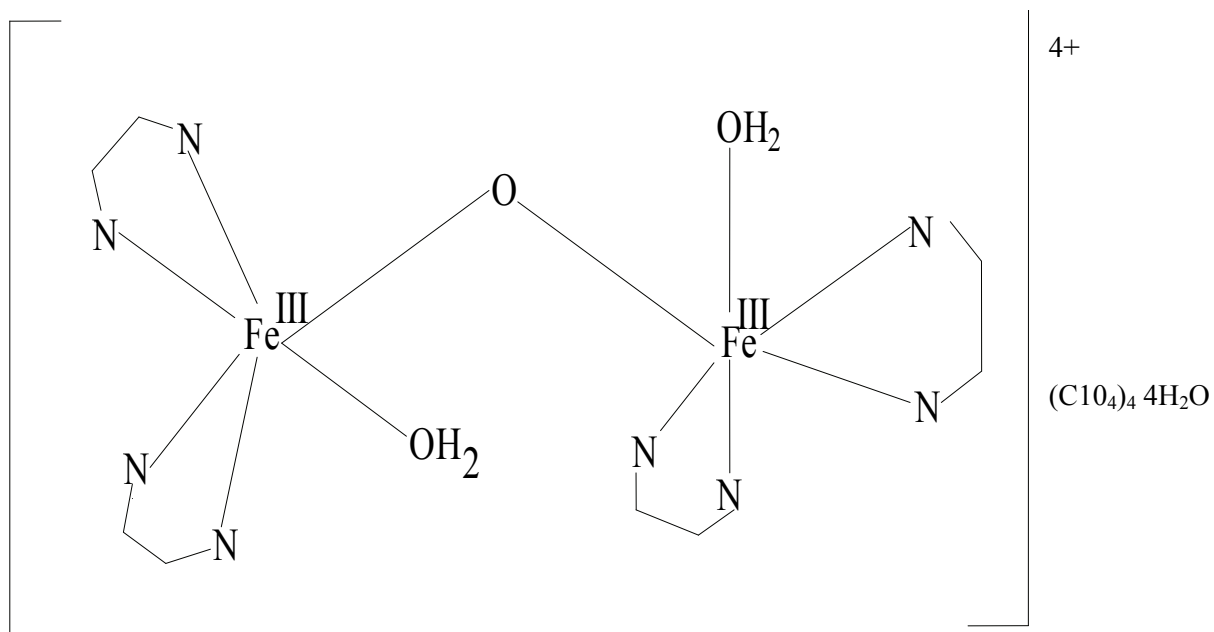


FIGURE 2 Diperoxa(diethylenetriamine)chromium(IV) monohydrate



= 2, 2' - bipyridyl or 1, 10' - phenanthroline

phen = 1, 10' - phenanthroline

bipy = 2, 2' - bipyridyl

FIGURE 3 Diperoxo(diethylenetriamine)chromium(IV) monohydrate

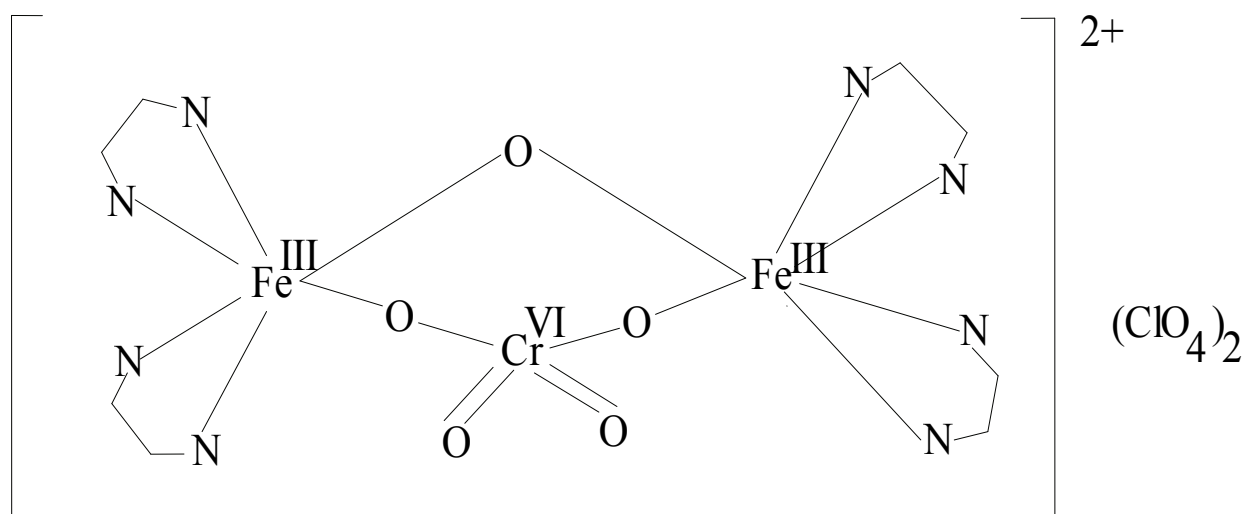


FIGURE 4 (m-oxo)(m-O, O'-chromato-bis[bis(1-10 phenanthroline) iron (III)]

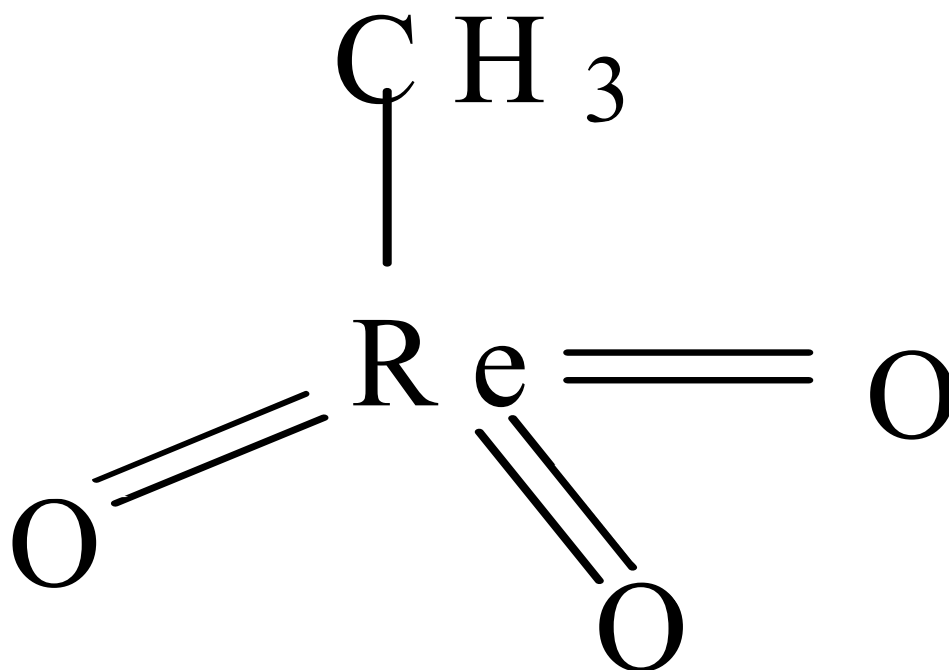


FIGURE 5 Methylrhenium Trioxide

EXPERIMENTAL

Materials

Neat Aroclor 1232, Aroclor 1248 and Aroclor 1260 were obtained from SUPELCO, Bellefonte, PA 16823, USA. The other reagents used were either general purpose reagents (GPR) or analytical grade reagents (AR) obtained from British Drug House Chemicals Limited (BDH), Aldrich and Sigma Chemical Companies. Pesticide grade solvents were used and these were obtained from commercial sources.

Distilled and deionized water were generated from a LABCONCO^R WATER PRO^{T.M.} PS and FISTREEN^{T.M.} CYCLON^{T.M.} deionization unit. High purity nitrogen gas (99.9999%) was supplied either locally by Jamaica Oxygen and Acetylene Limited or overseas by Air Products and Chemicals, Inc. Allentown, PA 18195, USA. Samples were collected from designated sites as indicated in the tables provided (see results).

PREPARATION OF COMPOUNDS

A: *Diperoxaqua(ethylenediamine)chromium (IV)*

The diperoxaqua(ethylenediamine)chromium (IV) was prepared and characterized according to published standard procedure¹². The purity was checked by uv/visible spectrophotometry and λ_{\max} was found to be 380 (literature value = 378 nm).

B: *Diperoxo(diethylenetriamine)chromium(IV) monohydrate*

The above compound was prepared by standard procedure published earlier¹². The purity was checked by uv/visible spectrophotometry and λ_{\max} was found to be 385 (literature value = 388 nm).

C: *(m-oxo)bis[aquabis(1-10 phenanthroline) iron (III)]*

The above compound was prepared by the

published standard procedure¹³. The purity was checked by uv/visible spectrophotometer and λ_{\max} was found to be 580 (literature value = 588 nm).

D: *(m-oxo)(m-O, O'-chromato-bis[bis(1-10 phenanthroline) iron (III)]*

The above compound was prepared by the published standard procedure¹³. The purity was checked by uv/visible spectrophotometer and λ_{\max} was found to be 602 (literature value = 610 nm).

E: *Methylrhenum Trioxide*

The above compound was prepared by the published standard procedure¹⁴. The purity was checked by uv/visible spectrophotometer in water and λ_{\max} was found to be 239 (literature value = 239 nm).

PROCEDURE FOR CHEMICAL DEGRADATION STUDY

5 mL of 20 ppm Aroclor or hexachlorobenzene were pipetted into each 50 mL round bottom flask and all the hexane were evaporated by placing in a water bath and 5 mL of solvent (Table 1-21) were added. Known amounts of catalysts were added and 0.1 mL of 30% w/v hydrogen peroxide was added to each flask. The resulting solutions were either allowed to stand and stirred or digested in a microwave oven for a known time after which two 10 mL portions of hexane were used to extract the analyte. 20 mL of concentrated sulfuric acid were then added and was shaken vigorously. After settling, the bottom layer was rejected. The top layer was placed in a round bottom flask which was then concentrated on a water bath and made up to 5 mL with distilled hexane. A 1/5 dilution was done and 1 μ L of hexane and 1 μ L of the diluted sample were injected into a Hewlett-Packard 5890 gas chromatograph attached to an electron capture detector and a Hewlett-Packard 3396A integrator. A HP-1 (methyl silicone gum) capillary column of 10 m x 0.53 mm x 2.65 μ m film thickness was employed. Oxygen free nitrogen was used as the carrier gas with a flow rate of 30 mL/min. The injector and detector temperatures were 220°C and 300°C respectively and the oven temperature

was maintained isothermally at 150°C. The chart speed and attenuation were 0.5 and 5 respectively while the peak width and area reject were 0.04 mm and 10,000 respectively. A PCB calibration curve was obtained by using the appropriate 1, 2, 3 and 4 ppm Aroclor standards versus the respective peak areas (Figure 6). The PCB results are recorded in Tables 1-8.

A HCB calibration curve was obtained by us-

ing 0.1, 0.2, 0.3, 0.4 and 0.8 ppm HCB standard versus the respective peak areas (Figure 7). The HCB results are recorded in table 9-21. Analysis of these data (including error analysis) were done using Microsoft Excel 97.

Porphrine was added to the PCB and the HCB in both acidic and basic solution using 5 mL of concentrated nitric acid and 0.5 g of sodium hydroxide respectively.

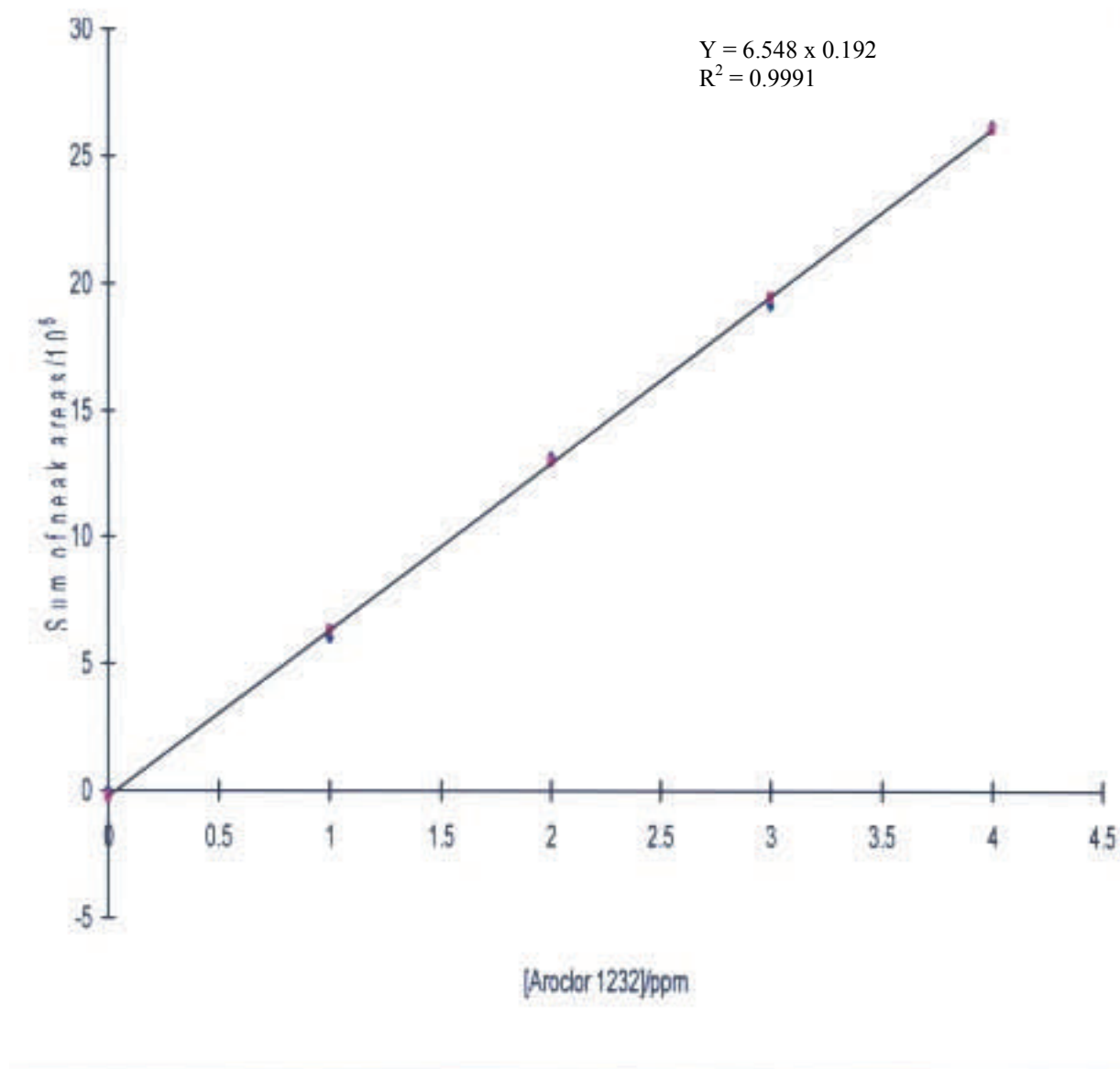


FIGURE 6 Construction of Calibration Curve using Aroclor 1232 Standards

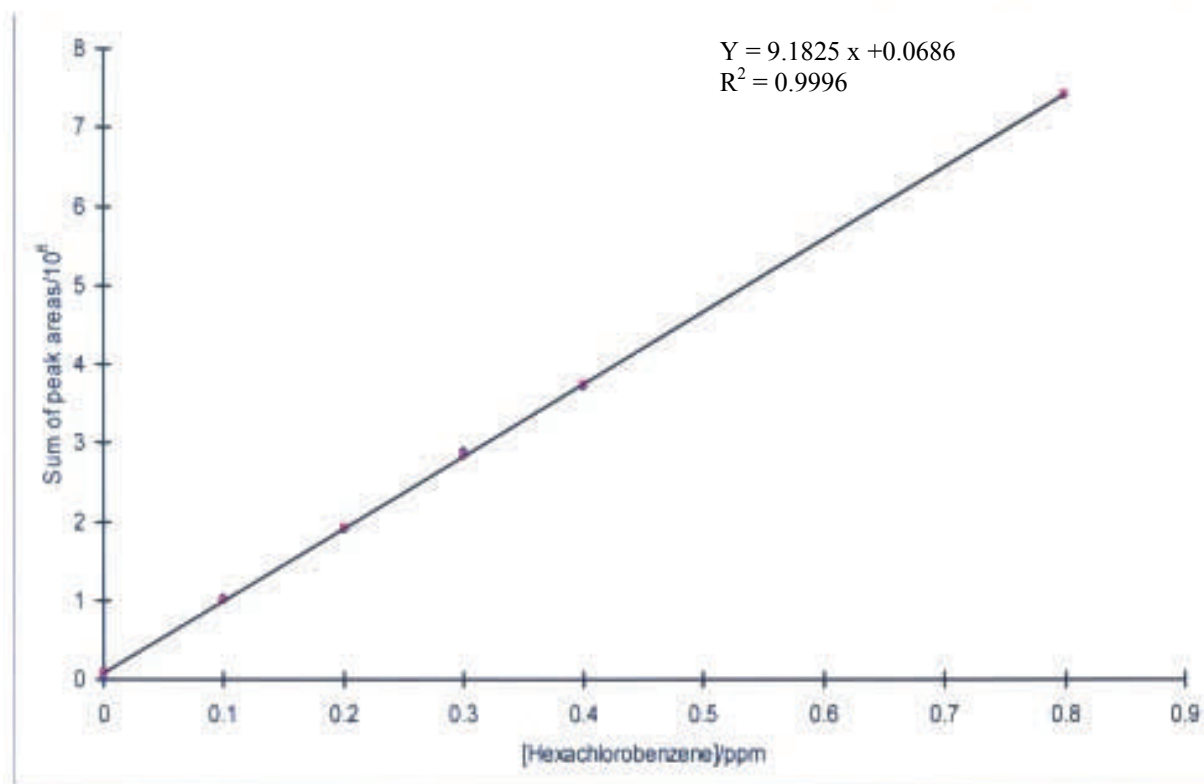


FIGURE 7 Construction of Calibration Curve using Hexachlorobenzene Standards

TABLE 1 Extent of PCB Degradation Using Various Catalysts in Hexane and Acetone/Water Solvent System.

Run Number	1	2
Solvent Used	Hexane	Acetone /Water
Duration of Stirring	24hrs	48hrs
Name of Sample	[PCB] _{av.} /(mg/kg)	[PCB] _{av.} /(mg/kg)
Sample before treatment	304	857
Sample with H ₂ O ₂ & No catalyst	278 (8.6)	855 (0.2)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	273 (10.2)	681 (20.5)
Sample with [Cr(O ₂) ₂ (dien)]. H ₂ O + H ₂ O ₂	262 (13.8)	798 (6.9)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	275 (9.5)	850 (0.8)

The values in brackets represent the average percentage degradation of PCBs.

TABLE 2 Extent of PCB Degradation Using Various Catalysts in Acetone/Water Solvent System

Run Number	1	2	3	4
Solvent Used	Acetone / Water			
Duration of Stirring	24hrs	48hrs	48hrs	48hrs
Name of Sample	[PCB] _{av.} / (mg/kg)	[PCB] _{av.} / (mg/kg)	[PCB] _{av.} / (mg/ kg)	[PCB] _{av.} / (mg/ kg)
Sample before treatment	278	148	86.1	65.3
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	275 (1.1)	146 (1.4)	68.2 (20.8)	64.2 (1.7)
Sample with [Cr(O ₂) ₂ (dien)]. H ₂ O + H ₂ O ₂	262 (5.8)	146 (1.4)	80.0 (7.1)	56.3 (13.8)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂] (ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	265 (4.7)	144 (2.7)	84.6 (1.7)	52.1 (20.2)

The values in brackets represent the average percentage degradation of PCBs.

TABLE 3 Extent of PCB Degradation Using Various Catalysts in Acetone/Water Solvent System

Run Number	1	2	3
Solvent Used	Acetone / Water		
Duration of Stirring	24hrs	48hrs	48hrs
Name of Sample	[PCB] _{av.} / (mg/ kg)	[PCB] _{av.} / (mg/kg)	[PCB] _{av.} / (mg/ kg)
Sample before treatment	71.4	331	560
Sample with H ₂ O ₂ & No catalyst	65.3 (8.5)	328 (0.9)	535 (4.5)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	70.3 (1.5)	228 (31.1)	456 (18.6)
Sample with [Cr(O ₂) ₂ (dien)]. H ₂ O + H ₂ O ₂	69.8 (2.2)	325 (1.8)	435 (22.3)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	58.5 (18.1)	327 (1.2)	555 (0.9)

The values in brackets represent the average percentage degradation of PCBs.

TABLE 4 Extent of PCB Degradation Using Various Catalysts in Isopropyl-alcohol

Run number	1	2	3
Solvent used	isopropyl-alcohol		
Duration of stirring/hrs.	48	31	41
Name of sample	Av. [PCB]/ mg/kg	Av. [PCB]/ mg/kg	Av. [PCB]/ mg/kg
Sample before treatment	660	232	609
Sample with H ₂ O ₂ and no catalyst	650 (1.5)	227 (2.2)	535 (12.1)
Sample with Cr(O ₂) ₂ (en). H ₂ O + H ₂ O ₂	650 (1.5)	227 (2.2)	456 (25.1)
Sample with [Cr(O ₂) ₂ (dien)].H ₂ O + H ₂ O ₂	561 (15.0)	225 (3.0)	435 (28.6)
Sample with [Fe ₂ O(phen) ₄ . (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O +H ₂ O ₂	557 (15.6)	173 (25.4)	535 (12.1)

The values in brackets represent the average percentage degradation of PCBs.

TABLE 5 Extent of PCB Degradation Using Various Catalysts in Isopropyl-alcohol

Run number	1	2	3	4
Solvent Used	Isopropyl-alcohol			
Duration of Stirring	24hrs.	24hrs.	24hrs.	24hrs.
Name of Sample	[PCB] _{av} / (mg/kg)	[PCB] _{av} / (mg/ kg)	[PCB] _{av} / (mg/ kg)	[PCB] _{av} / (mg/ kg)
Sample before treatment	20.0	20.0	20.0	20.0
Sample with H ₂ O ₂	17.2 (14.0)	16.4 (18.0)	19.2 (4.0)	18.4 (8.0)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	16.3 (18.5)	19.8 (1.0)	20.0 (0)	19.8 (1.0)
Sample with [Cr(O ₂) ₂ (dien)].H ₂ O + H ₂ O ₂	18.1 (9.5)	17.5 (12.5)	18.2 (9.0)	19.0 (5.0)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	16.3 (18.5)	18.3 (8.5)	19.1 (4.5)	18.4 (8.0)
Sample with PM catalyst + H ₂ O ₂	17.7 (11.5)	20.0 (0)	18.5 (7.5)	19.1 (4.5)

The values in brackets represent the average percentage degradation of PCBs.
Aroclor 1248 was used as standard. PM = [Cr₂FeO(OOCC₄H₉)₆(C₅H₅N)₃]ClO₄

TABLE 6 Extent of PCB Degradation Using Various Catalysts in Isopropyl-alcohol

Run number	1	2	3	4
Solvent Used	Isopropyl-alcohol			
Duration of Stirring	24hrs.	24hrs.	24hrs.	24hrs.
Name of Sample	[PCB] _{av.} / (mg/kg)	[PCB] _{av.} / (mg/ kg)	[PCB] _{av.} / (mg/ kg)	[PCB] _{av.} / (mg/ kg)
Sample before treatment	20.0	20.0	20.0	20.0
Sample with H ₂ O ₂	18.3 (8.5)	17.3 (13.5)	16.2 (19.0)	17.6 (12.0)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	17.0 (15.0)	15.4 (23.0)	14.6 (27.0)	16.1 (19.5)
Sample with [Cr(O ₂) ₂ (dien)].H ₂ O + H ₂ O ₂	18.2 (9.0)	16.2 (19.0)	19.0 (5.0)	15.1 (24.5)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	17.4 (13.0), 19.2 (4.0)	19.3 (3.5), 18.7 (6.5)	19.4 (3.0)	19.2 (4.0)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	18.4 (8.0)	18.1 (9.5)	19.2 (4.0)	17.3 (13.5)
Sample with PM catalyst + H ₂ O ₂	17.1 (14.5)	19.5 (2.5)	16.6 (17.0)	15.7 (21.5)

The values in brackets represent the average percentage degradation of PCBs.
Aroclor 1232 was used as standard. PM = [Cr₂FeO(OOCC₄H₉)₆(C₅H₅N)₃]ClO₄

TABLE 7 Extent of PCB Degradation Using CH₃ReO₃ in Hexane

Run Number	1	2
Solvent	Hexane	
Name of Sample	[PCB] _{av.} / (mg/kg)	[PCB] _{av.} / (mg/kg)
Sample before treatment	20.0	20.0
PCB + CH ₃ ReO ₃ + No Stirring	19.5 (2.5)	19.6 (2.0)
PCB + CH ₃ ReO ₃ + 48hrs. Stirring	19.8 (1.0)	19.0 (5.0)
PCB + CH ₃ ReO ₃ + H ₂ O ₂ + 48hrs. Stirring	16.4 (18.0)	17.1 (14.5)
PCB without stirring at room temperature	19.9 (0.5)	19.8 (1.0)
PCB stirred for 24hrs. at room temperature	20.0 (0)	19.8 (1.0)
PCB + CH ₃ ReO ₃ stirred for 24hrs. at room temp.	18.2 (9.0)	17.7 (11.5)
PCB + CH ₃ ReO ₃ + H ₂ O ₂ + Reflux for 24hrs.	15.3 (23.5)	15.6 (22.0)
PCB + CH ₃ ReO ₃ + H ₂ O ₂ + Refluxed for 48hrs.	17.4 (13.0), 19.2 (4.0)	18.0 (10.0), 19.5 (2.5)

The values in brackets represent the average percentage degradation of PCBs
Name of PCB used was Aroclor 1232

TABLE 8 Extent of PCB Degradation Using Various Porphrines

Initial [PCB]/ppm	Volume of PCB solution/mL	Volume of 30% H ₂ O ₂ used/mL	Proposed (~5mg)	Catalyst	Duration of re-flux/hrs.	Resulting *[PCB] av./ppm
20.0	5.0	5.0	MTMPP		24	19.4 (3.0)
20.0	5.0	5.0	MTMPP		24	19.6 (2.0)
10.0	5.0	5.0	PCM		24	9.5 (5.0)
10.0	5.0	5.0	PCM		24	9.2 (8.0)
10.0	10.0	5.0	H ₂ TPP		24	9.4 (6.0)
10.0	10.0	5.0	H ₂ TPP		24	9.1 (9.0)
10.0	10.0	5.0	H ₂ TPP + NaOH		24	9.1 (9.0)
10.0	10.0	5.0	H ₂ TPP + NaOH		24	9.3 (7.0)
10.0	10.0	5.0	H ₂ TPP + NaOH		48	9.1 (9.0)
10.0	10.0	5.0	H ₂ TPP + NaOH		48	9.5 (5.0)
10.0	10.0	5.0	H ₂ TPP + HNO ₃	Conc.	24	8.9 (11.0)
10.0	10.0	5.0	H ₂ TPP + HNO ₃	Conc.	24	8.7 (13.0)
10.0	10.0	5.0	H ₂ TPP + HNO ₃	Conc.	48	8.6 (14.0)
10.0	10.0	5.0	H ₂ TPP + HNO ₃	Conc.	48	9.0 (10.0)

The values in brackets represent the average percentage degradation of PCBs.

MTMPP = Meso-tetra(4-N-methylpyridyl)porphrine tetra-iodide

H₂TPP = Tetraphenylporphrine

PCM = Phthalocyanine Magnesium

*Aroclor 1232 was used as standard

TABLE 9 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts in Hexane, Water and Acetone/Water Solvent System

Run Number	1	2	3
Solvent Used	Hexane	Water	Acetone /Water
Duration of Stirring	24hrs	48hrs	48hrs
Name of Sample	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)
Sample before treatment	20.0	20.0	20.0
Sample with H ₂ O ₂ & No catalyst	19.4 (3.0)	19.6 (2.0)	19.3 (3.5)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	19.3 (3.5)	19.7 (1.5)	19.8 (1.0)
Sample with [Cr(O ₂) ₂ (dien)]. H ₂ O + H ₂ O ₂	19.6 (2.0)	19.5 (2.5)	19.7 (1.5)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	19.7 (1.5)	19.4 (3.0)	19.4 (3.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 10 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts in Acetone/Water Solvent System

Run Number	1	2	3	4
Solvent Used	Acetone / Water			
Duration of Stirring	24hrs	48hrs	48hrs	48hrs
Name of Sample	[HCB] _{av.} / (mg/L)	[HCB] _{av.} / (mg/L)	[HCB] _{av.} / (mg/L)	[HCB] _{av.} / (mg/L)
Sample before treatment	20.0	20.0	20.0	20.0
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	19.8 (1.0)	19.6 (2.0)	19.5 (2.5)	19.7 (1.5)
Sample with [Cr(O ₂) ₂ (dien)].H ₂ O + H ₂ O ₂	19.7 (1.5)	19.7 (1.5)	19.6 (2.0)	19.5 (2.5)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	19.4 (3.0)	19.7 (1.5)	19.3 (3.5)	19.6 (2.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 11 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts in Isopropyl-alcohol

Run number	1	2	3	4
Solvent Used	Isopropyl-alcohol			
Duration of Stirring	24hrs.	24hrs.	24hrs.	24hrs.
Name of Sample	Av. [HCB] / (mg/L)	Av. [HCB] / (mg/L)	Av. [HCB] / (mg/L)	Av. [HCB] / (mg/L)
Sample before treatment	20.0	20.0	20.0	20.0
Sample with H ₂ O ₂	19.6 (2.0)	19.7 (1.5)	19.4 ((3.0)	19.7 (1.5)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	19.1 (4.5)	19.5 (2.5)	19.8 (1.0)	19.8 (1.0)
Sample with [Cr(O ₂) ₂ (dien)].H ₂ O + H ₂ O ₂	19.6 (2.0)	19.6 (2.0)	19.1 (4.5)	19.5 (2.5)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	19.4 (3.0)	19.6 (2.0)	19.4 (3.0)	19.7 (1.5)
Sample with PM catalyst + H ₂ O ₂	19.2 (4.0)	19.5 (2.5)	19.7 (1.5)	19.0 (5.0)

The values in brackets represent the average percentage degradation of HCB

PM = [Cr₂FeO(OOCC₄H₉)₆(C₅H₅N)₃]ClO₄

TABLE 12 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts in Hexane

Run Number	1	2
Solvent	Hexane	
Name of Sample	[HCB] _{av} /(mg/L)	[HCB] _{av} /(mg/L)
Sample before treatment	20.0	20.0
HCB without stirring at room temperature	19.9 (0.5)	19.8 (1.0)
HCB + H ₂ O ₂ + No Catalyst or Stirring	19.8 (1.0)	19.7 (1.5)
HCB + CH ₃ ReO ₃ + No Stirring	19.8 (1.0)	19.8 (1.0)
HCB + CH ₃ ReO ₃ + 48hrs. Stirring	19.3 (3.5)	19.6 (2.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 48hrs. Stirring	18.7 (6.5)	19.2 (4.0)
HCB stirred for 24hrs. at room temperature	19.8 (1.0)	19.7 (1.5)
HCB + CH ₃ ReO ₃ stirred for 24hrs. at room temp.	19.6 (2.0)	18.8 (6.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + Reflux for 24hrs.	19.0 (5.0)	18.7 (6.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + Refluxed for 48hrs.	18.9 (5.5)	19.4 (3.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 13 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts in Acetone and Isopropyl-alcohol

Run Number	1	2
Name of Sample	[HCB] _{av} /(mg/L)	[HCB] _{av} /(mg/L)
Solvent	Acetone	Isopropyl-alcohol
Sample before treatment	20.0	20.0
HCB without stirring at room temperature	19.8 (1.0)	19.8 (1.0)
HCB + H ₂ O ₂ + No Catalyst or Stirring	19.6 (2.0)	19.8 (1.0)
HCB + CH ₃ ReO ₃ + No Stirring	19.7 (1.5)	19.6 (2.0)
HCB + CH ₃ ReO ₃ + 48hrs. Stirring	19.3 (3.5)	19.6 (2.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 48hrs. Stirring	19.4 (3.0)	19.5 (2.5)
HCB stirred for 24hrs. at room temperature	19.2 (4.0)	19.3 (3.5)
HCB + CH ₃ ReO ₃ stirred for 24hrs. at room temp.	19.7 (1.5)	19.0 (5.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + Reflux for 24hrs.	19.4 (3.0)	19.2 (4.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + Refluxed for 48hrs.	19.9 (0.5)	19.4 (3.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 14 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts in Acetonitrile and Dimethylsulfoxide

Run Number	1	2
Name of Sample	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)
Solvent	Acetonitrile	Dimethyl-sulfoxide
Sample before treatment	20.0	20.0
HCB without stirring at room temperature	19.9 (0.5)	19.7 (1.5)
HCB + H ₂ O ₂ + No Catalyst or Stirring	19.7 (1.5)	19.7 (1.5)
HCB + CH ₃ ReO ₃ + No Stirring	19.8 (1.0)	19.5 (2.5)
HCB + CH ₃ ReO ₃ + 48hrs. Stirring	19.6 (2.0)	19.3 (3.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 48hrs. Stirring	19.6 (2.0)	19.7 (1.5)
HCB stirred for 24hrs. at room temperature	19.0 (5.0)	19.5 (2.5)
HCB + CH ₃ ReO ₃ stirred for 24hrs. at room temp.	19.2 (4.0)	19.4 (3.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + Reflux for 24hrs.	19.3 (3.5)	19.5 (2.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + Refluxed for 48hrs.	19.6 (2.0)	19.1 (4.5)

The values in brackets represent the average percentage degradation of HCB

TABLE 15 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts and Microwave Radiation in Hexane, Water and Acetone/Water Solvent System

Run Number	1	2	3
Solvent Used	Hexane	Water	Acetone /Water
Duration of radiation	10 min.	10 min.	10 min.
Name of Sample	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)
Sample before treatment	10.0	10.0	10.0
Sample with H ₂ O ₂ & No catalyst	9.5 (5.0)	9.3 (7.0)	9.1 (9.0)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	9.6 (4.0)	9.2 (8.0)	9.4 (6.0)
Sample with [Cr(O ₂) ₂ (dien)]. H ₂ O + H ₂ O ₂	9.2 (8.0)	8.9 (11.0)	8.5 (5.0)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	9.5 (5.0)	9.2 (8.0)	8.7 (13.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 16 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts and Microwave Radiation in Acetone/Water Solvent System

Run Number	1	2	3
Solvent Used	Acetone / Water		
Duration of radiation	10 min.	10 min.	10 min.
Name of Sample	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)	[HCB] _{av.} /(mg/L)
Sample before treatment	20.0	20.0	20.0
Sample with H ₂ O ₂ & No catalyst	18.8 (6.0)	18.5 (7.5)	18.7 (6.5)
Sample with Cr(O ₂) ₂ (en).H ₂ O + H ₂ O ₂	19.0 (5.0)	18.7 (6.5)	18.9 (5.5)
Sample with [Cr(O ₂) ₂ (dien)]. H ₂ O + H ₂ O ₂	18.4 (8.0)	18.6 (7.0)	18.3 (8.5)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O + H ₂ O ₂	19.1 (4.5)	19.3 (3.5)	18.8 (6.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 17 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts and Microwave Radiation in Isopropyl-alcohol, Acetonitrile and Dimethylsulfoxide (DMSO)

Run number	1	2	3
Solvent Used	Isopropyl-alcohol	Aceto-nitrile	DMSO
Duration of radiation/min.	10	10	10
Name of sample	[HCB] _{av.} /mg/L	[HCB] _{av.} /mg/L	[HCB] _{av.} /mg/L
Sample before treatment	20.0	20.0	20.0
Sample with H ₂ O ₂ and no catalyst	18.8 (6.0)	18.5 (7.5)	19.1 (4.5)
Sample with Cr(O ₂) ₂ (en). H ₂ O + H ₂ O ₂	18.5 (7.5)	18.7 (6.5)	19.3 (3.5)
Sample with [Cr(O ₂) ₂ (dien)].H ₂ O + H ₂ O ₂	18.3 (8.5)	18.8 (6.0)	19.0 (5.0)
Sample with [Fe ₂ O(phen) ₄ (H ₂ O) ₂](ClO ₄) ₄ .4H ₂ O +H ₂ O ₂	19.0 (5.0)	18.8 (6.0)	19.4 (3.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 18 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts and Microwave Radiation in Acetonitrile and Dimethylsulfoxide (DMSO)

Run Number	1	2
Solvent Used	Acetonitrile	DMSO
Initial [HCB] /(mg/L)	20.0	20.0
Volume of HCB used/mL	20.0	20.0
HCB + CH ₃ ReO ₃ + 10 min. radiation	18.7 (6.5)	19.1 (4.5)
HCB + CH ₃ ReO ₃ + 30 min. radiation	18.3 (8.5)	18.5 (7.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 10 min. radiation	18.1 (9.5)	18.7 (6.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 30 min.	18.4 (8.0)	18.2 (9.0)
HCB + CrO ₃ + H ₂ O ₂ + 10 min. radiation	19.3 (3.5)	19.0 (5.0)
HCB + CrO ₃ + H ₂ SO ₄ + 30 min. radiation	19.1 (4.5)	19.4 (3.0)
HCB + NaOH + 10 min. radiation	19.0 (5.0)	19.5 (2.5)
HCB + NaOH + 30 min. radiation	19.6 (2.0)	19.3 (3.5)
HCB + 1:1 H ₂ SO ₄ /HNO ₃ + 10 min. radiation	19.5 (2.5)	19.4 (3.0)
HCB + 1:1 H ₂ SO ₄ /HNO ₃ + 30 min. radiation	18.9 (5.5)	19.3 (3.5)

The values in brackets represent the average percentage degradation of HCB

TABLE 19 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts and Microwave Radiation in Acetone and Isopropyl-alcohol

Run Number	1	2
Solvent Used	Acetone	Isopropyl-alcohol
Initial [HCB] /(mg/L)	20.0	20.0
Volume of HCB used/mL	20.0	20.0
HCB + CH ₃ ReO ₃ + 10 min. radiation	18.9 (5.5)	19.4 (3.0)
HCB + CH ₃ ReO ₃ + 30 min. radiation	18.1 (9.5)	18.3 (8.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 10 min. radiation	18.4 (8.0)	18.3 (8.5)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 30 min.	18.6 (7.0)	18.4 (8.0)
HCB + CrO ₃ + H ₂ O ₂ + 10 min. radiation	19.1 (4.5)	19.5 (2.5)
HCB + CrO ₃ + H ₂ SO ₄ + 30 min. radiation	19.4 (3.0)	19.0 (5.0)
HCB + NaOH + 10 min. radiation	19.3 (3.5)	19.4 (3.0)
HCB + NaOH + 30 min. radiation	19.2 (4.0)	19.5 (2.5)
HCB + 1:1 H ₂ SO ₄ /HNO ₃ + 10 min. radiation	19.7 (1.5)	19.5 (2.5)
HCB + 1:1 H ₂ SO ₄ /HNO ₃ + 30 min. radiation	18.4 (8.0)	18.7 (6.5)

The values in brackets represent the average percentage degradation of HCB

TABLE 20 Extent of Degradation of Hexachlorobenzene (HCB) Using Various Catalysts and Microwave Radiation in Water

Run Number	1	2
Solvent Used	Water	Water
Initial [HCB] /(mg/L)	20.0	20.0
Volume of HCB used/mL	20.0	20.0
HCB + CH ₃ ReO ₃ + 30 min. radiation	18.6 (7.0)	18.8 (6.0)
HCB + CH ₃ ReO ₃ + H ₂ O ₂ + 30 min.	18.4 (8.0)	18.2 (9.0)
HCB + CrO ₃ + H ₂ SO ₄ + 30 min. radiation	19.5 (2.5)	19.6 (2.0)
HCB + NaOH + 30 min. radiation	19.5 (2.5)	19.4 (3.0)
HCB + 1:1 H ₂ SO ₄ /HNO ₃ + 30 min. radiation	18.4 (8.0)	18.5 (7.5)
HCB + KMnO ₄ + 30 min. radiation.	19.6 (2.0)	19.4 (3.0)
HCB + K ₂ Cr ₂ O ₇ + 30 min. radiation	19.5 (2.5)	19.2 (4.0)

The values in brackets represent the average percentage degradation of HCB

TABLE 21 Extent of HCB Degradation Using Porphrines and Microwave Radiation

Initial [HCB]/ppm	Volume of HCB solution/ mL	Volume of 30% H ₂ O ₂ used/ mL	Proposed Catalyst (~5mg)	Duration of radiation/ min.	Resulting [HCB] av. /ppm
20.0	5.0	5.0	MTMPP	10	18.8 (6.0)
20.0	5.0	5.0	MTMPP	10	18.2 (9.0)
10.0	5.0	5.0	PCM	10	8.1(19.0)
10.0	5.0	5.0	PCM	10	8.4 (16.0)
10.0	10.0	5.0	H ₂ TPP	10	8.2 (18.0)
10.0	10.0	5.0	H ₂ TPP	10	8.5 (15.0)
10.0	10.0	5.0	H ₂ TPP + NaOH	10	9.0 (10.0)
10.0	10.0	5.0	H ₂ TPP + NaOH	10	9.1 (9.0)
10.0	10.0	5.0	H ₂ TPP + NaOH	30	8.8 (12.0)
10.0	10.0	5.0	H ₂ TPP + NaOH	30	8.5 (15.0)
10.0	10.0	5.0	H ₂ TPP + Conc. HNO ₃	10	8.3 (17.0)
10.0	10.0	5.0	H ₂ TPP + Conc. HNO ₃	10	8.3 (17.0)
10.0	10.0	5.0	H ₂ TPP + Conc. HNO ₃	30	8.2 (18.0)
10.0	10.0	5.0	H ₂ TPP + Conc. HNO ₃	30	8.4 (16.0)

The values in brackets represent the average percentage degradation of HCB.

MTMPP = Meso-tetra(4-N-methylpyridyl)porphrine tetra-iodide

PCM = Phthalocyanine Magnesium

H₂TPP = Tetraphenylporphrine

INSTRUMENTATION

Gas chromatographic analyses were performed using the following:

- (1) Hewlett Packard 5890 gas chromatograph equipped with a ^{63}Ni electron capture detector and a Hewlett Packard 3396A integrator.
- (2) Hewlett Packard 5890 Series II gas chromatograph equipped with a ^{63}Ni electron capture detector, a Hewlett Packard Vectra VL2 4/50 computer and a Hewlett Packard Laser Jet 4 Plus printer.
- (3) Hewlett Packard 6890 Series gas chromatograph with a Hewlett Packard 5973 Mass Selective Detector, a Hewlett Packard Vectra Xm Series 4 5/166 computer and a Hewlett Packard Laser Jet 5 printer.

A fused silica column of dimensions 10 m x 0.53 mm x 2.65mm film thickness (HP-1, methyl silicone gum) was used. The operating conditions were 150°C, 300°C and 200°C for oven, detector and injector temperatures respectively. The flowrate of the carrier gas was 30 mL/min. An Orion Research Expandable ion Analyzer, EA 920 pH meter fitted with a Cole Palmer combination electrode was employed for pH measurements. This was calibrated with standard buffers; 0.025 mol dm⁻³ Na₂HPO₄, 0.025 mol dm⁻³ K₂HPO₄ (pH 6.87) and 0.05 mol dm⁻³ potassium hydrogen phthalate (pH 4.01).

A METTLER TOLEDO AB104 analytical balance and a SARTORIUS top loading balance were used for weight determination. A PYE UNICAM SP3-300 infrared spectrophotometer was used to obtain infrared spectra. Spectrophotometric analyses were also carried out using a Hewlett Packard 8452A Diode Array attached to a Hewlett Packard Vectra ES112 computer and a Think Jet printer.

RESULTS AND DISCUSSION

An extensive amount of UV/VIS analyses were done using Aroclor 1232 and Aroclor 1248 before and after exposing them to degra-

ation reactions. Initially, some indications in the UV spectra were expected but there was no change in the absorbance. The absorbance remained the same before and after the addition of the complex. It could be that the percentage change in the Aroclor concentration did not reflect in the absorbance change in the spectra because the extinction coefficient was very high using ppm concentrations.

Aroclor 1232 and Aroclor 1248 were used in this research project because they have relatively short retention times which are about 8 and 20 minutes respectively under the instrument conditions employed and as a result, more samples were analysed than if Aroclor 1260 was used which has a retention time of about 60 minutes.

Experimental values for the polychlorinated biphenyl (PCB) degradation are tabulated in Tables 1 - 8. The experimental values for the hexachlorobenzene (HCB) degradation are tabulated in Tables 9 - 21. The average error associated with the results is 9.8%. In general, the average percentage decomposition was less than 25% with the percentage degradation ranging from 0.2 - 31% using ppm concentration unit. Based on samples spiked with standard Aroclors, the recovery was found to be 80% and the limit of detection was established using a hexane calibration matrix which was found to be 0.1 ppm. The detection limit is influenced by hydrocarbon matrix and may vary with different hydrocarbons. Calibration curves were used to determine the analyte concentration (Figures 6 and 7).

Acetone/water solvent system (Tables 2 and 3), isopropylalcohol (tables 4-6) and hexane (Table 7) were the solvents in which some amount of degradations of PCBs were observed. For example, Table 1 shows that PCB was degraded by 20.5% using Cr(O₂)₂(en).H₂O + H₂O₂ and an acetone/water solvent system. Also, PCB was degraded by 10.2% using the same catalyst with hexane being the solvent. The degradation of PCB was only slightly higher (13.8%) when [Cr(O₂)₂(dien)].H₂O + H₂O₂ was employed using hexane as the solvent. The results obtained using the acetone/water solvent system was encouraging and as a result, the reaction of PCB was monitored more closely using this solvent system. The greatest degradations of PCB were found to be 20.8% and 13.8% using Cr(O₂)₂(en).H₂O + H₂O₂

and $[\text{Cr}(\text{O}_2)_2(\text{dien})].\text{H}_2\text{O} + \text{H}_2\text{O}_2$ respectively (Table 2). This is consistent with the results obtained in Table 1. A degradation of 20.2% was obtained using $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2(\text{ClO}_4)_4.4\text{H}_2\text{O}] + \text{H}_2\text{O}_2$. In Table 3, the highest average degradations were found to be 31.1% and 22.3% for $\text{Cr}(\text{O}_2)_2(\text{en}).\text{H}_2\text{O} + \text{H}_2\text{O}_2$ and $[\text{Cr}(\text{O}_2)_2(\text{dien})].\text{H}_2\text{O} + \text{H}_2\text{O}_2$ respectively. These are the greatest degradations obtained using acetone/water solvent system. The reaction of PCB with $\text{Cr}(\text{O}_2)_2(\text{en}).\text{H}_2\text{O} + \text{H}_2\text{O}_2$ in acetone/water gave the most successful results in terms of PCB degradation. This could be explained by the fact that the presence of water facilitates the substitution and the electron transfer process involving the chromium complex and the PCB.

The results for the degradations of PCB using isopropylalcohol as solvent were recorded in Tables 4 - 6. These results were also encouraging. The highest average percent degradations were 27.0%, 28.6%, 25.4% and 21.5% for $\text{Cr}(\text{O}_2)_2(\text{en}).\text{H}_2\text{O} + \text{H}_2\text{O}_2$, $[\text{Cr}(\text{O}_2)_2(\text{dien})].\text{H}_2\text{O} + \text{H}_2\text{O}_2$, $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2(\text{ClO}_4)_4.4\text{H}_2\text{O}] + \text{H}_2\text{O}_2$ and $[\text{Cr}_2\text{FeO}(\text{OOC}_4\text{H}_9)_6(\text{C}_5\text{H}_5\text{N})_3]\text{ClO}_4 + \text{H}_2\text{O}_2$ respectively. Table 7 shows that when CH_3ReO_3 and H_2O_2 are added to PCB and stirred for 48 hours, the average PCB degradation is as much as 18%. Also, the average PCB degradation increased to as much as 23.5% when the latter reaction was carried out under reflux. Table 8 shows that the average degradations ranged from 2.0 - 14% with a mean of 7.9%. The highest PCB degradation observed using porphyrines was with tetraphenylporphyrine (H_2TPP) and concentrated nitric acid. Other reactions were tried involving sulfuric acid and nitric acid but the results obtained were different from what were reported in the literature.

The same solvents used in the degradation of PCB along with acetonitrile and dimethylsulfoxide were the solvents in which degradation of HCB was observed (Tables 9-21). For example, the average percentage degradation of HCB in water and acetone/water solvent systems ranged from 1 - 5% (Tables 9 - 11 and Table 13) while 6.5% was observed to be the highest average percent HCB degradation using hexane as solvent (see Table 12). Tables 13 - 14 show that the average percent HCB degradation is less than 5% when isopropylalcohol, acetonitrile and dimethyl

sulfoxide are used as solvents. It should be noted that the duration of stirring/refluxing did not show any consistent trend in degradation of PCBs or HCB (see Tables 7 and 12).

The results obtained from the investigations which involved microwave are shown in Tables 15 - 21. The average percent degradation of HCB using microwave radiation ranged from 1.5 - 13% with non-porphyrine type catalysts and solvents such as hexane, water, acetone/water, isopropylalcohol, acetonitrile, acetone and dimethylsulfoxide (Tables 15 - 20). The highest average HCB degradation observed with porphyrine was 18% using tetraphenylporphyrine (H_2TPP). Meso-tetra(4-N-methylpyridyl)porphyrine tetra-iodide (MTMPP), Phthalocyanine Magnesium (PCM) and Tetraphenylporphyrine (H_2TPP) were employed with and without microwave (Tables 8 and 21). If HCB was degraded using microwave, further investigations would have been done using PCB which is a more complex molecule.

Aroclor^(R) 1232 and Aroclor^(R) 1248 were the sources of PCB used because they are common PCB pollutant mixtures^{14,15} which contain a substantial fraction of environmentally persistent tetra-, penta- and hexachlorinated congeners which are ideal for our research. On the other hand, the more highly chlorinated congeners are more resistant to oxidation. Therefore, simple PCBs were recommended for initial investigations.

Although there are several instances in which chromium in its tetravalent state has been reported¹⁶ to be a substitution labile intermediate in Cr(IV) oxidation, there are relatively few stable complexes of Cr(IV) known. Among the few well characterized complexes of Cr(IV) are diperoxoqua(ethylenediamine)chromium(IV), $\text{Cr}(\text{O}_2)_2(\text{en})(\text{H}_2\text{O})^{(\text{A})}$ and diperoxo(diethylenetriamine)chromium(IV), $\text{Cr}(\text{O}_2)_2(\text{dien})^{(\text{B})}$ and the X-ray structure of the former complex reveals a 7-coordinate pentagonal bipyramid structure. It is known that $\text{Cr}(\text{O}_2)_2(\text{en})(\text{H}_2\text{O})$ undergoes reduction in highly acidic solutions with reductants to give Cr(III) products¹⁶. Since complexes (A) and (B) contain both Cr(IV) and O_2^{2-} ligands, which are capable of reduction as well as oxidation, the redox reactions of the diperoxo derivatives¹⁷ were of interest.

Iron complexes were found¹⁸ to catalyze many

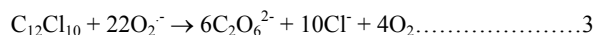
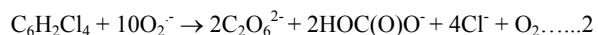
oxidation reaction and as a result $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$, $[\text{Fe}_2\text{O}(\text{phen})_4(\text{CrO}_4^{2-})](\text{ClO}_4)_2$ and $\text{Cr}_2\text{FeO}(\text{OOC}-\text{C}_6\text{H}_5)_6(\text{C}_5\text{H}_5\text{N})_3\text{ClO}_4$ were employed as catalysts. The compounds used as catalysts are shown in Tables 1 - 21. Various solvents were tried but only those in which both the analyte and the catalysts were soluble were employed.

The above iron compounds were added separately to the PCB or HCB solution and stirred and the effect was noted (Tables 1 - 21). Hydrogen peroxide was then added to the PCB or HCB solution containing these compounds in order to see what effect the hydrogen peroxide had on the rate of decomposition. No significant degradation was observed. According to Vassell and Espenson¹⁹, a family of organic sulfides was oxidized to the corresponding sulfoxides by hydrogen peroxide and these reactions were very slow and commercially meaningless without an effective catalyst. The oxidation was successfully catalysed by methylrhenium trioxide (CH_3ReO_3). Therefore, methylrhenium trioxide was employed in this research project. Unlike the above compounds, CH_3ReO_3 is stable far above its melting point (106°C). It is soluble in water as well as organic solvents. However, no significant degradation was observed with the addition of CH_3ReO_3 irrespective of various solvents.

Hexachlorobenzene which has one benzene ring and is saturated with six chlorine atoms, was employed in this research project because it is a relatively simple molecule to work with compare to PCB. If favourable results were obtained, then the same degradation procedure would have been applied to PCB.

Although primary and secondary haloalkanes and polychloroethenes are readily oxidized by superoxide ion (O_2^-) in aprotic media, chlorobenzene and monohalogenated aromatic hydrocarbons do not react at significant rates. This has prompted the belief that all halogenated aromatic hydrocarbons are unreactive. However, Sawyer¹⁹ reported that hexachlorobenzene, pentachlorobenzene, tetrachlorobenzene and trichlorobenzene as well as decachlorobenzene and other "heavy" polychlorobiphenyls (PCBs) are rapidly oxygenated by O_2^- in dimethylformamide, acetonitrile or dimethyl sulfoxide. The extent of the reactions for electrogenerated O_2^- and $(\text{Me}_4\text{N})\text{O}_2$ with poly-

chloro aromatics was determined by cyclic voltammetric assay of O_2^- concentrations and their decrease in the presence of excess polychloroaromatic substrates. Within the limits of a reaction time of 60 min or less, chlorobenzene and dichlorobenzene were not oxidized. Although the trichlorobenzenes reacted, the rates were too slow to ascertain the stoichiometries and the products. Sawyer¹⁹ also reported that although the substrates were degraded by O_2^- in acetonitrile and dimethyl sulfoxide, the rates of reaction were about one-tenth as great in MeOH and 20 times slower in Me_2SO . A reasonable initial step for these oxygenations was nucleophilic addition of O_2^- to the polyhalobenzene. Subsequent loss of chloride ion gave a benzoperoxy radical, which was reduced by a second O_2^- to form a peroxo nucleophile that could attack the adjacent carbocloro center with displacement of its chloride and apparent formation of an orthoquinone. The latter undergoes facile reactions with O_2^- to give peroxy dicarbonate ($\text{C}_2\text{O}_6^{2-}$) and chloride ions. The $\text{C}_2\text{O}_6^{2-}$ ions were hydrolysed by water to $\text{HOC}(\text{O})\text{O}^-$ and O_2 . When Aroclor 1268 (a commercial PCB fraction that contains a mixture of Cl_7 , Cl_8 , Cl_9 and Cl_{10} polychlorobiphenyls) was combined with excess O_2^- , the entire mixture was degraded. Samples taken during the course of the reaction confirmed that (a) the most heavily chlorinated members reacted first (the initial nucleophilic addition was the rate determining step) and (b) all components were completely dehalogenated as shown by the equations below.



Tests with other PCB mixtures established that those components with three or more chlorine atoms per phenyl ring were completely degraded by O_2^- within several hours. Even though Sawyer's¹⁹ attempt was successful in degrading PCBs, it was not economically viable and so we tried to generate O_2^- by non-electrochemical methods. No significant degradation was observed.

CONCLUSIONS AND RECOMMENDATIONS

The average percentage decomposition of PCB using Chromium(IV) complexes, iron-phenanthroline complexes and methylrhenium trioxide was less than 25% with the percentage degradation ranging from 0.2 - 31% using ppm concentration unit. The reactions were allowed to go to completion in a manner similar to a 'continuous process'. However, if an equilibrium exists, it is necessary to disrupt this equilibrium in order to increase the degradation of PCB. Also, at equilibrium, the presence of some degraded PCB can poison the catalyst causing it to be ineffective.

The existence of an equilibrium can be verified by doing product analysis. The starting material (PCB) and the catalyst should be removed and fed back into the reaction vessel in a manner similar to a 'batch process'. In so doing, a high degradation rate can be achieved. A pilot plant could be established and its efficiency determined. This recycling procedure could be found useful in remediation of highly contaminated soil.

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