

Degradation of Polychlorinated Biphenyls (PCBs) in Water Matrix Using UV/H₂O₂: Effect of Initial PCB Concentration and Analysis of Reaction Products

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This study investigated the effect of the different initial concentrations of polychlorinated biphenyls (PCBs) on its degradation in water matrix using UV/H₂O₂ and on the formation of reaction intermediates or products. Simulated PCB-contaminated water solution was subjected to irradiation with 17 W, 254 nm wavelength UV lamp in a batch tubular reactor. The ratio of oxidant to PCBs, in terms of Aroclor 1260, was based on 2,800 µL H₂O₂ is to 40 ppm PCB. Samples were extracted from the matrix by solid-phase extraction (SPE) method using C18 cartridges with hexane and ethyl acetate as solvents. The samples were analyzed using Gas Chromatography-Electron Capture Detector System (GC-ECD) to determine the concentration of PCBs in the samples and pH was monitored every sampling time. The analysis of chloride (Cl⁻) ion concentration in the samples was done using Argentometric titration. Determination of reaction intermediates and products was carried out with 40 ppm PCB concentration using Gas Chromatography-Mass Spectroscopy (GC-MS) system. A decrease in pH in the early stages of degradation was observed and the higher the initial concentration of PCB the greater was the drop in pH. The PCB degradation profile showed that from 1 to 40 ppm initial concentration, the degradation efficiency of UV/H₂O₂ increased with increasing initial PCB concentration. At 80 ppm, however, it was observed that there was a decrease in the efficiency of the system. The inorganic chloride ions produced indicate that dechlorination took place in the system. GC-MS analysis verified the decrease in concentration of PCBs in the solution and showed the preferential attack of the UV/H₂O₂ to PCBs over long chain saturated alkanes or waxes which contained the PCBs.

Keywords: Advanced oxidation processes (AOPs), GC-MS, hydroxyl radicals, polychlorinated biphenyls (PCBs), and UV/H₂O₂.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are mixtures of chlorinated derivatives of biphenyl with different structures depending on the number

and position of chlorine atoms on the biphenyl skeleton. They were widely used as electrical insulation and heat exchange fluids because of their chemical and thermal stability. However, prior to cessation of PCB production, evidence

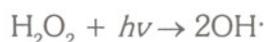
showed that the very properties that made these compounds industrially significant are also those that made them toxic and persistent organic pollutants.

Incineration is a standard method for the bulk destruction of PCBs. However, since these compounds are poor combustibles and that the formation of toxic by-products is a concrete possibility, incineration becomes an unattractive technology for PCB destruction. Thus, several non-burn treatment technologies were reviewed and considered as potential treatment options for PCBs (Centeno et al. 2003)

In the past decade, there has been considerable research on and commercial interest in the use of advanced oxidation processes (AOPs) for the treatment of organic contaminants in aqueous, gaseous, and solid phases. AOPs are typically characterized by the generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$) which are the principal agents responsible for the oxidation of numerous pollutants (Jardim et al. 1997).

THEORY

Among the AOPs, the UV/H₂O₂ system is considered the simplest in terms of mechanism, design, operation, and maintenance. It involves the production of $\text{OH}\cdot$ from the cleavage of O-O bond in hydrogen peroxide according to the following reaction:



The system has been proven effective in the degradation of various organic compounds in aqueous solutions such as 1,3,5-trinitrotriazaxyclohexane (RDX) (Bose et al. 1998), trichlorophenols (Hugul et al. 2000), n-methyl-p-aminophenol (Andreozzi et al. 1999), tetrachloroethylene (Alibegic et al. 2001), and p-chlorophenol (Ghaly et al. 2001).

The initial concentration of the solution being irradiated has a significant effect on the rate of pollutant degradation as well as on the kind and concentration of intermediates formed during reaction. Alnaizy and Akgerman (2000) reported that as the initial concentration of phenol is increased, the efficiency of the UV/H₂O₂ system

decreased. They further reported that p-benzoquinone was detected in all of their experimental runs except in those that were performed at low phenol concentrations. This indicates that initial pollutant concentration may be a factor in the mechanism of the reaction. The study by Wang et al. (2000) on the degradation of humic acids cited that, at a fixed concentration of hydrogen peroxide, increase in humic acid concentration decreases the rate of degradation. Wang et al. (2001) further elucidated that the higher the initial concentration of humic acid, the greater would be the competition between the H₂O₂ peroxide and the acid itself for the photons generated during irradiation. Thus, the major mechanism for humic acid degradation in this study was basically photolysis.

Start-up experimentations were conducted relative to this study wherein selected AOPs were applied for PCB degradation (Centeno et al. 2003). The UV/H₂O₂ peroxide system was chosen for its efficiency in degrading PCBs and ease of operation. Thus, this phase of the research was conducted to determine the effects of initial PCB concentration on the degradation of the compound and to determine the reaction intermediates and products of the degradation process.

EXPERIMENT

Reactor configuration

Batch experiments were carried out in a tubular photoreactor fitted with a 17 W Hg lamp (Sterilight, Canada) that emitted UV light at 254 nm intensity and had been encased in a quartz sleeve and jacketed with stainless steel. The UV lamp was positioned at the axial center of the reactor. A schematic representation of the reactor used in this study is illustrated in Figure 1.

The reactor had an effective volume of 1 liter. It was equipped with a recirculation pump (55–60 Hz, 0.25 HP) to facilitate the continuous mixing of the solution. Because the light source produced heat, the reactor was installed with a thermocouple to monitor temperature change. Ports had been provided for feeding the sample solution and withdrawing the samples for analysis.

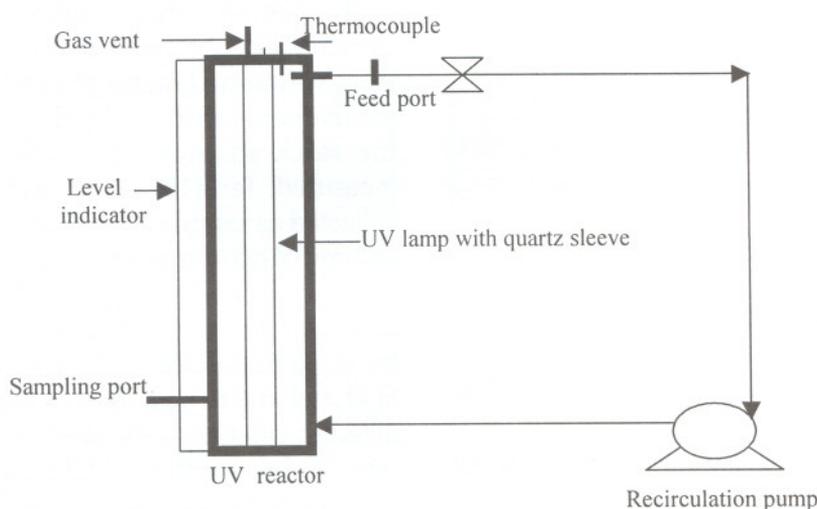


Figure 1. Schematic of Tubular Photoreactor

Materials and reagents

For the experimental runs, PCB stock solution was prepared using the PCB oil mixture obtained from an old transformer unit inside Clark Special Economic Zone. The oxidant used was a 30%-stabilized H_2O_2 solution (Riedel-de Haën, Germany). The pH of the solution was monitored every sampling time using a plastic electrode attached to a pH meter (Model 420, Thermo Orion, USA). Aroclor 1260 standard solution (Restek, USA) was used as basis in quantifying PCB concentration in the samples.

Extraction of the samples from the water matrix prior to analysis was done applying the Solid-Phase Extraction (SPE) Method. For this method, C18 cartridges (Varian, the Netherlands) were used as extracting media. Pesticide grade hexane, methanol, and ethyl acetate (Burdick & Jackson, USA) were used as solvents.

Instrumentations

The analysis of PCB concentration in the sample was done using Shimadzu GC 14B (Shimadzu, Japan) equipped with Electron Capture Detector (ECD). The gas chromatograph was installed with DB-5MS column (J&W Scientific, USA) with the following specifications: 30-m length, 0.25-mm inside diameter, and 0.25- μ m film thickness. The samples were injected using liquid tight glass syringe (Hamilton Model 701RN, USA), with Ultra High Purity (99.999% pure) Nitrogen (CIGI, Philippines) as carrier gas.

Shimadzu C-R7A plus integrator was used for data acquisition. The integrator was equipped with a system disk capable of storage, retrieval, and reprocessing of chromatographic data. The chromatographic conditions used for the analysis of samples were as follows:

- injector and detector temperature: 300°C;
- column oven temperature programming: 180°C initial temperature, step up to 260°C at 4°C/min, and
- step up to final temperature of 280°C at 10°C and the column was held at final temperature for 12 min.

Total analysis time was 34 minutes. The samples were injected in split mode. Split ratio was adjusted based on the expected lowest concentration to be analyzed. Column head pressure was set at 20 psig, which translates to column flow rate of approximately 3–5 ml/minute of carrier gas.

GC-MS analysis was carried out in Clarus500 GC-MS system (PerkinElmer, USA) equipped with an auto-injector and installed with DB-5MS (J&W Scientific, USA) with the following specifications: 30-m length, 0.25-mm inside diameter, and 0.25- μ m film thickness. High Purity Helium (CIGI, Philippines) was used as carrier gas. The samples obtained from 40 ppm initial concentration experimental run were subjected to GC-MS analysis. After collecting an untreated initial sample, the subsequent samples were drawn off after 30, 60, 120, and 180 min of

irradiation. Chromatographic conditions for GC-MS analysis are as follows:

- injector and detector temperature: 300°C;
- column oven temperature programming: 60°C initial temperature, step up to 80°C at 5°C/min, and
- step up to final temperature of 280°C at 12°C/min and the column was held at final temperature for 12 min.

Total analysis time was 32.67 min. The samples of 3 μ L volume were injected to the GC using an auto-injector in a splitless mode injector port. The mass spectra of each peak were matched using MS library to determine the compounds represented.

The chloride ion concentration in the samples was determined by Argentometric Method. In this method, the chloride ions present in the samples are titrated with silver nitrate solution. Potassium chromate was used to indicate the endpoint of titration. The pH of the sample should be between 7 to 10. Necessary adjustment was done using NaOH or H₂SO₄.

Preparation of stock solution and experimental run

The feed solution was prepared by spiking a definite volume of PCB oil mixture dissolved in methanol to 2 liters of distilled water according

to the desired concentration. The solution was stirred overnight under the fume hood. The UV lamp was turned on for about 10 min to stabilize the temperature inside the reactor. While stirring the stock solution, the initial pH was being measured. Ten (10) ml of the stock solution was collected as sample for $t=0$ min. The appropriate volume of hydrogen peroxide was spiked into the stock solution. The volume of H₂O₂ added was based on the optimum oxidant concentration in the study conducted by Centeno et al. (2004). The H₂O₂ volume to be added to the stock solution at different initial concentrations was determined by ratio and proportion. The samples for pH and PCB degradation were withdrawn from the reactor's sampling port every 15 min for 3 h. The samples for GC-MS analysis were drawn off after 30, 60, 120, and 180 min.

RESULTS AND DISCUSSIONS

Effect of initial PCB concentration

The results of the degradation of PCBs at different initial concentrations are shown in Figures 2 and 3. In all the initial PCB concentrations used, a decrease in the pH of the solution was observed as can be seen in Figure 2.

However, it may be observed that at a higher concentration, there would be a greater decrease in pH and this acidic range (about pH= 3.5) was

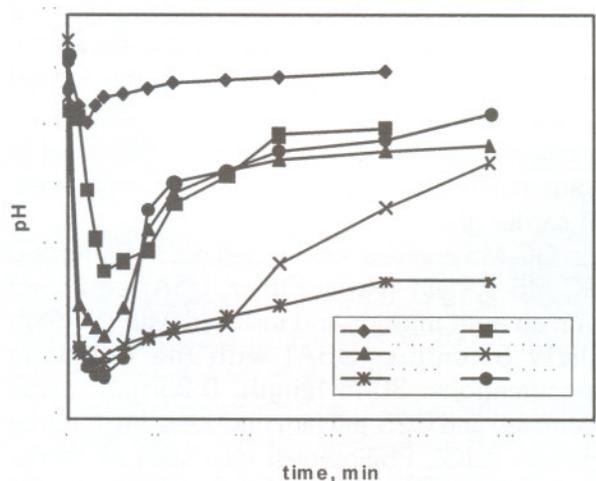


Figure 2. Change in pH Over Time at Different Initial PCB Concentrations
 $[pH_{soln} = 5.8-6.2; T_{reactor} = 28-33^{\circ}C; [H_2O_2]$
 based on 24.71 mM at 40 ppm]

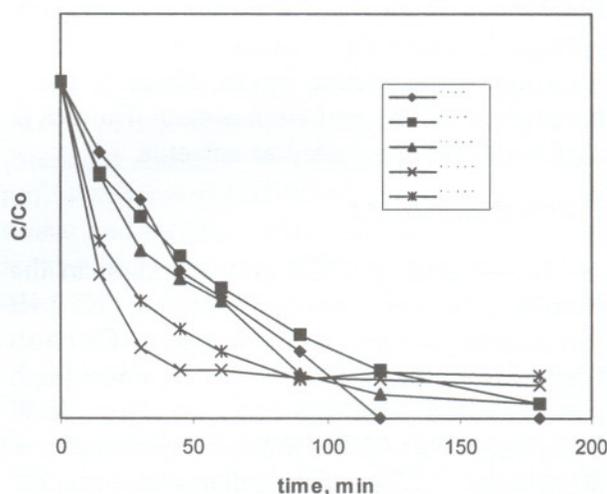


Figure 3. Concentration Profile at Different Initial PCB Concentrations
 $[pH_{soln} = 5.8-6.2; T_{reactor} = 28-33^{\circ}C [H_2O_2]$
 based on 24.71 mM at 40 ppm]

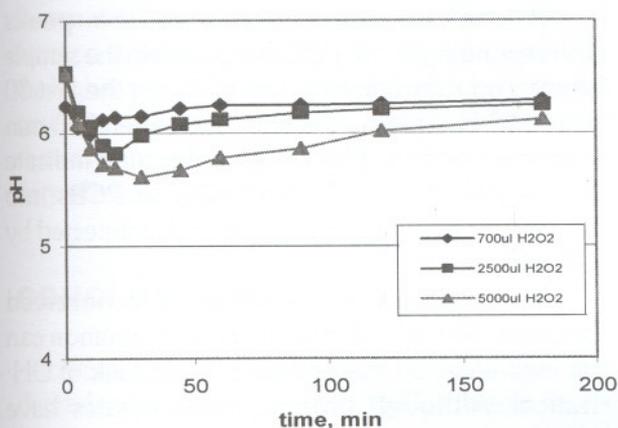


Figure 4. pH Profile of H_2O_2 Photolysis at Different Concentrations
 $[pH_{soln} = 6.2-6.5; T_{reactor} = 28-33^\circ C]$

seen longer during the reaction time than those at lower concentration runs. While there initially was a decrease in pH for the low concentration runs, this was immediately followed by an increase in pH. Again, this behavior may be explained by the possible dechlorination that occurred in the solution and that at higher concentration more Cl^- ions may have detached from the parent compound. Also, a greater concentration of acidic species may be obtained when a higher PCB concentration was used. The subsequent increase in pH may be explained either by the possible formation of intermediates or by the decrease in Cl^- ion concentration in the solution.

Since pollutants in the solutions were understood to play a dual role as UV light photon absorber and OH^\cdot scavenger, the higher the initial concentration, the lower would be the amount degraded. However, this was not quite consistent with the results presented in Figure 3. Percentage PCB degradation was observed to increase with increasing concentration.

The highest degradation efficiency of 86% after 60 min was obtained at a PCB concentration of 40 ppm. A plausible explanation for this would be the role of the intermediates in the reaction. It is possible that the fast formation of reaction intermediates occurred when low initial concentrations were used that the reaction favors the degradation of these intermediates rather than the parent compound.

A similar observation was reported by Wang et al. (2000) on the degradation of humic acids.

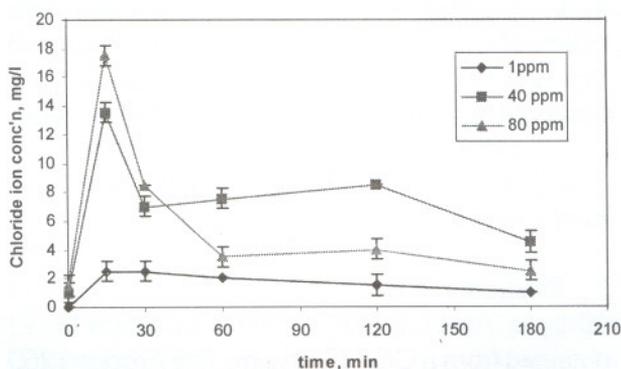


Figure 5. Chloride Ion (Cl^-) Concentration vs Time
 $[pH_{soln} = 5.8-6.2; T_{reactor} = 28-33^\circ C]$

Decrease in degradation efficiency, however, was observed at 80 ppm which gave a lower degradation efficiency of 79% after 60 min of reaction. The high initial concentration may have caused the inhibition of OH^\cdot formation, thus giving a slightly lower degradation efficiency than the 40 ppm run. Higher PCB concentration could compete with H_2O_2 for more UV light photons and thus reduce the light absorption of H_2O_2 to a greater degree. In this case, the primary mechanism at 80 ppm could be photolysis, which is a much slower reaction than the reaction with hydroxyl radicals.

To illustrate that the decrease in pH is indicative of the chemical degradation of PCBs and not of the decomposition of H_2O_2 , a blank run was carried out using H_2O_2 only. This was to determine the behavior of H_2O_2 during photolysis and the amount of residual H_2O_2 in the reactor at each sampling time. Different concentrations of H_2O_2 were used for this experiment. Figure 4 shows the change in pH vs. time during the photolysis of 700, 2500, and 5000 ul hydrogen peroxide. From the results of the experimental runs, it was observed that there was a slight decrease in the pH of the solution during the first few minutes of the run. This decrease in pH, however, was not significant enough to say that the drastic decrease in pH during the previous runs was due to H_2O_2 alone. In these previous runs, the pH of the solution decreased to about 3, which indicated that the decomposition of PCBs was responsible for the said reaction.

Chloride ion concentrations were monitored for 1, 40, and 80 ppm initial PCB concentrations. The results shown in Figure 5 demonstrate that

the highest chloride concentrations were detected during the first few minutes of the reaction. This observation agrees with the results shown in Figure 2, wherein the highest drop in pH was observed during the early stages of the reaction.

Analysis of reaction intermediates and products by GC-MS

Illustrated in Figure 6 is the chromatogram of 40 ppm Aroclor 1260 (dilution factor = 2) obtained from a GC-MS system. The Aroclor 1260 mixture is shown to contain pentachlorobiphenyls, hexachlorobiphenyls, heptachlorobiphenyls, and octachlorobiphenyls, with hexachlorobiphenyls and heptachlorobiphenyls as predominant congeners.

The mass spectra and specific congener structure of the six most prominent peaks used for the quantitative determination of the concentration of PCBs in the samples in terms of Aroclor 1260 are all shown in Figure 6.

The degradation profile for 40 ppm initial PCB concentration obtained by GC-MS analysis is shown in Figure 7. It can be seen that the peaks representing the PCBs in the samples have been eluted out and detected much later than the long chain alkanes, which are commonly waxes used to dissolve PCBs in the transformer oil mixture. This is due to higher molecular weight of PCBs compared to those of waxes.

It can be seen also that the peaks corresponding to the PCB congeners in the sample decreased dramatically in size during the first 30 min and has almost disappeared after 180 min into the reaction. This observation may indicate the degradation and conversion of PCBs into inorganic products, which cannot be detected by GC-MS.

No organic intermediates were observed between 30 and 120 min. This phenomenon can be explained by the non-selective attack of OH· radical. Although organic intermediates have been reported in some literatures (Hirvonen et al. 1996, Hugul et al. 2000), these species are *meta-stable*, or those that would occur only for a few seconds. Since OH· radical is known to be very reactive and indiscriminately attacks organic compounds in aqueous solutions, the degradation of PCBs and of organic intermediates occur almost simultaneously.

The UV/H₂O₂ system has preferential reaction to PCBs over long-chain saturated alkanes or waxes, which are represented by the early eluting peaks in the chromatogram in Figure 7. These peaks matched with decane (10 hydrocarbon chain), dodecane (12 hydrocarbon chain), heptadecane (17 hydrocarbon chain), and eicosane (20 hydrocarbon chain) in the MS library. Wahab et al. (1999) reported that PCB transformer oils are either *paraffinic* (long-chain saturated aliphatic hydrocarbons) or *naphthenic*

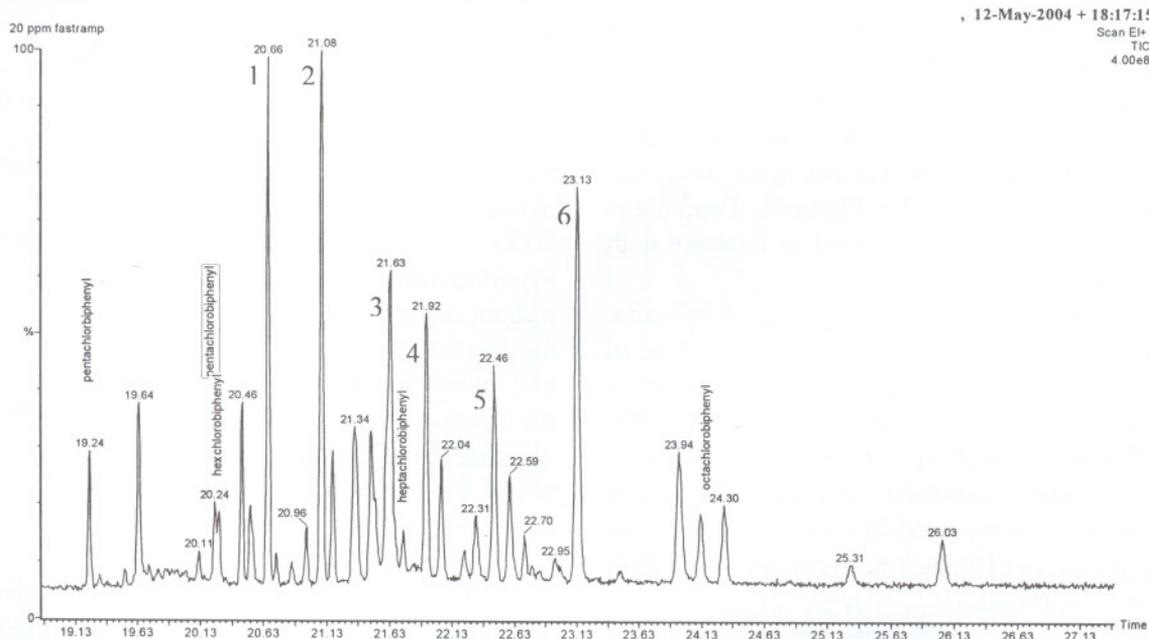


Figure 6. Chromatogram of Aroclor 1260 Showing Six Prominent Peaks

(aromatic hydrocarbons) based. The favored reaction towards PCBs may be brought about by the higher stability of long-chained saturated alkanes or waxes compared to PCBs. This observation also shows the possibility that PCBs in oil matrix can be degraded using the UV/H₂O₂ system.

CONCLUSIONS

From 1 to 40 ppm initial concentration, the degradation efficiency of UV/H₂O₂ towards PCBs (as Aroclor 1260) increases as the initial concentration increases. At 80 ppm, efficiency begins to drop due to the inhibition of high pollutant concentration to the H₂O₂ absorption of UV photon to form OH· radicals.

The decrease in pH at the early stages of the treatment from is attributed to the dechlorination of PCBs that produce inorganic chloride ions. The reaction intermediates may have formed but have not been detected by GC-MS from 30 to 120 min of the treatment. UV/H₂O₂ process has preferential degradation reaction to PCBs over long-chained saturated hydrocarbons present in the samples.

For future studies, it is worthwhile to consider a longer reaction time for the process to observe further formation of intermediates. It is recommended to conduct a study on the degradation of PCBs using a specific congener to determine the mechanism of degradation.

ACKNOWLEDGMENT

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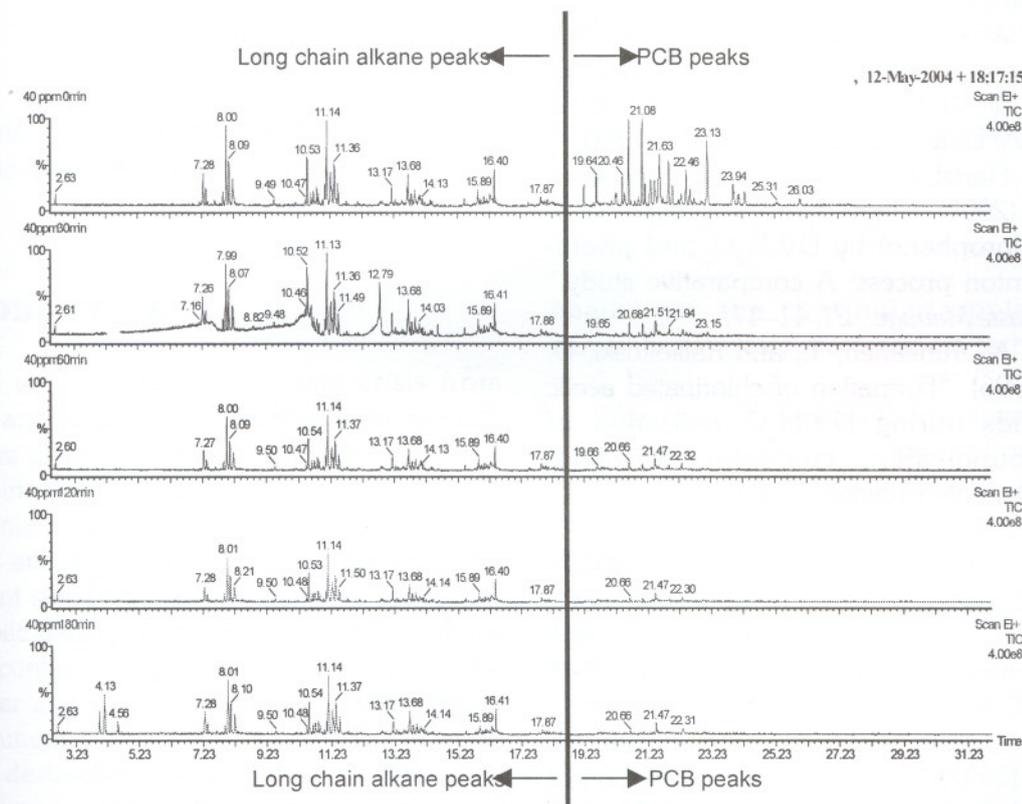


Figure 7. GC-MS Analysis Showing Preferential Reaction of the UV/H₂O₂ Process to PCBs over Alkanes/Waxes Containing PCBs

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