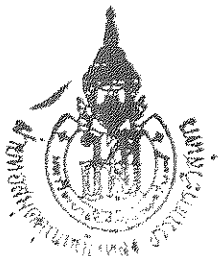

Trace Analysis of PCBs Residue in Water by Gas Chromatography – Mass Spectrometry

Pensiri Srichana

Master of Science Thesis in Analytical Chemistry

Prince of Songkla University

2002

Thesis Title	Trace Analysis of PCBs Residue in Water by Gas Chromatography – Mass Spectrometry
Author	Mrs. Pensiri Srichana
Major Prgram	Analytical Chemistry

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The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment for the Master of Science degree in Analytical Chemistry.

.....

(Piti Trisdikoon, Ph. D.)

Associate Professor and Dean Graduate School

ชื่อวิทยานิพนธ์	การวิเคราะห์สารประกอบพีซีบีที่ตกค้างปริมาณน้อยในน้ำ โดยเทคนิคแก๊สโครมาโตกราฟี – แมสสเปกโตรเมทรี
ผู้เขียน	นางเพ็ญศิริ ศรีชนะ
สาขาวิชา	เคมีวิเคราะห์
ปีการศึกษา	2545

บทคัดย่อ

การวิเคราะห์เชิงคุณภาพและปริมาณของสารพีซีบี 3 คอนจีเนอร์ (พีซีบี138 พีซีบี153 และพีซีบี180) ปริมาณน้อยที่ตกค้างในน้ำ โดยเทคนิคแก๊สโครมาโตกราฟี-แมสสเปกโตรเมทรีที่ใช้คาปิลลารีคอลัมน์ชนิดเอชพี-5เอ็มเอส (HP-5MS) ยาว 30 เมตร ขนาดเส้นผ่าศูนย์กลาง 0.25 มิลลิเมตร และความหนาของฟิลม์ 0.25 ไมโครเมตร ร่วมกับตัวตรวจวัดชนิดแมส ซีเล็กทีฟ (Mass Selective Detector) จากการศึกษาพบว่าสภาวะการทดลองที่เหมาะสม ได้แก่ อัตราการไหลของแก๊สพา (ฮีเลียม) 0.8 มิลลิลิตรต่อนาที อุณหภูมิคอลัมน์ ทำโปรแกรมโดยมีอุณหภูมิเริ่มต้น 130 องศาเซลเซียส เป็นเวลานาน 2 นาที จากนั้นเพิ่มอุณหภูมิด้วยอัตรา 40 องศาเซลเซียสต่อนาทีจนถึงอุณหภูมิ 250 องศาเซลเซียส แล้วเพิ่มอุณหภูมิต่อทันทีด้วยอัตรา 25 องศาเซลเซียสต่อนาทีไปจนถึงอุณหภูมิ 300 องศาเซลเซียส อยู่ที่อุณหภูมิสุดท้าย 10 นาที สำหรับอุณหภูมิหัวฉีด อุณหภูมิทรานเฟอร์ไลน์ (Transfer line) อุณหภูมิแหล่งกำเนิดอิเล็กตรอน (MS Source) และอุณหภูมิควอดรุโพล (MS Quadrupole) ที่เหมาะสม เท่ากับ 230, 290, 150 และ 230 องศาเซลเซียส ตามลำดับ จากสภาวะดังกล่าวทำให้ได้ขีดจำกัดต่ำสุดของการตรวจวัดสารพีซีบีทั้งสามคอนจีเนอร์คือ พีซีบี138 พีซีบี153 และพีซีบี180 อยู่ในช่วง 60 ถึง 70 นาโนกรัมต่อลิตร โดยมีช่วงความเป็นเส้นตรง 60 นาโนกรัมต่อลิตรถึง 1 มิลลิกรัมต่อลิตร ได้ศึกษาเทคนิคการเตรียมตัวอย่างที่เหมาะสมสำหรับการวิเคราะห์สารพีซีบีที่มีปริมาณที่ต่ำกว่าขีดจำกัดต่ำสุด พบว่าตัวอย่างต้องผ่านอุปกรณ์กรองที่ประดิษฐ์ขึ้นในห้องปฏิบัติการ ก่อนไปเพิ่มความเข้มข้นโดยเทคนิคการสกัดด้วยตัวดูดซับของแข็ง

ชนิดแบบแผ่นสกัด (C_{18} Empore Extraction Disk) โดยใช้ตัวชะที่เหมาะสมคือ ไดคลอโรมีเทน (Dichloromethane) 10.0 มิลลิลิตร ค่าเปอร์เซ็นต์การได้กลับคืนของสารพีซีบีทั้งสามคอนจีเนอร์อยู่ในช่วง 83-112 เปอร์เซ็นต์ ค่าเบี่ยงเบนมาตรฐานสัมพัทธ์ต่ำกว่า 4 เปอร์เซ็นต์ ในการทดลองได้กำจัดสารรบกวนอื่นๆ ได้แก่ กลุ่มสารพทาเลต (Phthlate compounds) ที่มาจากภาชนะบรรจุด้วยกรดซัลฟุริกก่อนทำการวิเคราะห์

ผลการวิเคราะห์ปริมาณสารประกอบพีซีบีที่ตกค้างในน้ำบ่อ ในพื้นที่บริเวณใกล้เคียงบ่อบำบัดน้ำเสียและหลุมฝังกลบขยะ เทศบาลเมือง จังหวัดสงขลา โดยเทคนิคแก๊สโครมาโตกราฟี-แมสสเปกโตรเมทรี ร่วมกับเทคนิคการสกัดด้วยตัวดูดซับของแข็งด้วยสภาวะการทดลองดังกล่าวข้างต้นพบว่าทุกพื้นที่มีการปนเปื้อนและตกค้างของสารพีซีบีทั้งสามคอนจีเนอร์อยู่ในช่วง 0.11-0.67 นาโนกรัมต่อลิตร จากผลการศึกษานี้สามารถจะนำมาเป็นเทคนิคที่มีความไวและจำเพาะเจาะจง รวมถึงประยุกต์ใช้สำหรับการตรวจวัดหาสารพีซีบีที่ตกค้างในตัวอย่างน้ำต่างๆได้อย่างรวดเร็ว (13 นาที) และประหยัดค่าใช้จ่าย

Thesis Title	Trace Analysis of PCBs Residue in Water by Gas Chromatography – Mass Spectrometry
Author	Mrs. Pensiri Srichana
Major Prgram	Analytical Chemistry
Academic Year	2002

Abstract

A qualitative and quantitative analysis of 3 PCBs congeners (PCB138, PCB153 and PCB180) residues in water by gas chromatography-mass spectrometry equipped with a 30 m. x 0.25 mm. x 0.25 μm. HP-5MS capillary column and a mass selective detector was conducted. From this study, optimum conditions were obtained, i.e. the carrier gas (Helium) flow rate at 0.8 ml/min; the column temperature programming at 130°C as the initial temperature held for 2 minutes, ramped at 40°C/min to 250°C and then continuously ramped at 25°C/min to 300°C and at the final temperature for 10 minutes. For the optimum injector, transfer line, MS source and MS quadrupole temperatures were 230°C, 290°C, 150°C and 230°C respectively. The system at optimum conditions showed a limit of detection of 3 PCBs congeners (PCB138, PCB153 and PCB180) in the range of 60-70 ng/l and a linear dynamic range of 60 ng/l to 1 mg/l. The water sample was filtered through the lab built prefiltration unit before being preconcentrated by Solid-Phase Extraction technique using a C_{18} Empore Extraction Disk. The suitable eluent was 10.0 ml of dichloromethane which provided high recovery in the range of 83-112% and high precision (%RSD < 4). The phthalate compounds from container interfered the analysis were eliminated by sulfuric acid.

Based on this study, trace analysis of PCBs residues from two sampling well water, which were collected from wells near the wastewater treatment pond and landfill of Songkhla municipally, showed all areas had been contaminated with three PCBs congeners in the range of 0.11-0.67 ng/l. According to observations, this method could be a sensitive and selective technique for rapid and economical analysis of PCBs at a trace level in water samples (13 min).

Acknowledgements

The completion of this thesis would be quite impossible without the help of many people, whom I would like to thank.

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And lastly, my friends in Analytical & Environmental Chemistry / Trace Analysis Research Unit and Biophysics Research Unit: Biosensors & Biocurrents who help in many ways.

Pensiri Srichana

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Chapter 1

INTRODUCTION

1.1 Introduction

Over the last two decades, the most serious of all environmental problems and poses a major threat to health and well being of human and global ecosystems has been widespread environmental occurrence. There are many toxic substances increased the environmental problems, including the carcinogenesis potential. The main concerns are Polychlorinated biphenyls (PCBs) that are toxic and persistence in the environment. Therefore it is necessary to understand the route of exposure in trace level of these compounds to environment such as air, soil, sediment, and water etc. and the analytical and environment chemists have been interesting in these compounds for more than twenty years (Erickson, 1997).

During 1994-1996, the Division of Food, Department of Medical Science (Thailand) reported that the contaminant in the import-export products for consumable in Thailand; a total of 1,503 samples had been contaminated by the chlorinated compounds including PCBs. Of these 703 samples were vegetables and fruits and 158 samples were meats. These were probably caused by the use of pesticides and herbicides to improve the product yields that could release the PCBs contaminant into a food chain (Thoopehom, 1998).

PCBs are a class of 209 discrete chemical compounds, called congeners, in which one to ten chlorine atoms are attached to a biphenyl nucleus. These compounds were first commercially produced in 1929 as a complex mixture for various uses including dielectric fluids in capacitors, heat transformer fluid, hydraulic fluid, lubricating and cutting oil, and as an additive in pesticides, paints, copying paper, carbonless copy paper, adhesives, sealant, plastics and many more. The PCBs were known under the trade name Aroclor® from 1930 to 1977 by the Monsanto Company. PCBs were most used in the industries due to their excellent chemical and physical stability included their electrical insulating properties. The open-ended applications such as ink inherently resulted in widespread, low level release to environmental compartments. In addition, the closed and controlled used such as dielectrics within electric equipment could be in environmental release because of spills, improper handling, or improper disposal. Most such releases tend to contaminate locally landfills, or elsewhere and can often result in relatively high, localized concentrations (Erickson, 1997). The Electrical and Electronics Institute of Thailand reported that the total imported electrical and electronics products during 1996-1998 were more than 700,000 units (The Electrical and Electronics Institute, 1999). As the quantity of electric equipment usage relates to the usage of PCBs, therefore, the increasing quantity of PCBs will be found in the environment.

Under these misused and mismanagement, PCBs have entered the environment through both legal and illegal use and disposal thus, the environment i.e. water, air, and soil, could be contaminated by PCBs. The PCBs are persistent and lipopillic, do not easily decompose or dissemination in the environment after disposal and tend to bioaccumulate in the biota.

Recently, the interest in analytical methods for analysis trace amount of PCBs in water are one of the most concerning for the environmental issue. Because PCBs were either directly or indirectly introduced into all environmental compartments and the water as a one source could run off from the agriculture and industrial sites, and transport from the atmosphere into surface water which is the source for drinking water. So it is possible to observe PCBs in the human (e.g. fat tissues and breast milk) after consumed the contaminated water.

The European Union 76/464/CEE Directive and the United State Environmental Protection Agency (U.S. EPA) have listed PCBs as toxic and persistent pollutants and set the maximum permissible levels in surface water. The practical limit of quantitation (LOQ) of PCBs was defined as 10 $\mu g/m^3$ per resolvable gas chromatography peak for air, 100 µg/l per resolvable gas chromatography peak for water and 2 µg/g per resolvable gas chromatography peak for any product and waste (Erickson, 1997). In Europe, member states were encouraged to comply with Directive 76/464/CCE regarding dangerous substances discharged into surface water. This Directive, also knew as the EU Black list, considered PCBs be a one of 22 different chemical classed of pollutants which followed the general parameters of toxicity, persistence, and input and therefore were to be removed from community waters and discharges (Lacorte *et al.*, 2000).

In contrast, the Thai government has not realized the toxicity problem of PCBs contaminated in water resources. No regulation has been implemented (since 1992) to include the PCBs into the law section 32(1) of the Enhancement and Conservation of National Environmental Quality Act BE.2535, 1992 (Water Quality Management Division, 1997). Therefore, Thai people could be at risk from PCBs residue in water since their toxicity can have undesirable effects on human and ecosystem.

Songkhla is a province where many communities are expanding at high rate as a result from several developing projects between the cities of Hat Yai and Songkhla. The industries in these areas are growing rapidly and continually, therefore, all towns and municipalities have several major sources of water pollution. In many public water systems, pollution exceeds safe levels and these were caused by industrial, agricultural, and human activities, accidental spill, and waste discharges. Most manufacturing facilities used huge quantities of freshwater to carry their waste discharge to the environment. The waste-bearing water, or effluent, was discharged into streams, lakes, or oceans, which in turn disperse the pollutants. The contaminant release into the water and food chains would include the PCBs.

PCBs have been measured in most environmental analytical laboratories in a variety of matrices and have been one of the most studied groups of organic contaminants for a period of time. The analytical method for trace level of PCBs residue in environment samples has been challenging for analytical and environmental chemists for many years. The investigation and monitoring at the PCBs contaminants or residues in water are most interesting since these would help to reduce the risk for people who need to use water. This study would also help to improve the analysis methodologies that will help to control the quality of water in this country.

This thesis emphasizes on trace analysis of PCBs residue in water using Gas Chromatography-Mass Spectrometry. The sample preparation is by solid phase extraction (SPE) technique. The purpose is to qualify and quantify the trace level of PCBs contaminated in well water near the wastewater treatment pond and landfill in order to accurately and reliably determine PCBs in water. The analytical results can provide the basic information that will help our

society to make decisions, initiate new regulation of the limit of contaminant level of PCBs in water and focus on the evaluation and maintenance of aquatic ecosystem onward. In addition, this work is focusing on the developing a method that will produce a minimum amount of waste in the process. In general, this has required a conversion of a sample preparation method from a traditional liquid-liquid based into solid phase based extraction.

The developing method when compared to current method should be achieve equivalent or better accuracy, precision, recovery, use less time and is more economical. In addition, it should be easy to use, be rugged enough to handle a wide variety of waters, and be amenable to high production output include capable of measuring contaminants at low levels from small sample volume.

1.2 Background

1.2.1 Chemical formula and structure

The chlorination of biphenyl can lead to replacement of 1-10 hydrogen atoms by chlorine; the conventional numbering of substituent position is shown in the Figure 1.

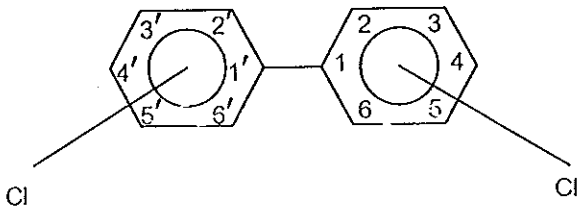


Figure 1 Chemical structure of Polychlorinated biphenyls (PCBs)

The chemical formula can be presented as $C_{12}H_{10-n}Cl_n$, where n, the number of chlorine atom in the molecule can range from 1-10 (see Appendix, Table A). The relative molecular mass depends on the degree of substitution. For example, monochlorobiphenyl has a relative molecular mass of 188, while completely chlorinated biphenyl ($C_{12}Cl_{10}$) has a relative molecular mass of 494 (Dobson and van Esch, 1993).

1.2.2 Common name

PCBs are listed in chemical abstracts under "1, 1-biphenyl, chloro derivatives" which a generic CAS registry number of 1336-36-3. The entire set of 209 PCBs forms a set of congeners.

Ballschmiter and Zell arranged the 209 congeners in ascending numberic order and assigned what are commonly term "Ballschmiter", "BZ", or "IUPAC" number from 1 to 209 as shown in Appendix, Table A (Erickson, 1997).

1.2.3 Chemical composition

The PCBs are chlorinated hydrocarbons, manufactured commercially by progressive chlorination of biphenyl with chlorine gas in the presence of suitable catalyst (e.g., iron chloride). Depending on the reaction condition, the degree of chlorination can vary between 21 to 68% (w/w). The yield is always a mixture of different isomers and congeners. Thus, a total of 209 theoretically different chemical compounds exist, but only about 130 of these are likely to occur in commercial product or mixtures of such compounds (Dobson and van Esch, 1993).

Individual manufactures have their own system of identification for their products. For example, in Aroclor series, a 4-digit code is used that biphenyls is generally indicated by 12 in the first 2 positions while the last 2 numbers indicate the percentage by weight of chlorine in the mixture, thus, Aroclor 1260 is a polychlorinated biphenyl mixture containing 60% of chlorine. The proportion of PCBs with 1-9 chlorine substituents in Aroclor are shown in Table 1.

1.2.4 Physical Properties

Most PCBs congeners are colorless, odorless crystal: the commercial mixtures are clear viscous liquids (the more highly chlorinated mixtures are more viscous), light yellow to dark color. They do not crystallize at low temperatures, but turn into solid resins because of the chlorine atoms in molecule and their density is rather high. They possess very low electrical conductivity and are extremely high resistance to thermal breakdown, and it is

on basis of these properties that they are used as cooling liquids in electrical equipment (Dobson and van Esch, 1993). Although the physical and chemical properties vary widely across the class, PCBs have low water solubility and low vapor pressure as shown in Appendix, Table B. The interaction of the various physical properties and their relevance to specific applications can be extremely complex and not well defined (Erickson, 1997).

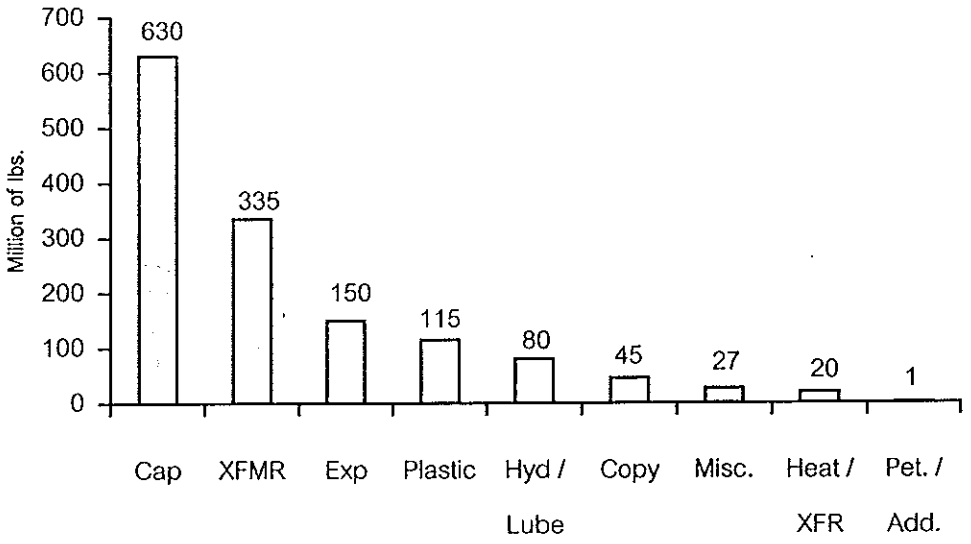
Table 1 Approximate percentage (w/v) of Aroclors with different degree of chlorination

Number of chlorine atoms in molecule	Chlorine weight (%)	Aroclor						
		1221	1232	1016	1242	1248	1254	1260
0	0	10	-	-				
1	18.8	50	26	2	3			
2	31.8	35	29	19	13	2		
3	41.3	4	24	57	28	18		
4	48.6	1	15	22	30	40	11	
5	54.4				22	36	49	12
6	59.0				4	4	34	38
7	62.8						6	41
8	66.0							8
9	68.8							1

Source: Environmental Health Criteria 140, World Health Organization, Geneva, 1993.

1.2.5 Application

Commercial PCB mixtures are used in a wide variety of applications, including dielectric fluid in capacitor and transformers; heater transfer fluids; hydraulic fluids; lubricating and cutting oils; and as additives in pesticides, paints, copying paper, adhesives and plastics. By far, the preponderance of the PCBs is used in capacitor and transformers as shown in Figure 2. Their commercial utility is based largely on their chemical stability, including low flammability and their desirable physical properties, including electrical insulating properties (Erickson, 1997). This information together with the report that during 1996-1998 Thailand imported more than 700,000 units of electrical and electronic products (The Electrical and Electronics Institute, 1999).



Note: Cap: Capacitor, XFMR: Transformer, Exp: Electronic equipments, Hyd/lube: Hydraulic fluid/ lubricant, Copy: Copy paper, Heat/XFR: Heat transfer fluid, Pet/Add.: Pesticides/Additives

Figure 2 Applications in the U.S. based on sales records 1930- 1975 (Erickson, 1997: 38)

1.2.6 Environmental contamination

PCBs are contaminated consistently in many environmental matrices, including marine, plants and animals, fish, mammals, birds, wildlife, soil, air and water. The contamination of PCBs has generally in level of parts per billion in soil, sediment and food, and subparts per trillion in water. Many PCB congeners, most abundant in human tissues and important, are compounds with IUPAC numbers: 28, 52, 74, 77, 99, 101, 105, 118, 126, 128, 138, 153, 156, 169, 170, 179 and 180. They comprise more than 70% of total PCBs and are of greatest toxicological significance (Dobson and van Esch, 1993). In addition, they are also found in human milk and these are shown in Table 2 (Erickson, 1997).

Table 2 The contribution of PCB Congeners in Human Milk

Proportion	Congener (IUPAC No.)
>10%	138, 153, 180
2-10%	15, 18, 28, 52, 66, 61/74, 99, 101, 105, 187, 156/202, 170
<2%	44, 119, 77/110, 82/151, 128, 149, 183, 188, 201

Source: Analytical Chemistry of PCBs, 2nd, Lewis Publication, New York, 1997:58

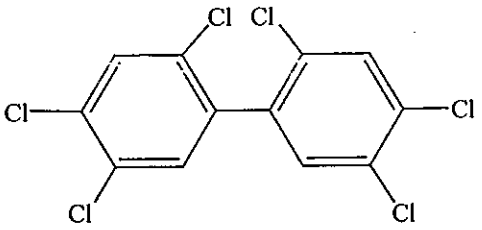
1.3 Literature Review

1.3.1 PCBs Contamination

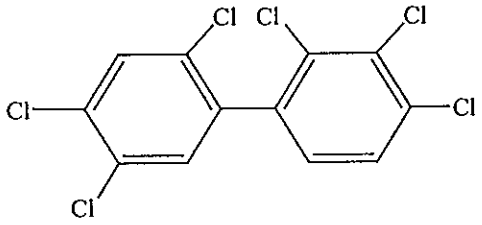
The determination of PCBs residue in water is necessary for solving various environmental and biological problems. Albaigés (1993) reported that PCBs had 209 possible chlorinated biphenyl configurations (congeners), but about 150 account for nearly all the environmental contamination attributable to PCBs and only a few congeners are both persistent and toxic. Recently, 36 congeners have been indicated as most environmentally threatening based on their most report contamination in environmental samples, their relative abundance in animal tissue, and the toxicity potential. The 36 priority PCB congeners that have the most toxic effect include PCBs .77, 126 and 169. Some PCB congeners were found in the environment at relative high concentrations such as 105, 118, 128, 138, 156 and 170. Particularly, some relative weak toxic PCBs was reported frequently in the environment or present in high concentrations in animal tissues relative to other PCBs 18, 44, 49, 52, 70, 74, 151, 177, 187 and 201.

In the Organochlorines Programme of New Zealand to characterizing the extent of contamination in the New Zealand environment, Buckland *et al.* (1998) reported that the relative abundance of PCBs in water samples PCB congener 138 and 153 were frequency detected in water samples and this correlated to previous report by Bush *et al.,* (1985). The concentration of PCBs in water from Hudson River (Buckland *et al.,* 1998) was reported in a range from non detectable to 1.2 ng/l for PCB153 while PCB138 was found in the range of 0.4-2.8 ng/l. Both congeners showed the concentration at level considerably higher than the current Australian and New Zealand and Conservation Council Water Quality Guideline for protection of aquatic life (1 ng total PCBs L^{-1}).

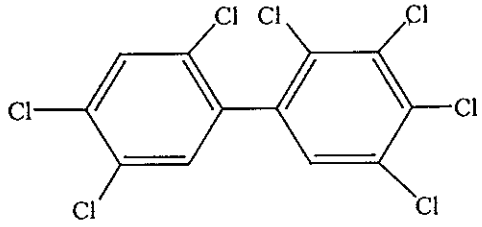
Taking into consideration the high level contamination of PCB138 and 153 in water (Buckland *et al.,* 1998), the abundance of PCB138, 153 and 180 in human milk (Erickson, 1997), and the fact that these PCBs are presented as a major composition in electronic wastes. Therefore, this thesis purposed to do trace analysis of PCBs residue in water focusing to congener number 153, 138 and 180. The chemical structures of these PCBs were shown in Figure 3.



2, 2′, 4, 4′, 5, 5′ – Hexachlorobiphenyl
(PCB153)



2, 2′, 3, 4, 4′, 5′ – Hexachlorobiphenyl
(PCB138)



2, 2′, 3, 4, 4′, 5, 5′ – Heptachlorobiphenyl
(PCB180)

Figure 3 Chemical structure of PCB153, 138 and 180

1.3.2 Analysis Methods

The accuracy and precision for the analysis of PCBs are dependent on both instrumental performance and sample preparation. Most of the determination techniques used for PCBs employ a chromatographic separation due to the complex nature of aqueous environmental samples. Industrial analysis of PCBs was performed on packed column gas chromatography using PCBs mixtures for calibration. But the lack of agreement between the composition of the mixtures and the environmental samples, especially the association of their toxicity to some specific isomer, gave rise to continuing need for measurement of individual components of PCBs (Albagiés, 1993). Thus, many powerful chromatographic separation methods, such as capillary gas chromatography (GC) or high-performance liquid chromatography (HPLC), are indispensable for analytical determination of PCBs (Mol *et al.*, 1995) and replaced the old method because of their far superior efficiency and sensitivity by factor of ten (Audunsson *et al.*, 1988).

However, some congener-specific analysis is required to determine the co-planar or ortho-PCB, thus, High Resolution Gas Chromatography (HRGC) or Capillary gas chromatography with an appropriate detector will be the technique of choice (Erickson, 1997). The HRGC is one of the most widely employed analytical techniques today (Grob, 1985). Due to the simplicity, rapidity of analysis, high sensitivity of detector systems, high efficiency of the separation varied applications and the use of very small samples. Moreover, presently HRGC is finding use in the concentration of impurities in the parts per million (ppm) and parts per billion (ppb) that is one interest advantage of trace analytical technique. In addition, as the consideration of high efficiency for analysis, the property of HRGC column was reviewed. The capillary column was made of fused silica, chemically bonded with various stationary phase to achieve a range of different selectivity toward complex samples. Liquid phases were "immobilized" or crosslinked, this allowed high

temperature operation with low bleeding, so labile and/or less volatile compounds could be analyzed and detector could be operated at high sensitivity (Muccio, 1995). Currently there are two general types of capillary columns, conventional (0.10-0.25 mm I.D.) and wide-bore capillary columns (0.53 mm I.D.) for suitably determining the retention time of PCBs. The complete set of retention time data for a capillary column that available for all 209 congeners were obtained by Mullin *et al.* (1984). The column was SE-54 (5% diphenyl-1%divinyldimethylsiloxane) and some analyses had been based on this phase (Erickson, 1997).

Larsen *et al.* (1995) has reported the property of various capillary columns where their performance and strength/weakness were identified for the co-eluting congener of PCBs in several Aroclors. Many classical columns for HRGC were studied such as SIL-8, SIL-5, SIL-9, SIL-88, HT-5, SIL-8/HT-5. The HT-5 column (5% diphenyl dimethylsiloxane, 25 m x 0.22 mm x 0.10 μm) was noted to be the best after seven major PCBs constituents (IUPAC no.28, 52, 101, 118, 138, 153 and 180) were determined. Later, Sukowski and Rosinska (1999) reported the determination of the seven PCB congeners (the same as Larsen *et al.* (1995)) by GC-MS. Separation was achieved on a DB-5 column (5% diphenyl dimethylsiloxane, 30 m x 0.32 mm x 1 μm). From a review by Font *et al.* (1996), the most commonly employed GC phase in the determination of PCBs in water is 5% phenyl methylsiloxane. Therefore, HP-5MS (5% diphenyl and 95% dimethylpoly siloxane, 30 m x 0.25 mm x 0.25 μm) was chosen for the separation of PCB153, 138 and 180 in the trace analysis of PCBs residue in water.

Another influencing factor for the analysis PCBs is detector. The GC detector is a transducer, converting a chemical signal (molecules in gas stream) to an electrical signal, some detectors (e.g. Flame ionization detector; FID) destroy the compounds in the detection process while others (e.g. Electron Capture Detector; ECD) are nondestructive (Skoog, 1985). GC detectors may

be categorized as either universal or selective. The ECD is selective toward halogenated compounds. The selectivity coupled with its extreme sensitivity has made ECD very popular for analyses of trace levels (residues) of pesticides and PCBs while FID is the most common GC detector and is as universal detector, giving similar responses for most organic compounds. Thus, FID will be unsuitable for detection PCBs in a complex matrix. However, the analysis of PCBs generally requires selectivity and sensitivity. Therefore, the detector often must selectively detect PCBs in the presence of other compounds present at an order of magnitude higher concentration. The levels typically observed in matrices of interest are in the parts-per billion ranges. These level strain the capability of even the most sensitive detection device, such as ECD, resulting in a large number of not detected values in many reports (Erickson, 1997).

The advantage of ECD can be observed from the determination PCBs in water by equipping with GC (as referred to ASTM D3534). In this case, ECD can give the limit of detection in range 0.1-0.5 ppb for Aroclor 1254 and 1260 where analyzing 1 liter of water. However, because of the high sensitivity and selectivity of ECD toward halogenated compounds, ECD can detect many other chlorinated and nonchlorinated compounds (halogenated pesticides, Chloroaromatics, phthalate, adipate esters and other compounds). These may be differentiate from PCBs on the basis of retention time such as very high levels of polynuclear aromatic hydrocarbon can give an ECD response with retention times in the PCB window (Vessman, 1980). Furthermore, some samples were tested positive by GC-ECD may require further confirmation by GC-MS (Singh *et al.*, 1998). Thus, mass spectrometer are becoming increasingly common as GC detectors as sensitivity, cost, performance, reliability and user friendliness improves. As the mass spectrometer is universal and selective GC detector. So it can represent secondary order which generate a three-dimensional matrix of data (Booksh and Kowalski, 1994). By focusing on a spectral property characteristic of a compound or class of

compounds, this detector can be rather specific because of the much higher information content of mass spectral. This is particularly useful for isomer differentiation, where good GC separation frequently compensates for difficulties encountered as the result of intermediate mass spectra (Harvey, 1995).

Moreover, the major advantage of GC-MS that allowed the instrument to be used in most sensitive mode for quantitative measurements was the selected-ion monitoring (SIM). It was first introduced in the 1960's under the name "mass fragmentography" by Hammar *et al.* (1954) and also owed its high sensitivity to the tuning of the mass spectrometer so as to focus only a few ions that were recorded continuously. In its most sensitive mode, a single ionic species was monitored for the duration of the experiment. Thus all the ion current from this ion was captures, whereas if the mass spectrometer were scanned, only small fraction of the ions at this mass per charge (m/z) value would be acquired (Harvey, 1995).

Yasuhara *et al.* (1997) reported the investigation of the presence of several organic substances in highly toxic wastes such as soils contaminated with polychlorinated biphenyls were burned in closed landfill leachates in Japan. The GC-MS was used to determine these compounds. A JEOL DX-303 MS equipped with HP570 GC column, crosslinked 5% phenyl methylsilicone (25 m x 0.31 mm x 0.52 μm) with temperature program: 10°C for 2 min followed by a 3°C/min ramp to 270°C for 10 min hold. The injector temperature was 250°C, carrier gas (He) flow rate: 2.0 ml/min, injector mode: splitless, ion source temperature: 250°C, ionizing energy: 70 eV. The results showed approximately 190 detected compounds and biphenyl was detected in a range 2.9-17 ng/l. Singh *et al.* (1998) also reported the use of GC-MS for the quantitative analysis of polychlorinated biphenyls, organochlorine insecticides, polycyclic aromatic hydrocarbons, polychlorinated hydrocarbons and polynitrohydrocarbons in spikes of soil, water and plasma. A HP5890 gas

chromatograph with 5970 mass selective detector and HP-5 column were used in their study. The column temperature was programmed: 75°C for 2 min, 3°C/min to 150°C, 5 min hold at 150°C, 5°C/min to 200°C, 5 min hold at 200°C, 3°C/min to 300°C and 10 min hold at 300°C. The helium flow rate was operated at 20 ml/min while injector temperature was 200°C and sample injection was made in splitless mode. The chromatogram profile of individual ion indicated good separation of each ion. The minimum detection limit was in range 1 - 4 pg injected when 1 or 2 ions were monitored or from 20 - 200 pg injected when 20 ions monitored. Then in year 2000, Lacorte *et al.* used the GC/EI/MS in selected ion monitoring (SIM) mode for tentative identification of 109 priority compounds listed in the 76/464/CEE Counçil Directive. GC-MS system was performed by gas chromatograph HP6890 connecting to a mass spectrometer HP5973 (Hewlett-Packard, Waldbronn, Germany). The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV and the emission current 300 μA. The temperature of ion source was heated to 230°C. A HP-5MS (30 m x 0.25 mm i.d. with 0.25 μm film thickness), containing 5% phenyl methyl siloxane was programmed from 40°C (keeping this temperature for 2 min) to 175°C at 3°C/min (keeping this temperature for 4 min), from 175 to 240°C at 3 °C/min and to 320°C at 7°C/min (keeping this temperature for 10 min). The total analysis time was 93 min. The GC/EI/MS with SIM mode permitted an accurate quantification of target analytes and the unequivocal identification through mass spectra and library confirmation, respectively. This multiresidue approach permitted one to follow EU regulations in terms of the number of analytes that could be simultaneously analyzed in different types of water. In this thesis the GC-MS system is used for the analysis of PCBs residue in water with SIM mode at extremely low concentration.

1.3.3 Sample preparation

The largest problems was how the analyst encountered in the case of organic micropollutants to cope with many different compounds occurring at trace concentrations. Thus, the need for reliable data on occurrence of organic micropollutants including PCBs in the environment is an important driving force initiating the development of modern analytical techniques and procedure. PCBs analyses are generally similar to other trace organic micropollutants of environmental analyses. Samples are collected and stored until extraction. The sample extract is often cleaned up to remove interference and then PCB composition and content is determined. Therefore, the use of an appropriate sample preparation technique is a must in an analysis of the contaminants in water prior to the determination.

As the traditional preconcentration is usually performed by extracting a large water sample with organic solvent (Liquid-liquid Extraction, LLE) and evaporating the extract to small volume and then further submitted to a suitable clean up operation before analysis. Thus, these procedures are solvent and time-consuming including difficult to automate (Font *et al.,* 1993) that there is a risk of contamination. Furthermore, many disadvantages in some methods for determination PCBs in spiked water sample were found such as, the liquid-liquid extraction causes incomplete recovery of high molecular mass from environmental samples, the GC and HPLC both provided incomplete separation of many pollutants, and also the quantitative analysis of the pollutants may be difficult due to the lack of pure standards and suitable internal standard (Singh *et al.,* 1998). Therefore, the efforts to use a solid phase for the recovery analytes from water matrix prior to their determination have been developed for a long history. Castillo and coworkers (1999) reported that the solid phase extraction (SPE) has turned to be an effective technique for isolation of contaminants from wastewater matrices. The SPE used in current water analysis including adoption into standardized analytical methods

(Liška, 2000) and its implemented to be an alternative of Liquid - Liquid Extraction (LLE). If the interference are not removed in the sample preparation process, they will be injected into the analytical system together with the PCBs component (e.g., HRGC, GC-MS, etc.), resulting in lower sensitivity, shorter column life and more frequency instrument maintenance (EPA3535A, 2000). Many adsorbents have been introduced for enrichment trace amount of PCBs such as Al_2O_3, mixture of Al_2O_3 and silica gel, silica gel, Bio-bead S-X_3, XAD-2 resin, graphitzed carbon black, florisil and C_{18} cartridges (Russo *et al.*, 1993). Octadecyl (C_{18})-bonded silica is one of the most used sorbent for off-line procedure since its procedure similar result when it was used online. Sulkowski and Rosińska (1999) determined the polychlorinated biphenyls from city sewage-treatment plant sludge by extracting with different methods of extraction. Seven chosen PCB congeners (28, 52, 101, 118, 138, 153 and 180) were extracted by SPE kit from J.T. Baker including Bakerbond SPE C_{18} octadecyl column (500 mg) then analyzed by GC-MS, worked on SIM mode. The recoveries of all congeners showed more than 60%. In addition, Lacorte *et al.* (2000) developed a single multiresidue method to determine 109 priority organic compounds included in the 76/464/EEC Council Directive on Pollution of the European Union. By using automated off-line solid phase extraction that selected polymeric sorbent Oasis 60 mg cartridge to trap 109 compounds including PCBs, the preconcentration of 200 ml water sample has an achievement of limits of detection at the low nanogram/liter level and recoveries between 70 and 120%. In 2001, Dmitrovic and Chan reported a determination of Polychlorinated biphenyl congeners in human breast milk by gas chromatography - negative chemical ionization mass spectrometry technique after clean - up by solid phase extraction. A bond Elut C_{18}, a Sep-Pak Plus NH_2 and a Bond Elut PCB cartridge were used sequentially to extract 25 congeners in human milk sample. The limit of quantitation was 0.1 ppb for five less chlorinated congeners (PCB70, 74, 87, 99 and 101) and 0.01 ppb for

remaining 20 congeners (PCB77, 105, 118, 126, 128, 138, 151, 153, 156, 169, 170, 180, 183, 187, 191, 194, 205, 206, 208 and 209). Besides that Weigel *et al.* (2001) reported the unsatisfactory recovery rates and poor reproducibility were observed for XAD resins although the sorption capacity of these polymer was 10-fold higher than C_{18} sorbent. Especially for the XAD resins excessive cleaning procedures were required prior to their use.

However, in the 1990s the membrane extraction disk, new SPE types of material replaced the cartridge, was developed by 3M (Liška, 2000). The C_{18} extraction disk is a commercially available, very suitable for extraction, and can be performed in a short time. These advantages have led to its extensive use for sample pretreatment in various applications. Albanis and Hela (1995) reported a multi-residue analysis of 25 pesticides comprising PCBs in some formulations that was developed as a rapid screening method for organic contaminants in river, lake and sea water. The extraction of various natural waters spiked with pesticides mixtures was effective when C_{18} Empore solid phase extraction disks were used with filter-aid glass beads. The use of C_{18} Empore disks was found to be an effective mean for the trace determination of pesticides in natural waters at detection limit at least ten times below the drinking water limit (0.1 μg/l) for individual pesticides. In addition, Michor *et al.* (1996) investigated the Empore disk as an extraction medium for 23 polynuclear aromatic hydrocarbon from 1 liter ambient water sample at the ppt level. The method was shown to achieve equivalent or better detection limits (range 9-56 ng/l) than traditional liquid-liquid base methods, reduce the amount of solvent required, eliminate the use of chlorinated solvents, and the work-up time. Therefore, in this work, the C_{18} Empore extraction disk was chosen to enrich the three PCB congeners residue in water and then analyzed by GC-MS.

1.4 Objectives

1. To study the appropriate sample preparation technique and to analyze trace level of polychlorinated biphenyls residue in water using Gas Chromatography - Mass Spectrometry Technique.
2. To implement the appropriate sample preparation and analysis of PCBs for real water samples.

Chapter 2

EXPERIMENT

2.1 Chemicals and materials

2.1.1 Standard chemicals (Certified solutions with purity 99 - 100%, Accustandard Inc.,USA) :

- 2, 2′, 3, 4, 4′, 5′- Hexachlorobiphenyl (IUPAC No.138): 35 μg/ml
- 2, 2′, 4, 4′, 5, 5′-Hexachlorobiphenyl (IUPAC No.153): 35 μg/ml
- 2, 2′, 3, 4, 4′, 5, 5′-Heptachlorobiphenyl (IUPAC No.180): 35 μg/ml

2.1.2 General Solvents and Chemicals

- Isooctane ($(CH_3)_3CCH_2CH(CH_3)_2$, AR Grade: LAB-SCAN, Thailand)
- Perfluorotributylamine (PFTBA, MS.grade: Hewlette Packard, USA.)
- n-Hexane ($CH_3(CH_2)_4CH_3$, AR Grade: LAB-SCAN, Thailand)
- Dichloromethane (CH_2Cl_2, AR Grade: LAB-SCAN, Thailand)
- Ethyl acetate ($CH_3COO\ C_2H_5$, AR Grade: LAB-SCAN, Thailand)
- Acetone (CH_3COCH_3, A.C.S – ISO- For analysis: Carlo Erba, USA)
- Acetonitrile (CH_3CN, AR GRADE: LAB-SCAN, Thailand)
- Methanol (CH_3OH, GR GRADAE: Merck, USA)

- Ultra pure water (H_2O, Synthesis in laboratory by Maxima, ELGA, England)
- 1:1 v/v Sulfuric / water solution (H_2SO_4, A.C.S Reagent: J.T.Baker, USA)

2.1.3 Materials

- ENVI^{TM}-18 DSK 47 mm Solid Phase Extraction Disks (Supelco, USA)
- Filter Aid 400 (3M, USA)
- Glass fiber filter 47 mm (Whatman, USA)

2.1.4 Samples

Water samples were taken from the wells near wastewater treatment pond and landfill area at Songkhla municipal, Songkhla.

2.2 Instruments and Apparatus

2.2.1 Gas Chromatograph-Mass Spectrometry System (GC-MS)

- Gas chromatograph model 6890 Series (Agilent Technologies, USA)
- An auto-sampler injection model 7683 Series (Agilent Technologies, USA)
- Capillary Column: HP-5MS, 30 m x 0.25 mm ID. x 0.25 μm film thickness of 5% diphenyl and 95% dimethylpolysiloxane
- Helium Carrier Gas: Ultra High Purity, 99.99999% (Sounthern Liquid Oxygen Ltd., Thailand)
- Mass Selective Detector (MSD) model 5973 (Agilent, Technologies, USA)
- Computer system model KAYAK (Hewlette Packard, USA)

2.2.2 Apparatus

- Syringe 10 µl (Agilent Tecnologies, USA)
- Vial 2 ml with Polypropylene screw cap and red rubber septa (Agilent Tecnologies, USA)
- Vial 2 ml with Silver aluminum cap (Agilent Tecnologies, USA)
- 11-mm Crimper (Agilent Tecnologies, USA)
- Standard Filter apparatus (Wheaton, USA): 47 mm ID, consisting of a sample reservoir, clamp, fritted disk and filtration head with drip tube (Figure 5)
- Glass collection tube 60 ml (Pyrex, USA)
- Glass filter flask 500 ml (Pyrex, USA)
- Glass round bottom flask 50 ml (Pyrex, USA)
- Microliter pipette 200 µl , 1000 µl (Gilson, France)
- Evaporating rotator (EYELA, Japan)
- Vacuum pump (Sargent-welch, USA.): Capable of maintaining a vacuum of approximately 22 inches of mercury (150 ml/min.)
- Multimeter model Check-mate 90 (Mettler-Toledo Ltd., USA)

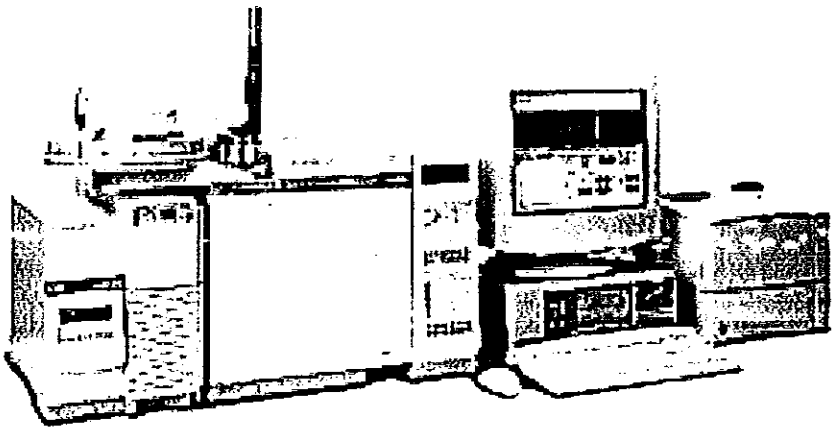


Figure 4 Gas Chromatography-Mass Spectrometry (HP6890-HP5973) with auto-sampler injection (HP7683)

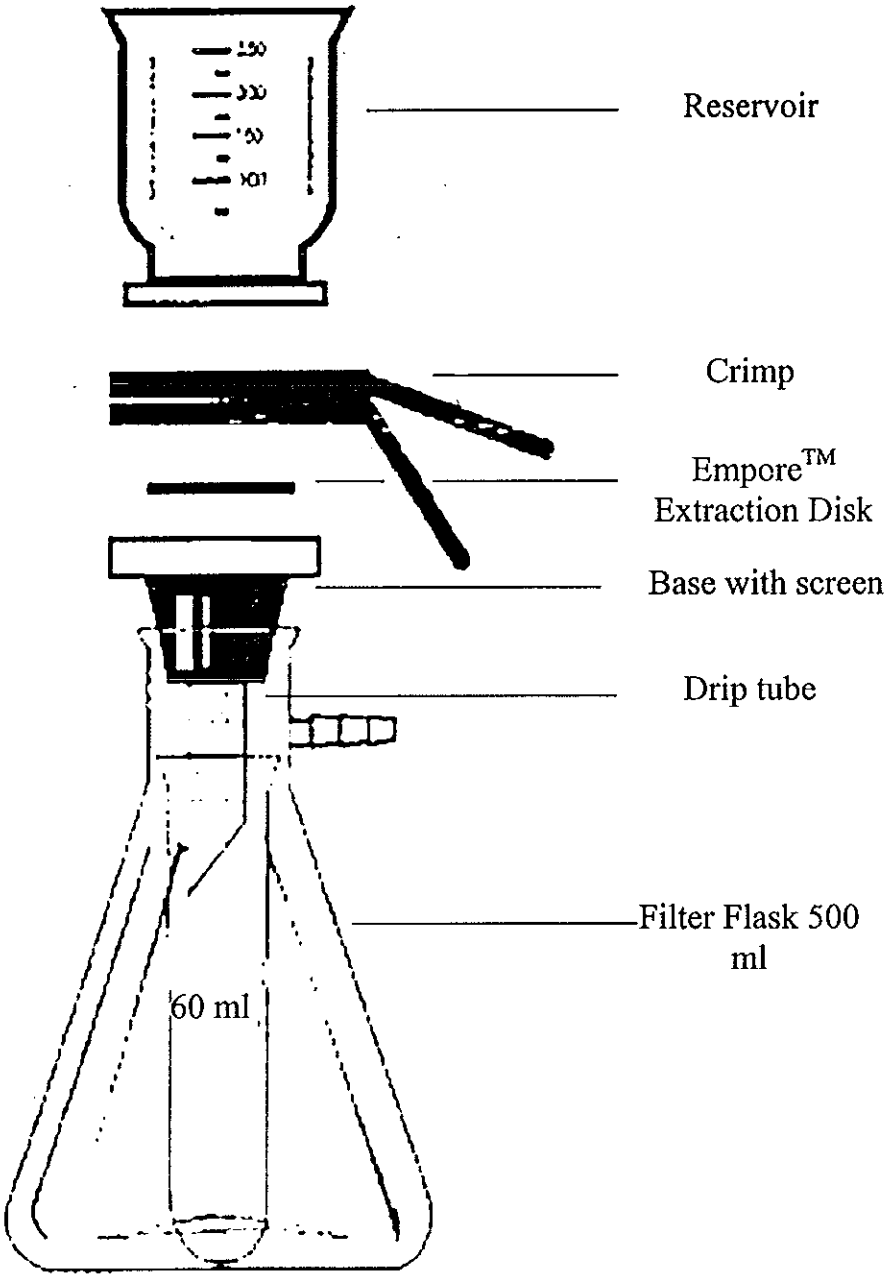


Figure 5 The standard filter apparatus

2.3 Methods

2.3.1 Preparation of PCBs standard stock solutions

The standard stock solution of individual PCB was prepared from standard chemical (2.1.1) at a concentration of 3.50 μg/ml where 1μg/ml correspond to 1 ppm. The solution was accurately dissolved in isooctane and diluted to 10-ml in the volumetric flask. They were then transferred into amber glass bottles with PTFE-lined screw caps, stored as 4°C as recommended by the manufacturer and also protected from light.

2.3.2 Preparation of the PCBs working standard solutions

The working standard solutions were prepared by serially diluting each PCBs standard stock solution (2.3.1) with isooctane to give the desired PCBs mixture concentrations over the range 1.0 ppb – 1.0 ppm.

2.3.3 Optimization of the analysis conditions

To optimize the GC-MS system for trace analysis of PCBs residue in water sample, the following parameters were studied: carrier gas flow rate, temperature program, injector temperature, GC-MS interface temperature, relative response factor, limit of detection, linearity, sample preparation and recovery.

2.3.3.1 Optimize carrier gas flow rate

A 1-μl aliquot of the working standard solution at a concentration of 100 ng/ml (ppb) was injected into the GC-MS system. The optimum carrier gas flow rate was investigated by varying the flow rate of helium carrier gas at 0.5, 0.8, 1.0, 1.2 and 1.5 ml/min respectively. The retention time, peak height and peak area from the chromatogram of three components were determined from graph. From the Van Deemter graph, the optimum flow rate was obtained from the lowest HETP in the graph.

Initially, the injector, MS source, MS quadrupole and transfer line temperature typical setpoint were maintained at 250°C, 230°C, 150°C and 280°C respectively, the recommended setpoint for operating in HP5973 Mass Selective Detector Hardware Manual (Hewlett-Packard, 1998). Therefore, for this work the MS source and MS quadrupole temperature would not be optimized since they have to be set to the requirement in order to operate the GC-MS.

The column temperature programming was performed following the application note of Gas Chromatography (Meng and Szelewski, 2000): 70°C(2min), 25°C/min, 150°C(0 min), 3°C/min, 200°C(0 min), 8°C/min, 280(10 min). Throughout this investigation we used a 1-µl aliquot of the working standard solution at a concentration of 100 ppb to inject into the GC-MS system (Figure 4) via splitless mode. The MS mass was scanned from m/z 45 to 450 amu by the scan mode (full range) to obtain the qualitative information.

2.3.3.2 Optimize the column temperature programming

As this work was a multiresidue analysis, it was not possible for all the PCB congeners to have the same optimum conditions at the same point or to be able to separate them with equal efficiency in the same system.Therefore, we have to choose one representative to study the optimum column temperature programming. Since, PCB153 congener or 2, 2′, 4, 4′, 5, 5′- Hexachloro biphenyl congener gave the highest abundance (Figure 6), it was chosen to investigate all optimum parameters throughout this experiment.

In the GC-MS system, temperature is one of the main variables for the separation. To obtain a good resolution, response and less analysis time, the temperature program was studied as follow.

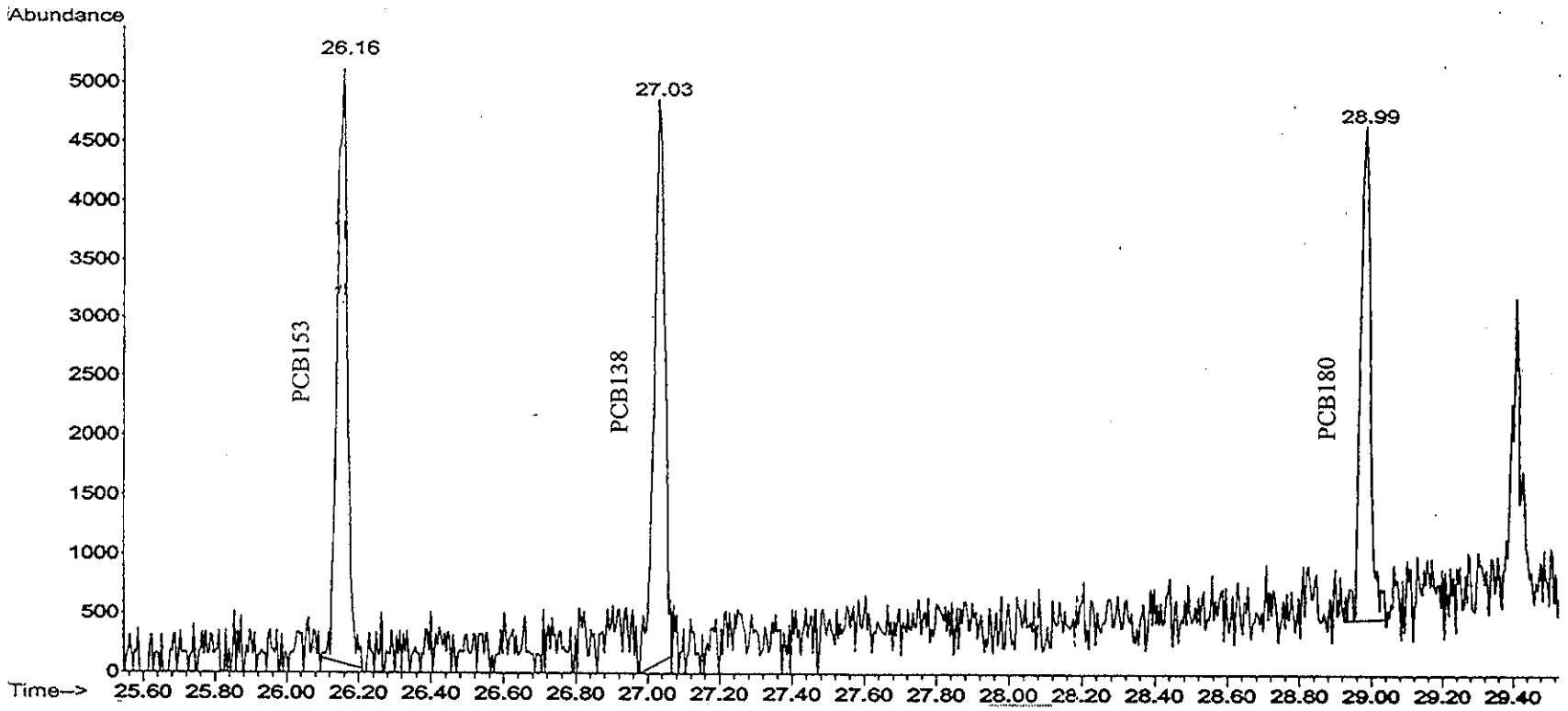


Figure 6 Total ion current chromatogram after auto injection 1-µl of 100 ppb the PCBs working standard solution into the GC-MS with condition 70°C(2min), 25°C/min, 150°C(0 min), 3°C/min, 200°C(0 min), 8°C/min, 280(10 min). Flow rate 1.0 ml/min

Step I Optimize the initial temperature

The optimum initial temperature was investigated by varying temperature from 80 to 150°C with increment of 10°C; held at that temperature for 1 minute; programmed the temperature to 300°C with the ramp rate 20°C/min and held at 300°C for 10 minutes. abundance and resolutions obtained from the different of temperature program were compared and the optimum initial temperature was selected from a highest abundance of PCB153.

Step II Optimize the hold time at the initial temperature

The initial temperature was set at 130°C (an optimum setpoint from Step I). The hold time at 130°C was investigated by varying time from 0 to 4 minutes with increment of 1 minute; programmed the temperature to 300°C with the ramp rate 20°C/min and held at 300°C for 10 minutes. The abundance and resolutions obtained from the different of temperature program were compared and the optimum hold time at the initial temperature was selected from a highest and constantly abundance of PCB153.

Step III Optimize the first stage of ramp rate

The initial temperature was set at 130°C and held for 2 minutes (results from Step I and II respectively). The temperature was then programmed to 300°C by varying the ramp rate from 10 to 50°C/min with increment of 10°C/min and held temperature at 300°C for 10 minutes. The abundance and resolutions obtained from the different of temperature program were compared and the optimum first ramp rate was selected from a highest abundance of PCB153.

Step IV Optimize the second stage of temperature

The initial temperature was set at 130°C and held for 2 minutes. The temperature was programmed to the second stage of temperature that was investigated by varying the temperature from 180 to 260°C with increment of 10°C with the ramp rate 40°C/min as obtained from step III. The temperature was then programmed from the second stage of temperature to 300°C with the ramp rate 20°C/min and held at 300°C for 10 minutes. The abundance and resolutions obtained from the different of temperature program were compared and the optimum of the second stage of temperature was selected from a highest abundance of PCB153.

Step V Optimize the hold time at second stage of temperature

The initial temperature was set at 130°C; held for 2 minutes and then programmed the temperature to 250°C with the ramp rate 40°C/min as obtained from step III and IV. The hold time at 250°C was investigated by varying time from 0 to 4 minutes with increment of 1 minute. The temperature was then programmed to 300°C with the ramp rate 20°C/min and held at 300°C for 10 minutes. The abundance and resolutions obtained from the different of temperature program were compared and the optimum hold time at the second stage of temperature was selected from a highest abundance of PCB153.

Step VI Optimize the second stage of ramp rate

The initial temperature was set at 130°C; held for 2 minutes and then programmed the temperature to 250°C with the ramp rate 40°C/min as obtained from step III and IV. Next, the temperature was programmed to 300°C immediately without a hold time at 250°C (as obtained from step V). The second stage of ramp rate was investigated by varying from

10 to 30°C/min with increment of 5°C/min and then held at 300°C for 10 minutes. The abundance and resolutions obtained from the different of temperature program were compared and the optimum of second stage of ramp rate was selected from a highest abundance of PCB153.

Step VII Optimize the final temperature

The initial temperature was set at 130°C; held for 2 minutes and then programmed the temperature to 250°C with the ramp rate 40°C/min as obtained from step III and IV. The temperature was then programmed to a final temperature immediately without the hold time at 250°C (as obtained from step V) with the ramp rates 25°C/min as obtained from step VI and held at that temperature for 10 minutes. The final temperature was investigated by varying the temperature from 270 to 310°C with increment of 10. All of the responses and resolutions obtained from the different of temperature program were compared and the optimum final temperature was selected from a highest and constantly abundance of PCB153.

2.3.3.3 Optimize the injector temperature

The temperature program and carrier gas flow rate were set at the optimum conditions obtained earlier. Other parameters (MS source, MS quadrupole and transfer line temperature) were fixed at defaults as described in 2.3.3.1. The injector temperature was investigated by varying the temperature from 210°C to 260°C with increment of 10°C. The abundance and resolutions obtained from the different temperature were compared and the optimum injector temperature was selected from a highest abundance of PCB153.

2.3.3.4 Optimize the transfer line temperature

The temperature program, carrier gas flow rate and injector temperature were set at the optimum conditions obtained earlier. Other parameters (MS source and MS quadrupole temperature) were fixed at defaults as described in 2.3.3.1. The transfer line temperature was investigated by varying the temperature from 260°C to 300°C with increment of 10°C. The abundance and resolutions obtained from the different temperature were compared and the optimum GC-MS interface temperature was selected from a highest abundance of PCB153.

2.3.3.5 Limit of detection

The working standard solution at a concentration of 1.0 ppm was diluted with isooctane to obtain the concentration in the range 50.0 ppt - 100.0 ppb. A 1-µl aliquot of each standard solution was injected into the GC-MS system that was set at the optimum conditions were obtained from 2.3.3.1-2.3.3.4.

The lowest concentration or amount of analytes that mass selective detector can detect and has a signal was taken from the total ion chromatogram using the SIM data acquisition. The Signal to Noise ration (S/N) was calculated automatically by the Chemstation Operating Software.

2.3.3.6 Linear dynamic range (linearity)

The working standard solution at a concentration of 1.0 ppm was diluted with isooctane to obtain the concentration in the range 50.0 ppt - 1.0 ppm. A 1-µl aliquot of each standard solution was injected into the GC-MS system with the optimum conditions that were obtained from 2.3.3.1-2.3.3.4.

Linearity was determined by ploting a calibration curve. The linearity of the response was determined by considering the correlation coefficient.

2.3.3.7 The response factor

Five concentrations of working standard solution were prepared by diluting the standard stock solution (2.3.1) with isooctane to give a desired mixture concentration at 0.01, 0.05, 0.10, 0.50 and 1.00 ppm. A 1-µl aliquot of each solution at various concentrations was then injected into the GC-MS system that was set at the optimum conditions were obtained from 2.3.3.1-2.3.3.4.

The response factors (RF) were determined using the integrated peak response of each analyte at various concentrations compared with the integrated peak response of PCB153 (Assigned RF = 1).

2.3.3.8 Quantitative analysis by Internal Standard Plot Method

Five concentrations of working standard solution were prepared by diluting the standard stock solution (2.3.1) with isooctane to give a concentration at 0.01, 0.05, 0.10, 0.50 and 1.00 ppm and then added the internal standard (Chrysene-d_{12}) 0.10 ppm in each solution. A 1-µl aliquot of each solution at various concentrations was then injected into the GC-MS system that was set at the optimum conditions were obtained from 2.3.3.1-2.3.3.4. The relationship between the concentration of three PCBs congeners and the ratio of analyte to internal standard peak was plotted for quantitative analysis of PCBs.

2.3.3.9 Sample preparation by Solid-Phase Extraction

A blank was prepared from ultra pure water similar to that being used for the water samples. A 500-ml of blank was collected in a 500-ml volumetric flask. A 100-µl of the working standard solution at a concentration of 100 ppb was then spiked into the blank, stirred and mixed well. The concentration of PCBs in the blank solution 500 ml was equal to 20 ppt. Methanol (0.5%, v/v) was then added to the aqueous solution before they were

loaded onto disk extraction. All samples and blank had the same amount of methanol. The matrix spike samples were mixed and allowed to stand for 10 minutes. The pH of the aqueous sample was checked with pH paper and if necessary, adjusted to pH 5-9 according to EPA3535A (Environment Protection Agency, 2000).

Figure 8 shows a scheme of sample preparation and preconcentration PCBs in water sample. The water samples before spiking with standard were prefiltered by pumping through a lab built prefiltration unit (Figure 7) to reduce particulate matter, then through 47 mm glass fiber filter 0.45 μm and collected in a 2-L amber glass bottle before loading to extraction unit. A lab-built prefiltration unit composed of 3 parts

Part 1: Consist of polyethylene top, middle and end covers with o-rings to prevent water leakage.

Part 2: Two glass tubes 1.85 cm. i.d. x 3.50 cm. filled with glass wool and filter aid 400 (50 g) respectively.

Part 3: Polyethylene screen

After prefiltering of the water sample, the standard filter apparatus was assembled for SPE disk extraction using 47-mm of C_{18} Empore extraction disk (Figure 5).

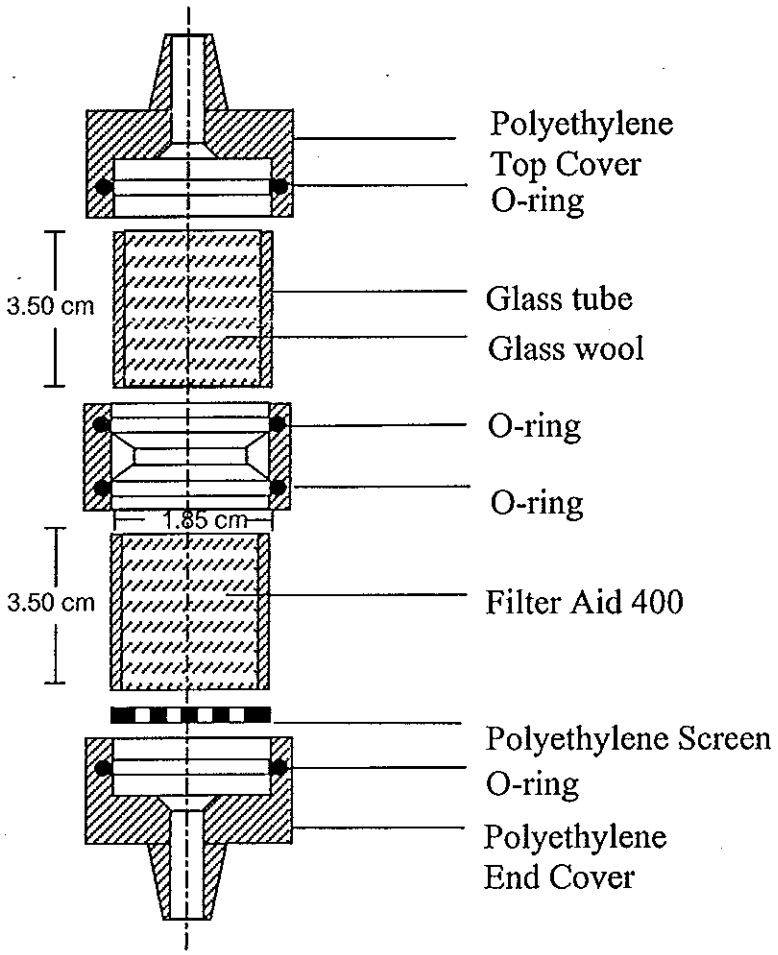


Figure 7 A lab built prefiltration unit

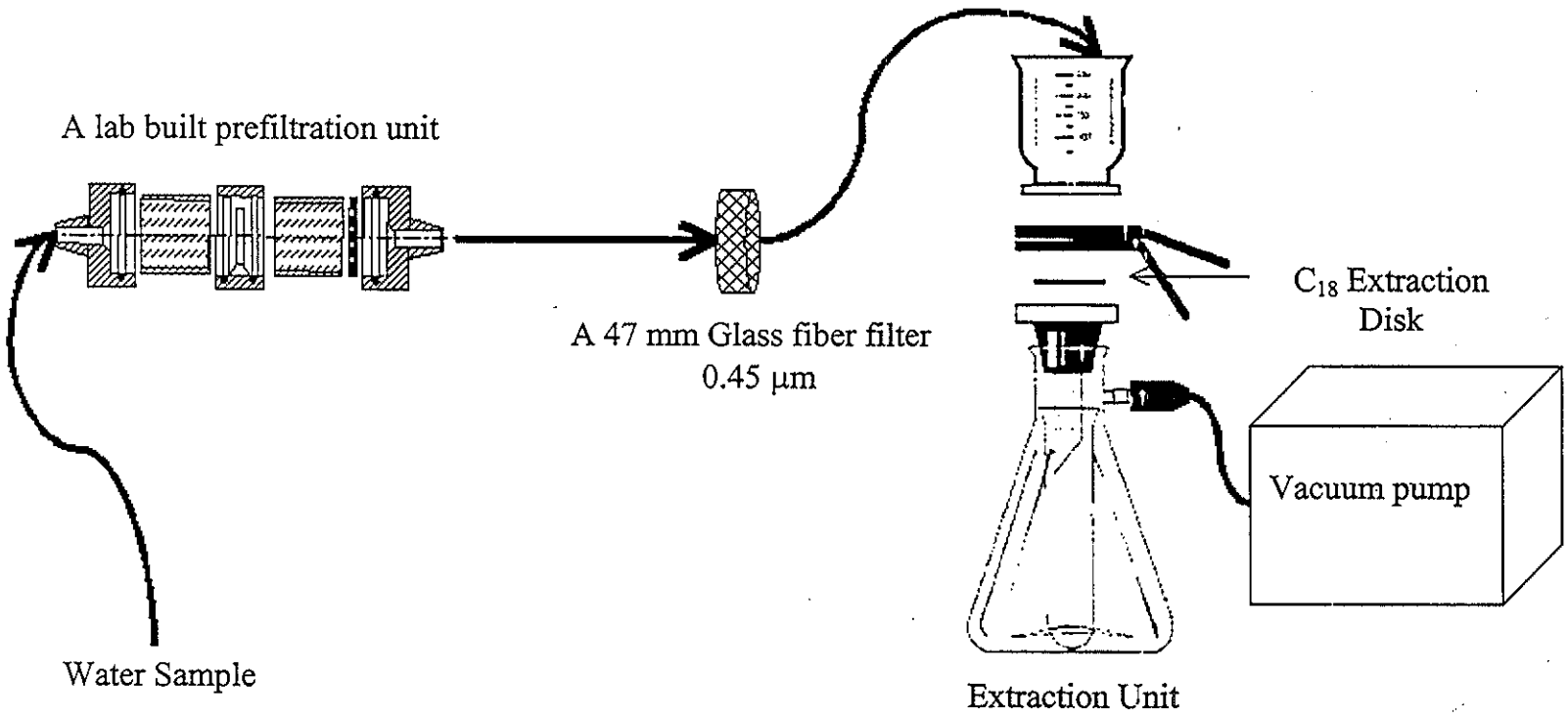


Figure 8 Scheme of sample preparation and preconcentration

The procedures for C_{18} Empore disk based on solid phase extraction consisted of disk washing, disk conditioning, sample extraction, and sample elution respectively.

Disk preconditioning, the extraction disk was washed with 10.0 ml dichlromethane and 5.0 ml ethyl acetate by rinsing the solvent down the sides of the glass reservoir. The small amount of solvent was pulled through the disk under vacuum (15″Hg). The vacuum was then turned off to allow the disk to soak with solvent for one minute. The remaining solvent was then pulled through the disk and the disk was allowed to dry. Since, the extraction disk composed of hydrophobic materials that did not allow water to pass. The disk was conditioned by pre-wetting with water-miscible solvent (10.0 ml methanol, soaked 1 minute and 10.0 ml ultra pure water respectively) before using for sample extraction and also after disk washing. The methanol was added to the extraction apparatus where a vacuum was applied (1-2″Hg) until a few drops of solvent pass through the disk. The disk was then allowed to soak with solvent for a minute after the vacuum was turned off. Once the soaking time was over, the vacuum was applied again. The remaining solvent was drawn through the disk but the vacuum and stopped before the disk went dry. The water sample was added to the extraction apparatus. A vacuum was applied to draw the water through the disk and stopped before the disk went dry. A 2-3 mm of water was left above the surface of the disk. The disk surface must avoid air exposure until the entire sample had been drawn through the disk.

After the washing and conditioning steps, 500 ml of water sample was transferred into the reservoir and, under full vacuum (approximately 7.5″Hg or 75-100 ml/min for clean water), loaded as quickly as the vacuum would allow. This took about 10 minutes. A 500 ml of water sample was transferred through the C_{18} Empore disk media. The extract disk was then allowed to dry by maintaining the vacuum for 3 minutes. After the

disk was completely dried, the entire standard filter assembly was removed and a 60-ml collection tube was inserted to receive the eluate. The drip tip of the filtration apparatus was sealed below the neck of the collection tube to prevent the analyte loss due to splattering when vacuum was applied. Three target analytes of polychlorinated biphenyls were initially eluted from the disk with 5.0 ml acetone. Then, the disk was allowed to soak with solvent for 15-20 sec. The sample flask was rinsed with 10.0 ml acetonitrile and added to disk. Finally, 2 x 5.0 ml of methylene chloride was used to be the last elution solvent for PCBs extraction from C_{18} Empore disk. The resulting solvent extract was transferred to a 50-ml round bottom flask, dried by evaporation. Two ml of isooctane was then cleaned up and analyzed by GC-MS respectively.

2.3.3.10 Clean up

Two ml of isooctane extractant from 2.3.3.9 was transferred to a 10-ml vial with a PTFE-lined screw cap and, in a fume hood, carefully added 5.0 ml of the 1:1 sulfuric acid/water solution as indicated by EPA3665A (Environmental Protection Agency, 1996). The vial was then capped tightly and shook for one minute. The phases were allowed at least 1 minute to separate. The isooctane layer was transferred to a clean 10-ml vial with a PTFE-lined screw cap. This was done by carefully to avoid acid layers since any acid contamination could cause damage to the analytical instrument. Once the isooctane layer was removed, a second "extraction" of the acid layer was performed as describe below. This second extraction was done to ensure quantitative transfer completeness of the PCBs. The second isooctane layer was removed and combined with the first isooctane extractant from the previous part. The combined isooctane layers was transferred to 50-ml round bottom flask. The solvent was evaporated to dry and the final volume was modified to 1.0 ml using an automicrolitter pipette.

2.3.3.11 Recovery

To obtain the absolute recovery of PCBs, the appropriate elution solvents from literature reviews were studied. Methylene chloride (Lacorte *et al.*, 2000 and Singh *et al.*, 1998), hexane (Sulkowaski *et al.*, 1999 and Molina *et al.*, 2000), ethyl acetate (Russo *et al.*, 1999), hexane-ethyl acetate 1:1 v/v (Weigel *et al.*, 2001) and methylene chloride-ethyl acetate 1:1 v/v were selected to study the recovery of PCBs by using as a last eluent. The experiment was done in fifth replicates.

2.3.4 Qualitative and quantitative analysis of PCBs residue in water

- Selecting Sampling sites

Two wells near the wastewater treatment pond and landfill of Songkhla municipal were selected as the sampling site. In order to get information and the characteristic of draining water into environment from the contaminant source. We used the municipal map and interviewed people who lived in those areas.

- Sample collection

The water samples were collected from the wells that were used for consumable and non-consumable. All sampling sites were within 1 km. of the wastewater treatment pond and landfill.

Four liters of water sample per sampling site was pumped through a lab built filtration unit (Figure 7) using a small fish tank pump. This was to eliminate the particulate matter before extraction. The physical and chemical properties of water sample (pH, total dissolved solid (TDS), conductivity and temperature) were measured at site by a multimeter (CHECK-MATE 90, Mettler-Toledo Ltd., USA). Water sample was then collected in clean amber glass containers and stored at $\leq 4^{\circ}C$ from the time of collection until extraction. The sample was extracted within 7 days after collection and

analyzed within 40 days after extraction as set by EPA3535A (Environmental Protection Agency, 2000).

- Qualitative and Quantitative Analysis

The qualitative analysis of the contaminants was determined based on retention time and comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. The contaminants were identified according to the following criteria.

a) simultaneous detection of a peak for all ions monitored were within the expected retention time window for each compound;

b) The relative retention time (RRT) of the sample component was within ± 0.01 RRT units of the RRT of the standard component;

c) The relative intensities of the characteristic ions agreed within 20% of the relative intensities of these ions in the reference spectrum or the ion intensity ratios of the peak were within 20% of the mean values of reference standards as referred to EPA8270D (Environmental Protection Agency; 1998)

d) signal to noise ratio ≥ 3:1

The quantification analysis based on SIM mode that PCB138 was monitored at m/z 218$[M-4Cl]^+$, 290$[M-2Cl]^+$, 360$[M]^+$; PCB153 was monitored at m/z 218$[M-4Cl]^+$, 290$[M-2Cl]^+$, 360$[M]^+$ and PCB180 was monitored at m/z 252$[M-4Cl]^+$, 324$[M-2Cl]^+$, 396$[M]^+$

For the quantitative analysis, an individual concentration of PCB congeners in a water sample was calculated against a calibration curve that obtained from five-point concentration of the working standard solutions.

Chapter 3

RESULTS AND DISCUSSION

3.1 Optimization of the analysis conditions

3.1.1 The optimum carrier gas flow rate

The optimum gas flow rate was determinated by considering the relationship between height equivalent to a theoretical plate (HETP) and the carrier gas flow rate. The HETP was calculated by the van Deemter equation.

$$HETP = A + \frac{B}{\bar{u}} + C\bar{u} \qquad (1)$$

where A is eddy diffusion term, represents the band broadening that occurs because of random choices of multiple paths available for analytes in packed columns. The $B/\bar{u}$ is the longitudinal diffusion term, represents the diffusivity of the analyte in the mobile phase and the $C\bar{u}$ is mass- transfer rate term, refers to the resistance to mass transfer of the analyte between the two phases.

However, in this study a 30 m. open tubular column (0.25 mm i.d.) was used. In this column a liquid phase is coated on fused silica with no material packs into it. Therefore, all molecules in the chromatograph would followed the same path and the multiple path term could be eliminated thus

$$HETP = \frac{B}{u} + C\bar{u} \qquad (2)$$

which is known as the Golay equation (Townshend, 1995).

The above equation showed that HETP is proportional to the flow rate of carrier gas (ū). It is also known that an optimum carrier gas flow rate will give an optimum column resolution would give the narrowest HETP (Grob, 1985). To indicate column efficiency the term H (i.e. HETP) is determined according to the equation

$$H = \frac{L}{N} \qquad (3)$$

where L is length of column in centimeters and N is the number of theoretical plates. The plate number N of a column may be determined directly from a chromatogram as shown in Figure 9 by the relation

$$N = (\frac{4t_R}{W_b})^2 \qquad (4)$$

where t_R is the retention time and W_b is the base peak width as shown in Figure 7 Another common way to determine N makes use of the relation

$$N = 5.54\,(\frac{t_R}{W_{1/2}})^2 \qquad (5)$$

where $W_{1/2}$ is the width at half the peak height.

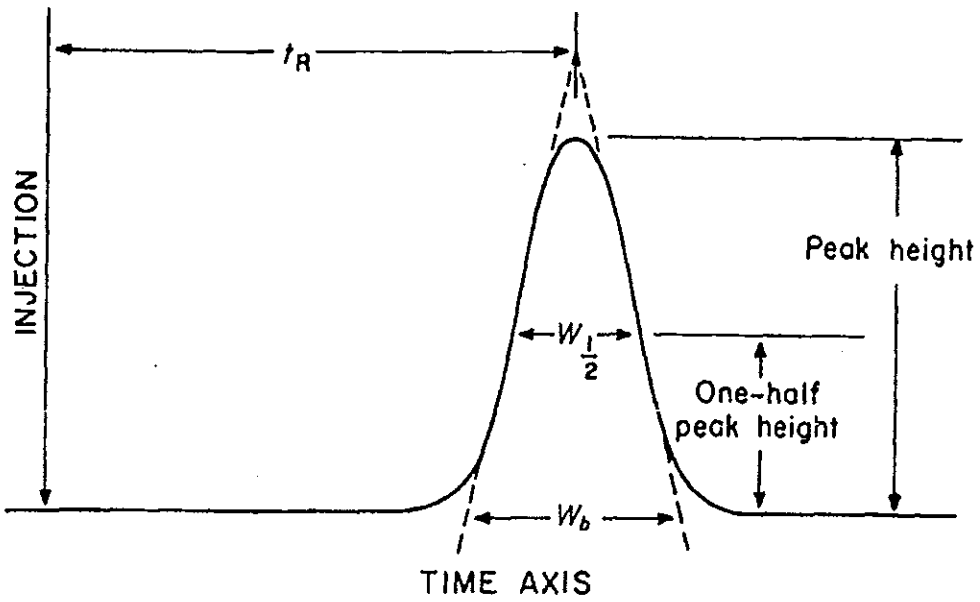


Figure 9 Measurement of t_R, W_b and $W_{1/2}$

So in this study, Equation (5) was used to calculate the HETP at various flow rates. The value N is then substituted in equation (3) to obtain H. A plot between HETP and carrier gas flow rate was done to find the optimum carrier gas flow rate at minimum HETP.

Table 3 and Figure 10 show the relationship between the carrier gas flow rate and HETP of three Polychlorinated biphenyl congeners. Each of the van Deemter graph of PCB congeners gives the HETP value at various flow rates does not differed from each other due to a long length of capillary column (30 meter) and a high number of theoretical plates. The graphs show the lowest of HETP value for PCB153, 138 and 180 at flow rates of 0.8, 0.8, 1.0 ml/min respectively.

Since, this study would be for multiresidue analysis Therefore, the optimum flow rate of carrier gas was considered from the best of flow rate that gave the lowest HETP and high efficiency to separate the three PCB congeners. Refer to Table 3, both congeners (PCB153 and 138) show the lowest HETP value at the flow rate of 0.8 ml/min, that is, this flow rate gave the highest

number of theoretical plates. The efficiency of separation PCB153 and 138 was excellent while PCB180 shows the lowest HETP value at 1.0 ml/min.

Typically a high flow rate of carrier gas will reduce the analysis time without significantly changing the efficiency of the analysis. Although at the flow rate of 1.0 ml/min the column gave a good separation similarly to the flow rate at 0.8 ml/min, but the chromatogram of PCB153 peak was eluted at the position near the solvent peak (delay time 6.00 min). This may lead to an interference by a solvent peak or other compounds in the real matrix. Therefore, the optimum carrier gas flow rate for three PCB congeners at 0.8 ml/min was chosen.

In Figure 10, the van Deemter graph of the three PCB congeners is plotted to establish the correlation between the carrier gas flow rate and height equivalent to a theoretical plate (HETP) using Golay equation (2) that rearranged from van Deemter equation (1).

Table 3 The height equivalent to a theoretical plate (HETP) of three PCB congeners (100 ppb) at various of carrier gas flow rate

Flow rate (ml/min)	Height Equivalent Theory Plate or HETP (cm.)		
	2, 2′, 4, 4′, 5, 5′-Hexachloro biphenyl (PCB153)	2, 2′, 3, 4, 4′, 5′-Hexachloro biphenyl (PCB138)	2, 2′, 3, 4, 4′, 5, 5′-Heptachloro biphenyl (PCB180)
0.5	0.412	0.320	0.263
0.8	0.368	0.261	0.237
1.0	0.394	0.269	0.209
1.2	0.387	0.273	0.246
1.5	0.382	0.312	0.251

* 5 replication, RSD < 4%

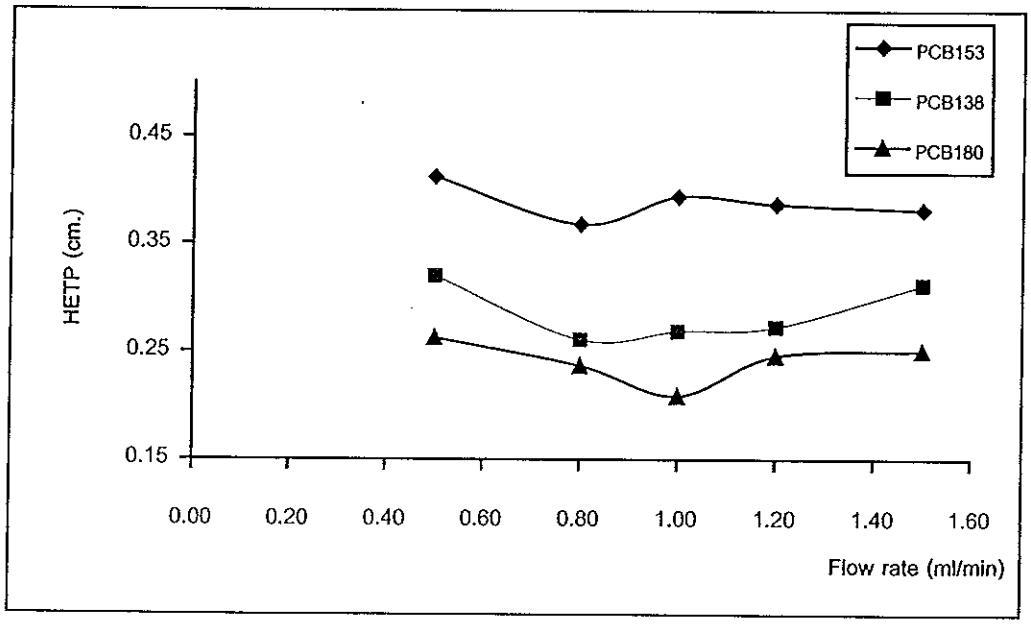


Figure 10 The van Deemter plot of three PCB congeners

3.1.2 The optimum column temperature programming

The results of the investigated parameters in the column temperature programming were shown in Tables 4-11 and Figures 11- 20.

Table 4 and Figure 11 show the relative response of the retention time and abundance of PCB153 congener at various initial temperatures. The retention decreased when the initial temperature increased. By comparing the abundance from MSD, the initial temperature at 130°C provides a highest value and a good separation. Therefore, the temperature at 130°C is chosen to be an optimum initial temperature. Although in many literatures, the initial temperature was generally recommended to be lower than the boiling point of the solvent about 10-20°C (Grob, 1985). Because at that temperature the analyte would volatilize gradually and gone into the column without lost of the gas phase yield. However, the boiling points of the three congeners are very high (Appendix, Table B) therefore the above criteria can not be followed.

Table 4 Relative response of PCB153 (100 ppb) at various initial temperature with the retention time and abundance from MSD

Temperature	Retention time (Min.)	Abundance from MSD* (10^4)
80	11.05	3.87
90	10.55	3.93
100	10.04	4.08
110	9.54	4.20
120	9.04	4.18
130	8.54	4.27
140	8.04	4.01
150	7.54	3.54

* 5 replication, %RSD < 4

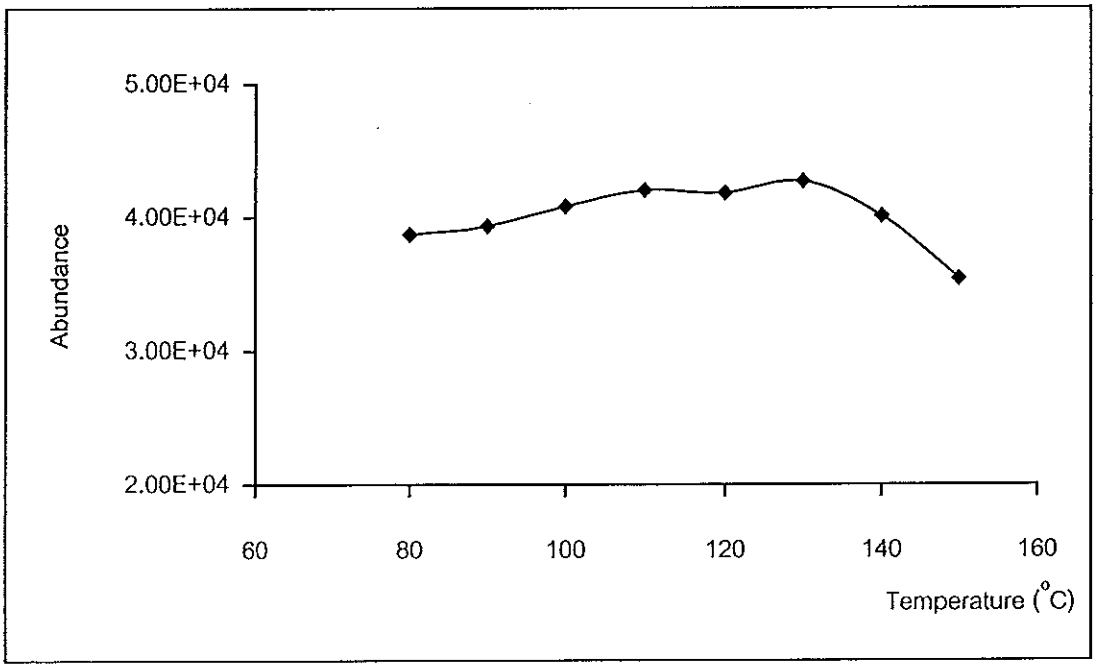


Figure 11 The abundance of PCB153 at various initial temperature showing 130°C was the optimum initial temperature

Table 5 and Figure 12 show the abundance of PCB153 congener at initial temperature (130°C) with the hold time between 0 to 4 minute. The abundance of PCB153 congener is higher when there is some hold time between 1, 2, 3 and 4 minutes the abundance are approximately the same, differ less than 10%. To ensure the efficiency of separation thus, the hold time for 2 minutes is chosen to be an optimum hold time at initial temperature.

After holding the temperature at 130°C for 2 minutes, the column temperature was programmed to increase rapidly to 300°C with different ramp rate. Thc abundance of the PCB153 congener (Table 6 and Figure 13) at 40°C/min showed the highest response. Although the abundance observed at the ramp rate 40°C/min and 50°C/min are approximately the same value but the latter ramp rate fail to separate the second (PCB138) and third (PCB180) peaks. They were eluted out too rapidly and were overlapping. Moreover, the first peak (PCB153) was eluted near the solvent delay time (6.0 minutes) and the peak would not appear in the chromatogram. So, the ramp rate at 40°C/min is chosen to be an optimum ramp rate for this investigation.

However, it was found that the last chromatogram (PCB180) showed a low abundance compared to the others. This is because the MS response decreases with increase level of chlorination (EPA608, Environmental Protection Agency, 1985). To increasing the response or abundance of the last chromatogram, the column temperature programming was divided in two steps the above ramp rate was used in the first stage and then the second stage of temperature was investigated (Figure 14).

Table 5 Relative response of PCB153 (100 ppb) at various hold time at 130°C with abundance from MSD

Hold time (Min)	Abundance from MSD* (10^4)
0	3.67
1	4.64
2	4.61
3	4.83
4	4.78

* 5 replication, %RSD < 4

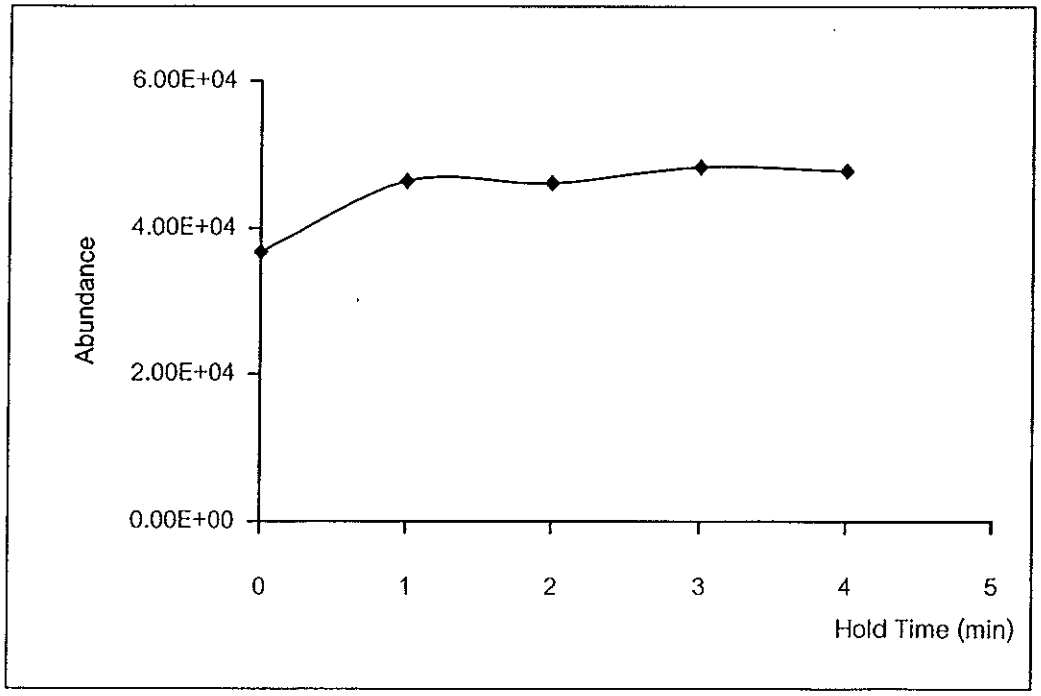


Figure 12 The abundance of PCB153 at various hold time at 130°C showing 2 minutes was the optimum hold time

Table 6 Relative response of PCB153 (100 ppb) at various of first stage of ramp rate with the retention time and abundance from MSD

Ramp rate (°C/min)	Retention time	Abundance from MSD* (10^4)
10	13.64	2.65
20	9.53	5.05
30	8.16	6.64
40	7.42	7.79
50	7.05	7.65

* 5 replication, RSD < 4%

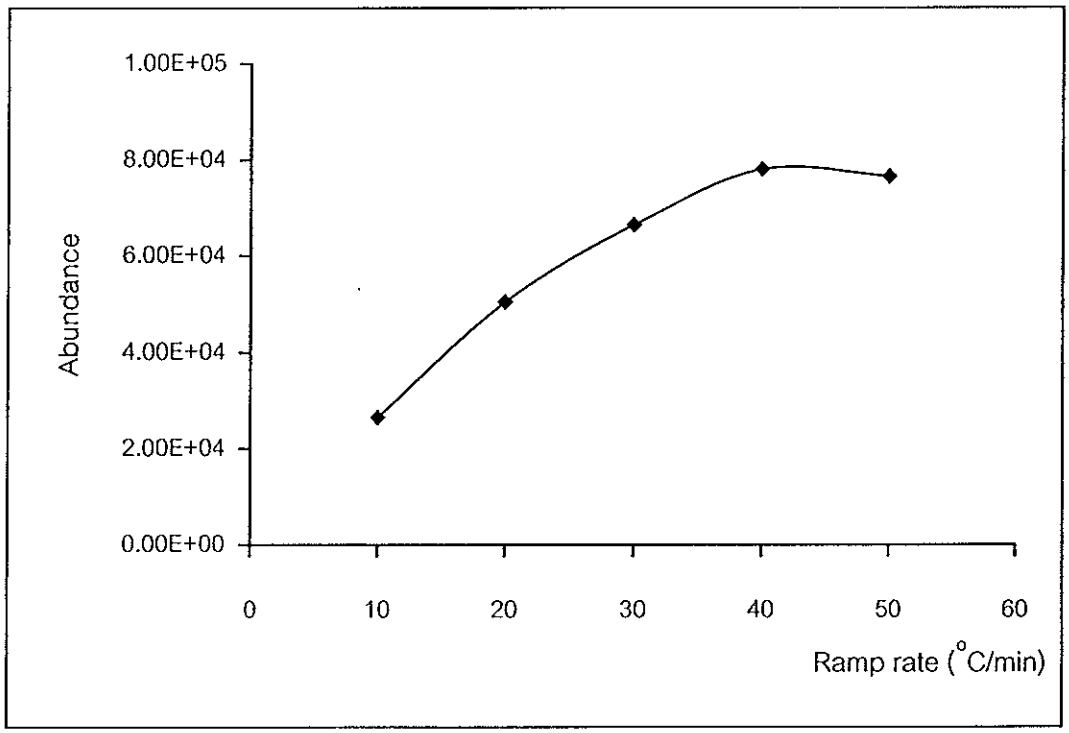


Figure 13 The abundance of PCB153 at various of first stage of ramp rate showing 40°C/min was the optimum first stage of ramp rate

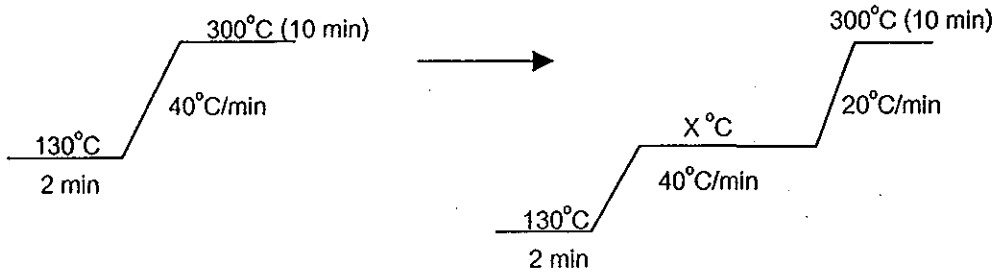


Figure 14 The column temperature programming changed to be 2 stages for increasing abundance of third peak (PCB180)

Table 7 and Figure 15 show the abundance of PCB153 congener when the second stage of temperature was investigated between 180°C to 260°C. The results show the highest abundance of the PCB153 congener at 250°C. Therefore, the temperature at 250°C was chosen to be an optimum of the second stage of temperature.

The purpose of dividing the column temperature programming into two steps was to increase the abundance of PCB180. However, in doing this the abundance of the PCB153 decreased about 35%. Therefore, in order to re-improve the abundance of PCB153 and other congeners simultaneously, other parameters were investigated at this second stage to obtain temperature program that would be suitable for all analytes.

Table 7 Relative response of PCB153 (100 ppb) at various of the second stage of temperature with abundance from MSD

Temperature	Abundance from MSD* (10^4)
180	3.92
190	4.13
200	4.38
210	4.28
220	4.44
230	4.58
240	4.85
250	5.08
260	4.45

* 5 replication, %RSD < 4

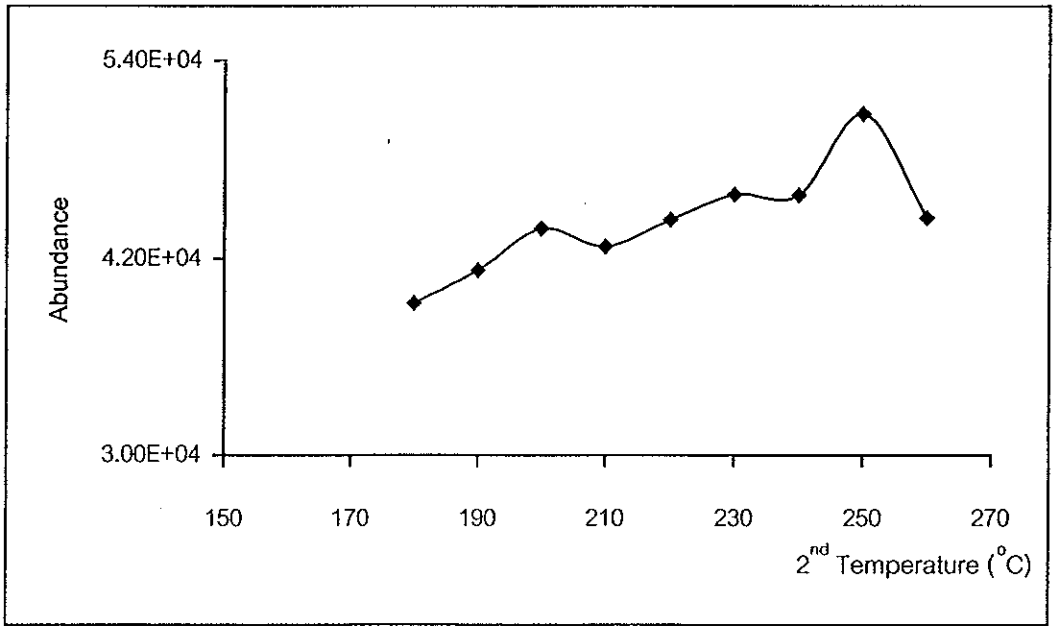


Figure 15 The abundance of PCB153 at various of the second stage of temperature showing 250°C was the optimum second stage of temperature

Table 8 and Figure 16 show the abundance of PCB153 congener at various hold time at the second stage of temperature (250°C). MSD gives the highest abundance of the PCB153 without holding at 250°C and the abundance decreases when increases the hold time. Therefore, at this second stage of temperature no hold time would be used as optimum condition.

The second stage of ramp rate was investigated between 10 to 30°C/min with increment of 5°C/min in order to find the highest resolution between the second (PCB138) and third (PCB180) peaks. The results (Table 9 and Figure 17) show that the abundance of PCB153 congener increases continually when increases the ramp rate, this is because this congener has a high boiling point and low polarity. However, an optimum is chosen at the ramp rate 25°C/min, instead of 30°C/min which gave the highest value, because the chromatogram showed a better resolution and the first peak (PCB153) would not be eluted out too rapidly and near the solvent delay time (Figure 18).

Table 8 Relative response of PCB153 (100 ppb) at various hold time at 250°C with abundance from MSD

Hold time (Min)	Abundance from MSD* (10^4)
0	5.31
1	4.32
2	3.51
3	2.60
4	2.50

* 5 replication, %RSD < 4

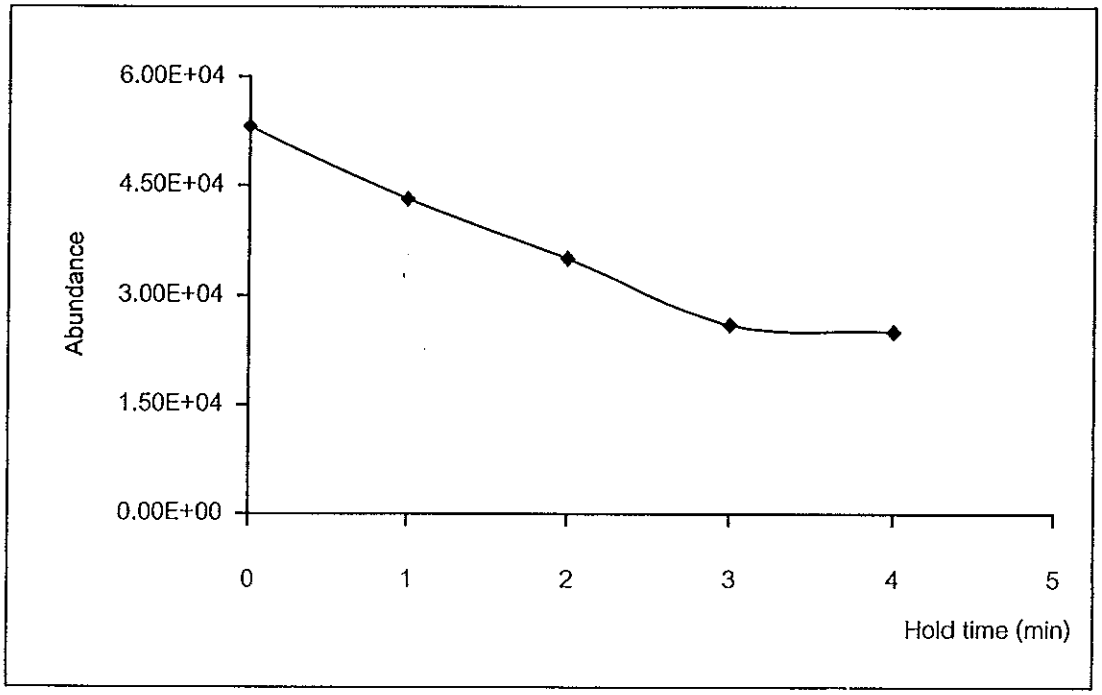


Figure 16 The abundance of PCB153 at various hold time at 250°C showing no hold time as an optimum condition

Table 9 Relative response of PCB153 (100 ppb) at various of second stage of ramp rate with the retention time and abundance from MSD

Ramp rate (°C/min)	Retention time	Abundance from MSD* (10^4)
10	7.30	4.19
15	7.24	4.86
20	7.19	5.54
25	7.10	6.09
30	7.02	6.44

* 5 replication, %RSD < 4

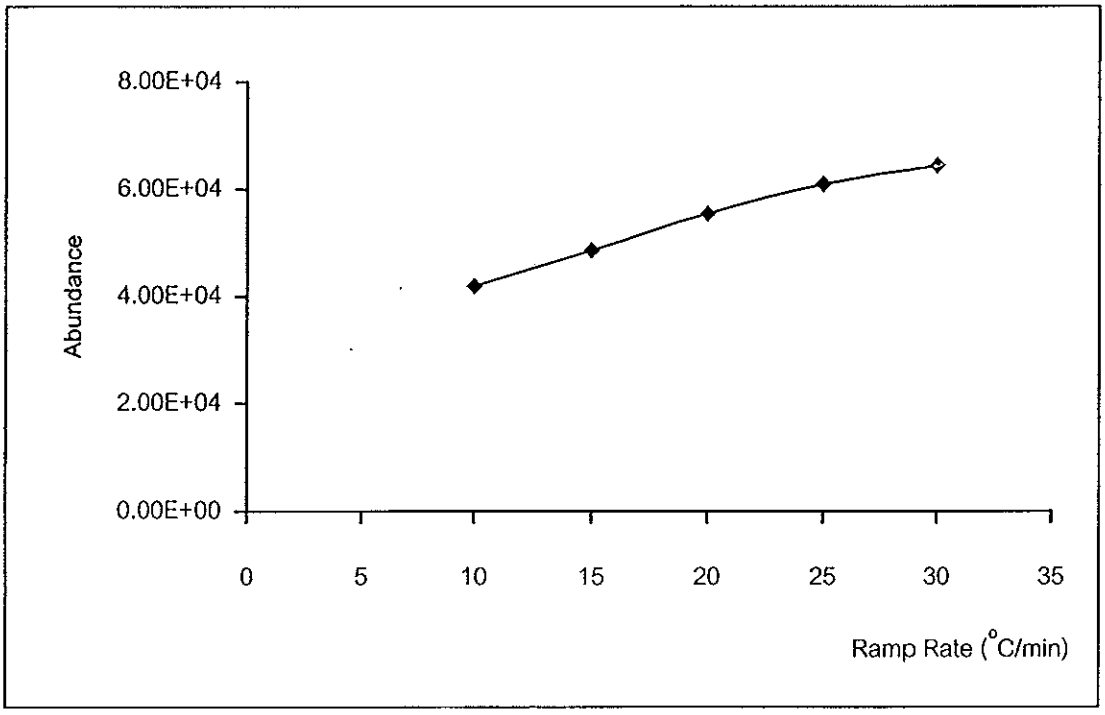


Figure 17 The abundance of PCB153 at various second stage of ramp rate showing 25°C/min was the optimum second stage of ramp rate

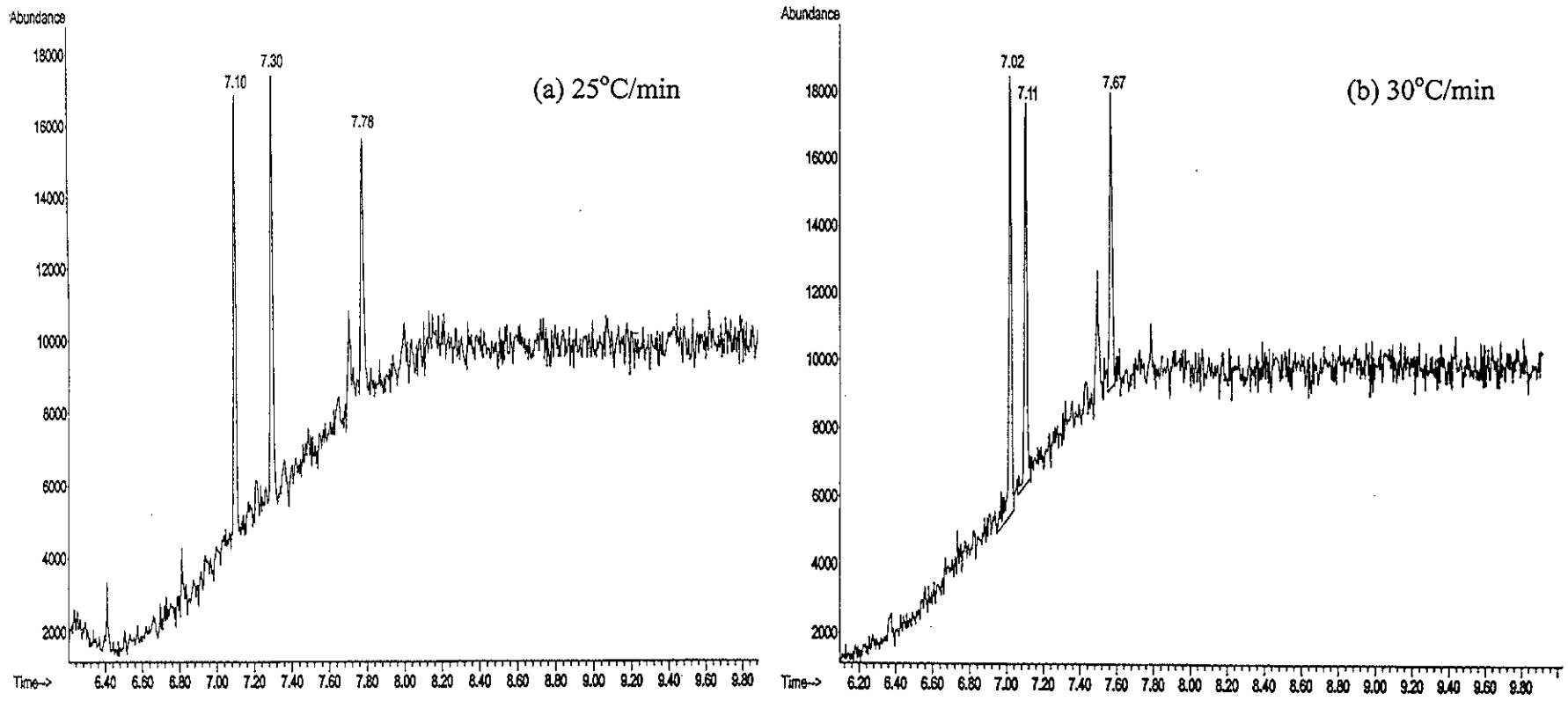


Figure 18 Comparison the resolution of three PCB congeners analysis between using the ramp rate at 25°C/min and 30°C/min

To investigate the optimum final temperature, it was varied from 260 to 310°C. The abundance increased with temperature until 280°C and then leveloff (Table 10 and Figure 19). In this case the temperature at 300°C is chosen to be an optimum final temperature to ensure the high abundance and maintain the lifetime of the column since the maximum acceptable temperature of HP-5MS column is 325°C. The optimum temperature should not be over this value (Grob, 1985).

In conclusion the optimum condition of the column temperature programming is 130°C, hold for 2 min, then rampped at 40°C/min to 250°C, immediately ramp 25°C/min to 300°C, and hold 10 min to let signal went back to the baseline (Figure 22).

3.1.3 The optimum injector temperature

Table 11 and Figure 20 show the abundance of PCB153 congener at injector temperatures between 210 to 260°C. The MSD gave the highest abundance of PCB153 congener at 230°C. Therefore, the temperature of 230°C is chosen to be an optimum injector temperature for analysis.

Table 10 Relative response of PCB153 (100 ppb) at various final temperature with abundance from MSD

Temperature	Abundance from MSD* (10^4)
270	4.00
280	4.52
290	4.50
300	4.55

* 5 replication, %RSD < 4

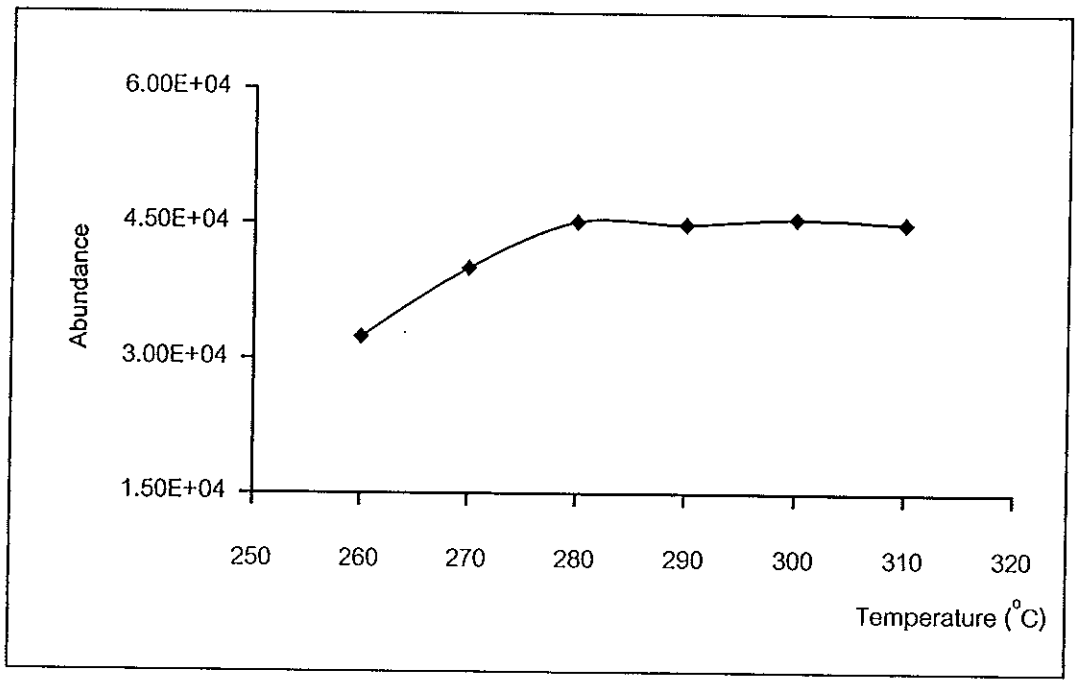


Figure 19 The abundance of PCB153 at various final temperature showing 300°C was the optimum final temperature

Table 11 Relative response of PCB153 (100 ppb) at various injector temperature with abundance from MSD

Temperature	Abundance from MSD* (10^4)
210	4.93
220	4.99
230	5.20
240	5.11
250	5.07
260	5.05

* 5 replication, %RSD < 4

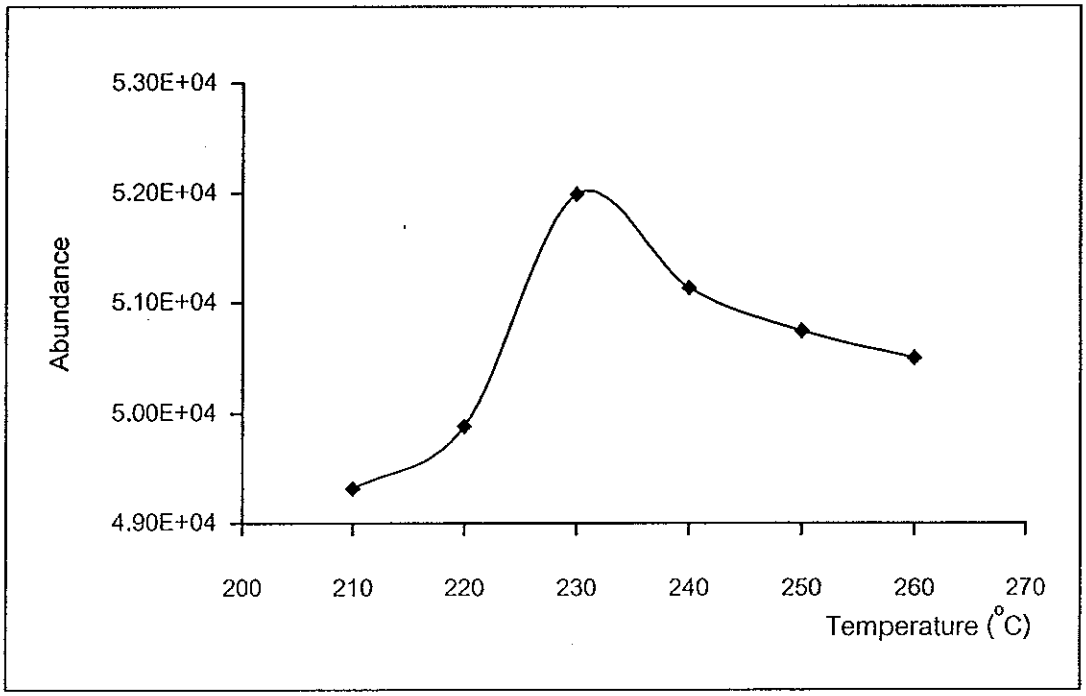


Figure 20 The abundance of PCB153 at various injector temperature showing 230°C was the optimum injector temperature

3.1.4 The optimum transfer line temperature

Table 12 and Figure 21 show the abundance of PCB153 congener after investigated the transfer line temperature by varying temperature from 260 to 300°C with increment of 10°C as described in 2.3.3.4. The highest abundance of PCB153 congener was obtained at 290°C. Therefore, the temperature at 290°C is chosen to be an optimum temperature for the analysis.

In conclusion the optimum conditions of analysis are obtained as follow.

Carrier gas flow rate:	0.8 ml/min
Column temperature program:	130°C, hold for 2 min, then rampped at 40°C/min to 250°C, immediately ramp 25°C/min to 300°C, and hold 10 min
Injector temperature:	230°C
Transfer line temperature:	290°C
MS source:	230°C
MS Quadrupole:	150°C

The total ion current chromatogram after completing the optimization of conditions for analysis three PCB congener is shown in Figure 22.

Table 12 Relative response of PCB153 (100 ppb) at various transfer line temperature with abundance from MSD

Temperature	Abundance from MSD* (10^4)
260	5.46
270	5.46
280	5.50
290	5.62
300	5.57

* 5 replication, RSD < 4%

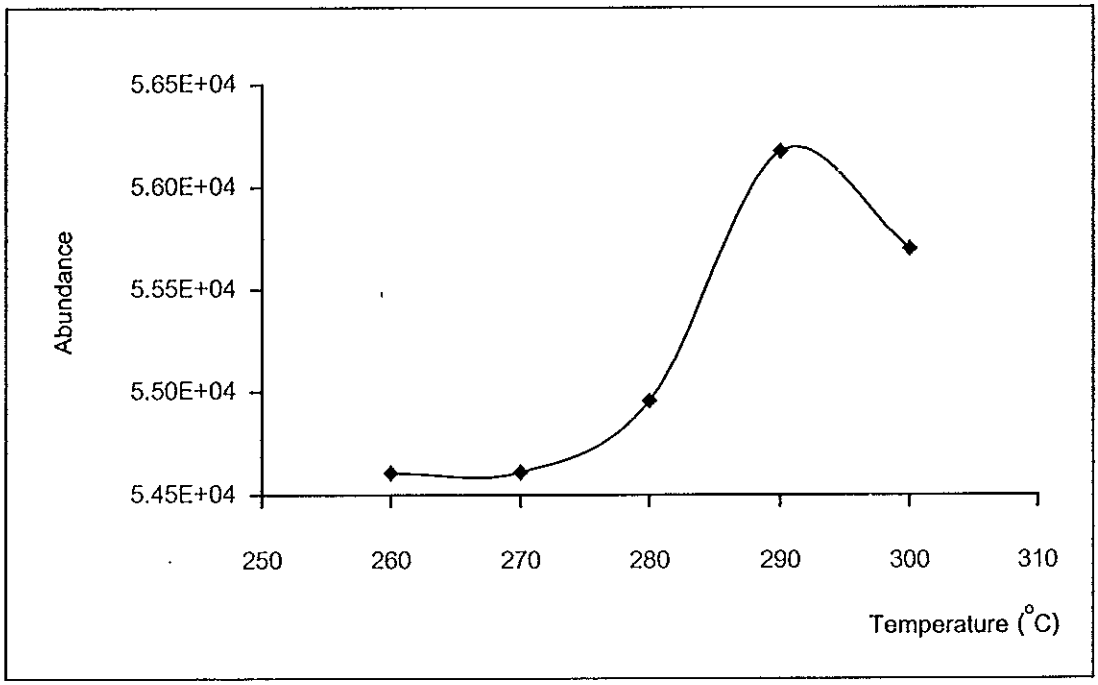


Figure 21 The abundance of PCB153 at various transfer line temperature showing 290°C was the optimum transfer line temperature

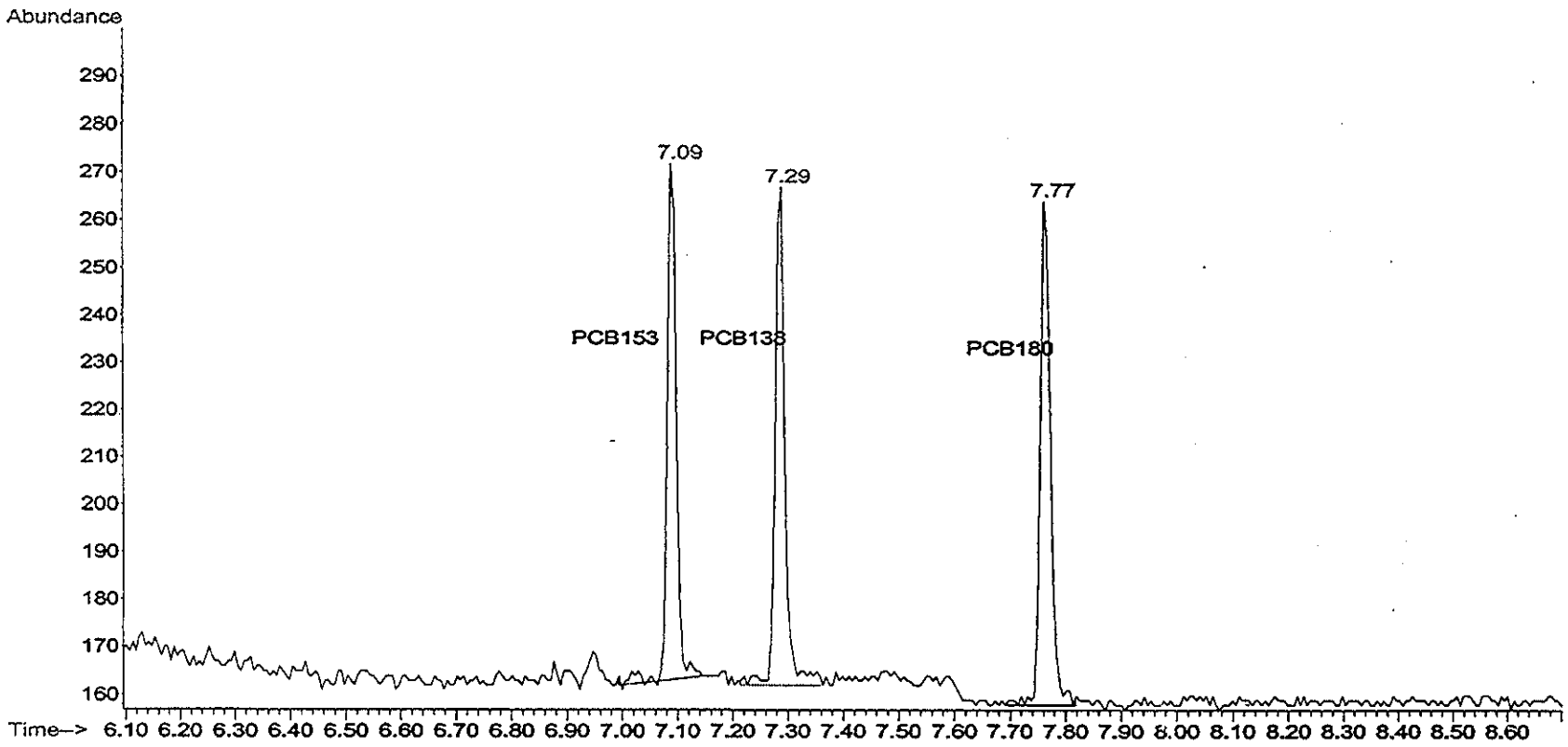


Figure 22 Total ion current chromatogram after autoinjection 1-µl of 10 ppb the PCBs working standard solution into GC-MS with condition 130°C, hold 2 min, ramp 40°C/min, 250°C, ramp 25°C/min, 300°C, hold 10 min; flow rate 0.8 ml/min; injector 230°C, transfer line 290°C, SIM mode

3.1.5 Limit of detection

In the trace analysis of PCBs by this GC-MS system, the S/N ratio was calculated automatically by the Chemstation Operating Software. The concentrations of the PCB congeners where a S/N is more than 3.0 were shown in Table 13. In addition to the S/N the limit of detection in the table were also considered by the relative retention time (within ± 0.01) and the relative intensities of mass ratio (within 20% of the mean values) as EPA's quality and quantity requirement (Environmental Protection Agency, 1998).

The limit of detection of each PCBs congener is shown in Table 13. The different efficiency of the mass selective detector to each congener was due to the different structure of the compounds (Figure 3). It can be seen that the limit of detection for individual PCB congeners increased when the number of chlorine atoms increased. This correlated well with the information given in EPA680 (1985). The limit of detection of PCB153 and 138 are at the same concentration, 0.06 ppb or 60 ppt, while PCB180 is at 0.07 ppb or 70 ppt. These are similar to those reported by Larcorte *et al.* (2000).

Table 13 The limit of detection of the mass selective detector for three PCB congeners with S/N ≥ 3.

Concentration (ppb)	Abundance from Mass selective detector		
	2, 2′, 4, 4′, 5, 5′-Hexachloro biphenyl (PCB153)	2, 2′, 3, 4, 4′, 5′-Hexachloro biphenyl (PCB138)	2, 2′, 3, 4, 4′, 5, 5′-Heptachloro biphenyl (PCB180)
0.05	N.D	N.D	N.D
0.06	43.86	46.85	N.D
0.07	46.81	58.15	32.93
0.08	53.06	59.85	41.18
0.09	70.45	73.22	47.59
0.10	73.23	80.55	53.70
1.00	653.20	626.87	547.61
10.00	5780.81	5507.23	4229.43

3.1.6 Linear dynamic range (linearity)

The linear dynamic range is the characteristic of the detector. It is the concentration where the range detector response is linear. Over this linear range the response factor of a detector (peak area units per weight of sample) is constant.

Table 14 and Figure 23 show the linear dynamic range of the response of the mass selective detector to each PCB congeners at six concentrations of standard solution. The system is linear over the concentration range 50 ppt – 1.0 ppm with correlation coefficient of all congeners (R^2) ≥ 0.99. This was agreed well with Larcorte *et al.* (2000). These results indicated that the MSD gave a high sensitivity over the range being studied.

However, to follow the quality assurance criteria for PCBs analysis (EPA680, 1985). To provide the correct and reliable data, the identification of the lowest of the linear range must take into consideration. Therefore, the dynamic range for PCB138 was in the range from 60 ppt – 1.0 ppm, PCB153: 60 ppt -1.0 ppm and PCB180: 70 ppt – 1.0 ppm. Each range will provide the high reproducibility and repeatability for analysis.

Table 14 The correlation coefficient of three PCB congeners

PCBs congener	r^2
2, 2′, 3, 4, 4′, 5′ - Hexachlorobiphenyl (PCB138)	0.9978
2, 2′, 4, 4′, 5,5′ - Hexachlorobiphenyl (PCB153)	0.9989
2, 2′, 3, 4, 4′, 5, 5′ - Heptachlorobiphenyl (PCB180)	0.9985

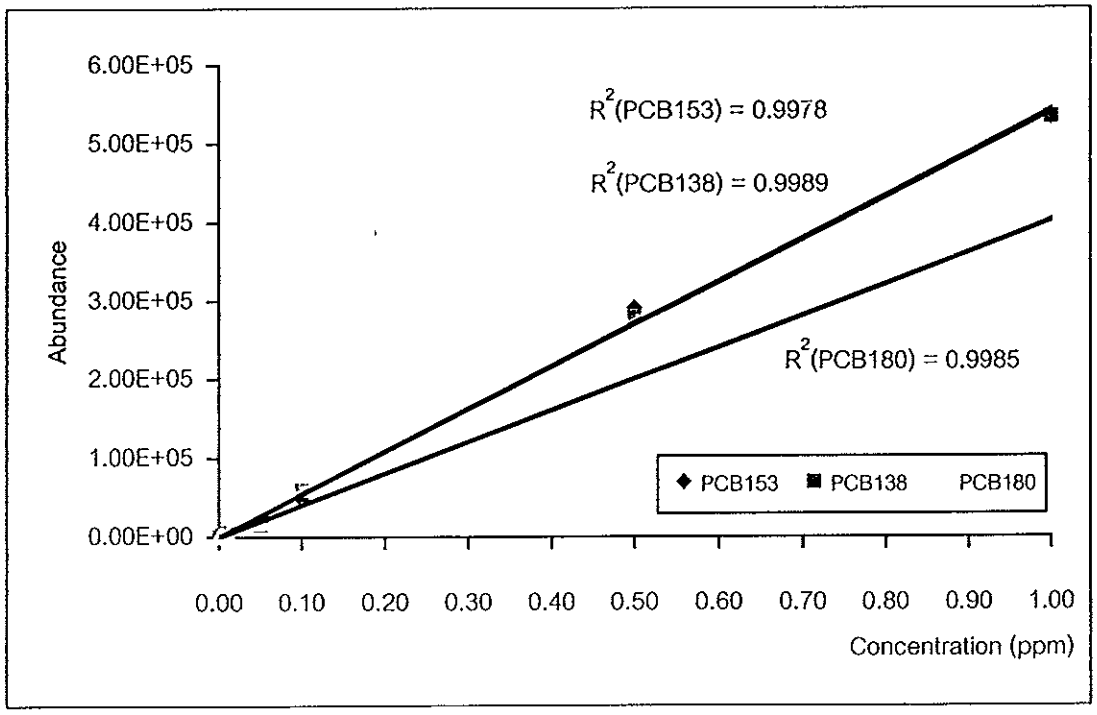


Figure 23 The linear dynamic range of three PCB congeners

3.1.7 The response factor

Response factors (RF) were determined by using the integrated peak response of each analyte at various concentrations, comparing with the integrated peak response of PCB153 congener that was assigned the RF equal to 1.00. The results are shown in Table 15.

Each congener when compared to PCB153 (assigned RF=1.00), gives a value of response factor nearly 1.00 with a mean 1.00 ± 0.01. These result agreed well with those found by Sauter et.al.(1986). Sauter and coworker reasoned that because of the separation has according to the PCB shape. All congeners have the ortho substitution in their structure. Correlation to the model for the estimation of electron impact radio frequency utilized terms for ion transmission, fractional ion abundance, ionization cross section, and molecular weight after studied ten PCB congeners, it gave an observed the RF in range from 0.86-1.13 with a mean of 1.05 ± 0.088.

Table 15 Relative Response factor of three PCB congeners at various concentration

Concentration (ppm)	2, 2′, 4, 4′, 5, 5′-Hexachloro biphenyl (PCB153)	2, 2′, 3, 4, 4′, 5′-Hexachloro biphenyl (PCB138)	2, 2′, 3, 4, 4′, 5, 5′-Heptachloro biphenyl (PCB180)
0.01	1.00	0.98	1.02
0.05	1.00	1.02	1.22
0.10	1.00	1.03	1.00
0.50	1.00	1.04	0.91
1.00	1.00	1.02	0.79

3.1.8 Quantitative analysis by Internal Standard Plot Method

From the study in 2.3.3.8, the relationship between concentration of the three PCB congeners and the ratio of analyte to internal standard (Chrysene-d_{12}) peak area is shown in Table 16 and Figure 24.

In chemical analysis, the internal standard plot method was performed by adding another compounds which was different to the analyte with known concentration into the sample in order to compare the signal intensity of the instrument. For this study, chrysene-d_{12} (0.10 ppm) was used to be an internal standard as recommended by EPA8082 and EPA680.

Figure 24 shows that the internal standard method can provide a better correlation coefficient (0.9999-1.000) than the external standard method (0.9979-0.9989) and gives a calculated resolution of more than 1.00 comparing to the adjacent peaks. Thus, the internal standard method was used for quantitative analysis of PCBs since it could provide a high precision with $R^2 >$ 0.99 for the quantification of all congeners.

For the determination of PCBs in the unknown by internal standard method, the signal intensity is converted to concentration. The mass or concentration of analyte in a peak area, M_a is proportional to the signal for the analyte, A_a according to the equation.

$$M_a = RF \times A_a \qquad (a)$$

Table 16 The relation between the concentration of three PCB congeners and the ratio of peak area of analyte to internal standard (Chrysene-d_{12})

Concentration (ppm)	2, 2′, 4, 4′, 5, 5′- Hexachloro biphenyl (PCB153)	2, 2′, 3, 4, 4′, 5′- Hexachloro biphenyl (PCB138)	2, 2′, 3, 4, 4′, 5, 5′- Heptachloro biphenyl (PCB180)
0.010	0.089	0.087	0.054
0.050	0.617	0.629	0.508
0.100	1.310	1.346	1.005
0.500	6.326	6.600	5.496
1.000	12.855	13.091	11.075

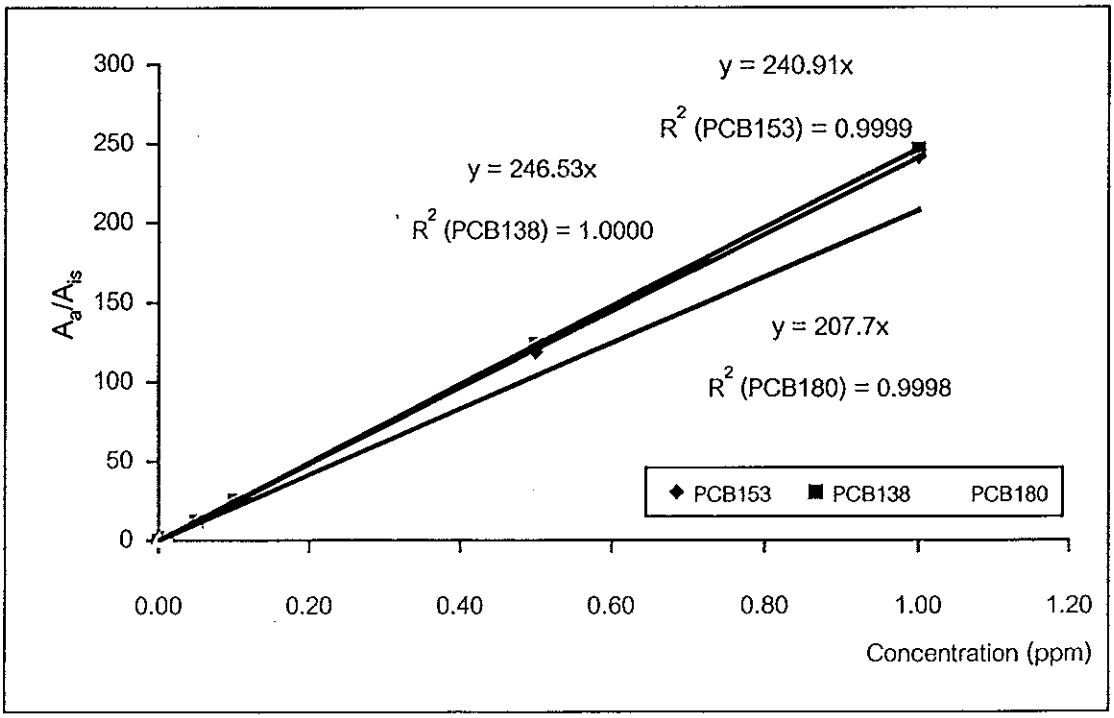


Figure 24 The relation concentration of three PCB congeners and the ratio of analyte to internal standard (Chrysene-d_{12}) peak

3.1.9 Interference effect

During the study it was found that there was an interfering peak from the phthalate group (t_R = 7.81) and this could affect the PCB180 peak integration (t_R = 7.77) as shown in Figure 25. It was thought that the phthalates might come from the distilled water in the plastic container used for the solid phase extraction technique. Phthalates are a ubiquitous laboratory contaminant since they are used as releasing agents when molding rigid plastic (e.g., PVC) and as plasticizers for flexible tubing (EPA8082, 1996).

Therefore, amber glass bottles were used instead and it was found that this could reduce the signal of phthalate by more than 50%. However, it was still affect the analyte peak thus, a cleanup method using sulfuric acid was use to eliminate this compounds from the water matrix followed EPA8082 recommendation. After that the phthalate peak disappeared from the chromatogram.

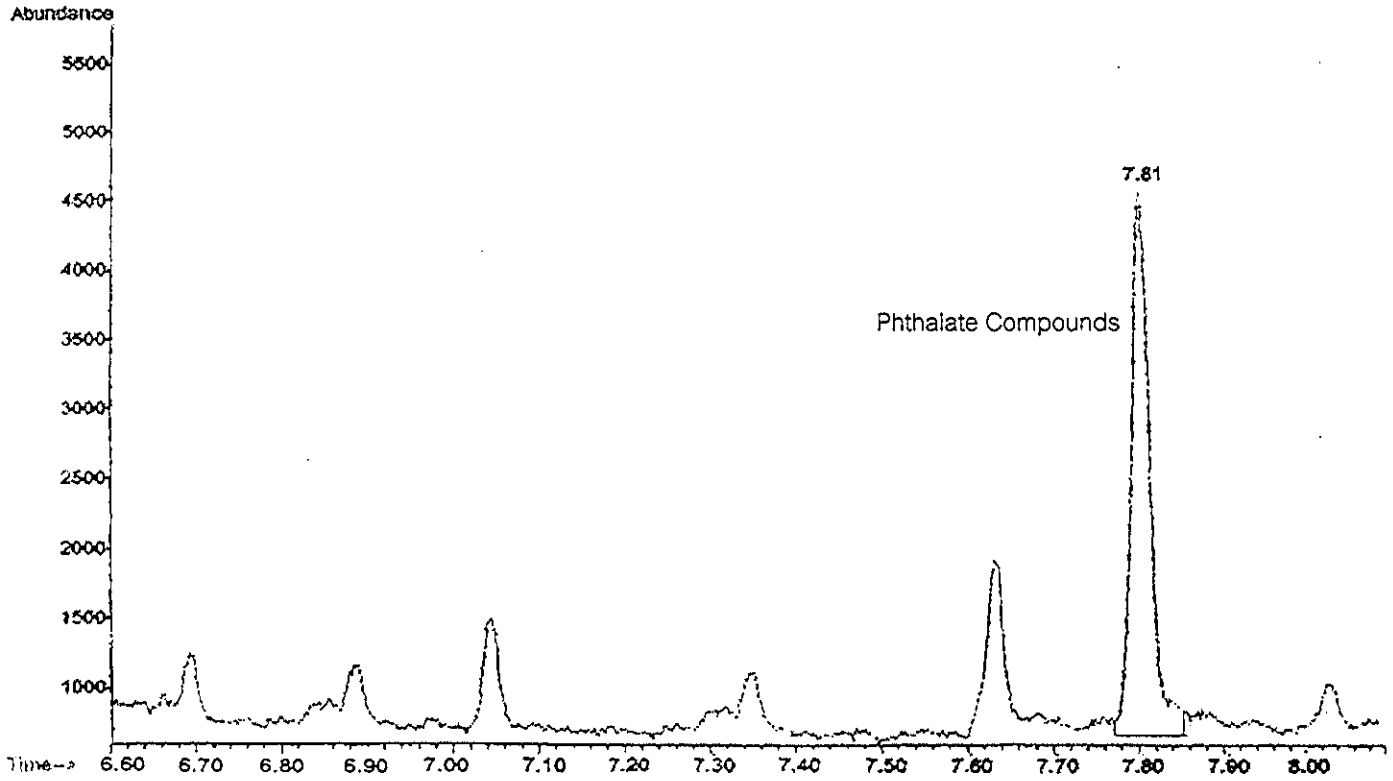


Figure 25 Total ion current chromatogram of phthalate compound in distilled water which was contained in plastic container

Another interference was the suspended particle matters (SPM) which normally presented in water matrix that would clog the disk during the isolation and preconcentration of the analyte. The removal of the SPM therefore was necessary. In this work, a lab built prefiltration unit (Figure 7) was used. This unit contained the Filter Aid 400, a non porous material comprising of glass bead with typical diameter of 40 micrometer. It is inert, resistant to leaching and providing low interference and more consistent recoveries. The suspended particle matters with large particle size would be trapped on this filter unit. The water sample would then pass through a 47 mm glass fiber filter (0.45 micrometer pore size) to remove the small size of particles before the PCBs were extracted by C_{18} Empore extraction disk. It was found that the prefiltration unit could reduce the filtration time of a 1 liter of water sample about 30% or 20 min with a flow rate 40-45 ml/min compared to the conventional method. The required filtration time was around 40-60 min per 1 liter sample. This is better than the work by Wolska *et al.* in 1999 i.e. the analysis time was 3 times less. Therefore, this is a good alternative method to separate and preconcentrate PCBs from water sample.

3.1.10 Recovery

Table 17 and Figure 26 show a comparison of the recovery of each congeners after the investigation of the extraction efficiency with five organic solvents (e.g. dichloromethane (Lacorte *et al.*, 2000 and Singh *et al.*, 1998), hexane (Sulkowaski *et al.*, 1999 and Molina *et al.*, 2000), ethyl acetate (Russo *et al.*, 1999), hexane-ethyl acetate 1:1 v/v (Weigel *et al.*, 2001) and methylene chloride-ethyl acetate 1:1 v/v). Dichloromethane provided the highest recovery (83-112%) for extraction all congeners with a percentage of relative standard deviation (%RSD) of less than 4 comparing to hexane: 74-91%, ethyl acetate: 68-101%, dichloromethane: ethyl acetate (1:1): 73-100% and hexane: ethyl acetate (1:1): 70-88%.

Table 17 The percentage recovery of extraction PCB153, 138 and 180 with hexane, ethyl acetate, dichloromethane, hexane:ethyl acetate (1:1) and dichloromethane:ethyl acetate (1:1)

Analyte	Hexane		Ethyl Acetate (EtOAc)		Dichloromethane (DCM)		Hexane : EtOAc (1:1)		DCM : EtOAc (1:1)	
	%Recovery	%RSD (n=4)	%Recovery	%RSD (n=4)	%Recovery	%RSD (n=4)	%Recovery	%RSD (n=4)	%Recovery	%RSD (n=4)
PCB153	74	8	68	10	83	3	73	5	70	2
PCB138	85	6	75	6	91	1	86	5	77	1
PCB180	91	7	101	2	112	2	100	8	88	4

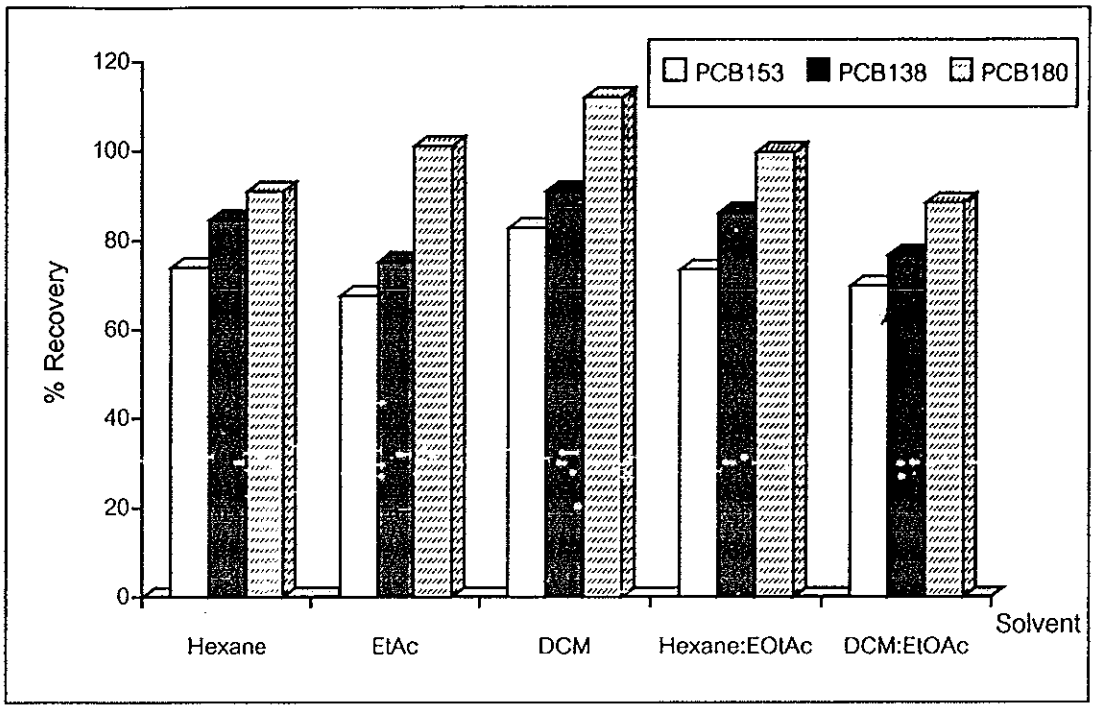


Figure 26 The recovery of extraction PCB153, 138 and 180 with hexane, ethyl acetate, dichloromethane, hexane:ethyl acetate (1:1) and dichloromethane:ethyl acetate (1:1)

It is necessary to evaluate various organic solvents for suitably extraction PCBs because the quantitative analysis of PCBs was performed simultaneously and the polarity of each PCB congener was different. The extraction by organic solvent is arisen from the partition between two immiscible liqiuds. The ratio of solute concentration in solvent to the solute concentration in water at equilibrium is called "Partition Coefficient" and is a constant value (Morison and Fresier, 1965). Therefore, the extraction efficiency of PCBs will depend on the solubility of compound in the two solvents system. If the polarity of solvent is considered, the dielectric constant could be used to find an appropriate solvent to extract PCBs from water. Normally, organic solvents with high polarity will have high electric constant and in contrast, solvents with low polarity will have low dielectric constant. The dielectric

constant of hexane, dichloromethane and ethyl acetate is equal to 1.88, 8.93 and 6.02 respectively (Honeywell Burick & Jackson company, 2000). In addition, in the term of dipole moment, the molecules that have high dipole moment will have strong polarity. The dipole moment of hexane, dichloromethane and ethyl acetate is equal to 0.08, 1.14 and 1.88 respectively (Honeywell Burick & Jackson company, 2000) these are corresponded to the polarity index, 0.1, 3.1 and 4.4 respectively (Honeywell Burick & Jackson company, 2000). Looking at the structure of PCB153, 138 and 180 and their physical properties, these compounds were moderately polar due to their weak solubility in water which are in the range of 0.014-0.038 g/m^3 at 25°C depended on the content of chlorine substituents on biphenyl nucleus (Erickson, 1997). Thus, by considering either properties as described above can be seen that PCBs could partition into dichloromethane better than hexane, ethyl acetate, DCM:EtOAc (1:1) and hexane:EtOAc (1:1). Ethyl acetate has high polarity from its carbonyl group and this decreases the efficiency of the mixture solvent that contains ethyl acetate in the extraction of PCBs and hence, the low recovery. Therefore, the dichloromethane was chosen to be an appropriate solvent for extraction PCBs in water. The results that were similar to EPA680, 1985; Federal register 40 CFR Part136, 1995; Font *et al.,* 1996; Espadaler *et al.*, 1997; Wolska *et al.,* 1999 and EPA method 3535A, 2000.

constant of hexane, dichloromethane and ethyl acetate is equal to 1.88, 8.93 and 6.02 respectively (Honeywell Burick & Jackson company, 2000). In addition, in the term of dipole moment, the molecules that have high dipole moment will have strong polarity. The dipole moment of hexane, dichloromethane and ethyl acetate is equal to 0.08, 1.14 and 1.88 respectively (Honeywell Burick & Jackson company, 2000) these are corresponded to the polarity index, 0.1, 3.1 and 4.4 respectively (Honeywell Burick & Jackson company, 2000). Looking at the structure of PCB153, 138 and 180 and their physical properties, these compounds were moderately polar due to their weak solubility in water which are in the range of 0.014-0.038 g/m^3 at 25°C depended on the content of chlorine substituents on biphenyl nucleus (Erickson, 1997). Thus, by considering either properties as described above can be seen that PCBs could partition into dichloromethane better than hexane, ethyl acetate, DCM:EtOAc (1:1) and hexane:EtOAc (1:1). Ethyl acetate has high polarity from its carbonyl group and this decreases the efficiency of the mixture solvent that contains ethyl acetate in the extraction of PCBs and hence, the low recovery. Therefore, the dichloromethane was chosen to be an appropriate solvent for extraction PCBs in water. The results that were similar to EPA680, 1985; Federal register 40 CFR Part136, 1995; Font *et al.,* 1996; Espadaler *et al.*, 1997; Wolska *et al.,* 1999 and EPA method 3535A, 2000.

3.2 Qualitative and quantitative analysis of PCBs residue in water sample

The concentration level of PCBs residue in water was at trace level and this was lower than the limit of detection of the GC-MS system as described in 3.1.5. Therefore, the sample preparation (SPE) was used to separate and preconcentrate the PCBs residue in well water so they could be analyzed. The extraction well water by SPE was performed following the procedure described in 2.3.3.9-2.3.3.10.

Four liters of water sample was collected in amber glass bottle from the wells near the wastewater treatment pond and landfill, stored in ice and transferred to the laboratory. All physical and chemical parameters of water sample were measured at the sampling site with multimeter (Check mate 90, England) as shown in Table 18. The water samples were then prefiltered by through a lab built prefiltration unit (as shown in Figure 7 Chapter 2) before being extracted by 47 mm C_{18} Empore extraction disk. In the extraction process, 500 ml of water sample was loaded into the reservoir where vacuum was applied to the disk. All of the analytes were adsorbed on the disk and then eluted by 2 x 5.0 ml of dichloromethane and processed as described in 2.3.3.9-2.3.3.10. The extractant final volume was 1.0 ml. The concentration ratio was 500. This factor could make the signal of all analytes detectable in the linear dynamic range of this system. The analysis results show in Table 20 and the total ion current chromatogram of three PCB congeners in well water sample in Figure 27.

Table 18 Parameters of water sample at all sampling sites

Sampling Site	Temperature (°C)	pH	Conductivity (µs)	Total Dissolve Solid (mg/l)	Depth (m)
WWT (S1)	28.2	7.65	269	134	1.5-2.0
Landfill (S2)	28.1	7.54	326	168	1.2-2.5

* Average per two day.

S1 : Wastewater treatment pond

S2 : Landfill

The quality and quantity of PCBs residue in well water were determined using retention time and comparing the mass spectrum with characteristic ions in a reference mass spectrum. Compounds were identified when the following criteria must be met.

a) Simultaneous detection of a peak for all ions monitored within the expected retention time window for each compound;

b) The relative retention time (RRT) of the sample component was within ± 0.01 RRT units of the RRT of the standard component;

c) The relative intensities of the characteristic ions agreed within 20% of the relative intensities of these ions in the reference spectrum or ion intensity ratios of the peak were within 20% of the mean values of reference standards as specified by EPA8270D (Environmental Protection Agency; 1998)

d) Signal to noise ratio ≥ 3:1

Quantification was based on SIM mode where PCB138 was monitored at m/z 218[M-4Cl]$^+$, 290[M-2Cl]$^+$, 360[M]$^+$; PCB153 at m/z 218[M-4Cl]$^+$, 290[M-2Cl]$^+$, 360[M]$^+$ and PCB180 at m/z 252[M-4Cl]$^+$, 324[M-2Cl]$^+$, 396[M]$^+$. The quantification ion and ion intensity of the three PCB congeners residue in well water near the wastewater treatment pond and the landfill of Songkhla municipal are shown in Table 19.

Table 19 The quantification ion and ion intensity of three PCB congeners residue in well water near the wastewater treatment pond and the landfill of Songkhla municipal.

Quantification Ion	**PCB153**	**PCB138**	**PCB180**
[M]$^+$	360(100)	360(100)	394(100)
[M-2Cl]$^+$	290(65.60)	290(69.90)	396(88.50)
[M-4Cl]$^+$	218(22.20)	218(25.90)	324(61.80)

Table 20 The quantity of PCBs residue in well water near wastewater treatment pond and landfill of Songkhla municipal

Sampling Site	Date	PCB153	PCB138	PCB153
		Concentration (ppt)	Concentration (ppt)	Concentration (ppt)
WWT	5 Feb, 16 Feb (2002)	0.13-0.14	0.16-0.59	0.20-0.25
Landfill	11 Feb, 16 Feb (2002)	0.11-0.14	0.58-0.67	0.20-0.44

* 5 replications , % RSD < 4

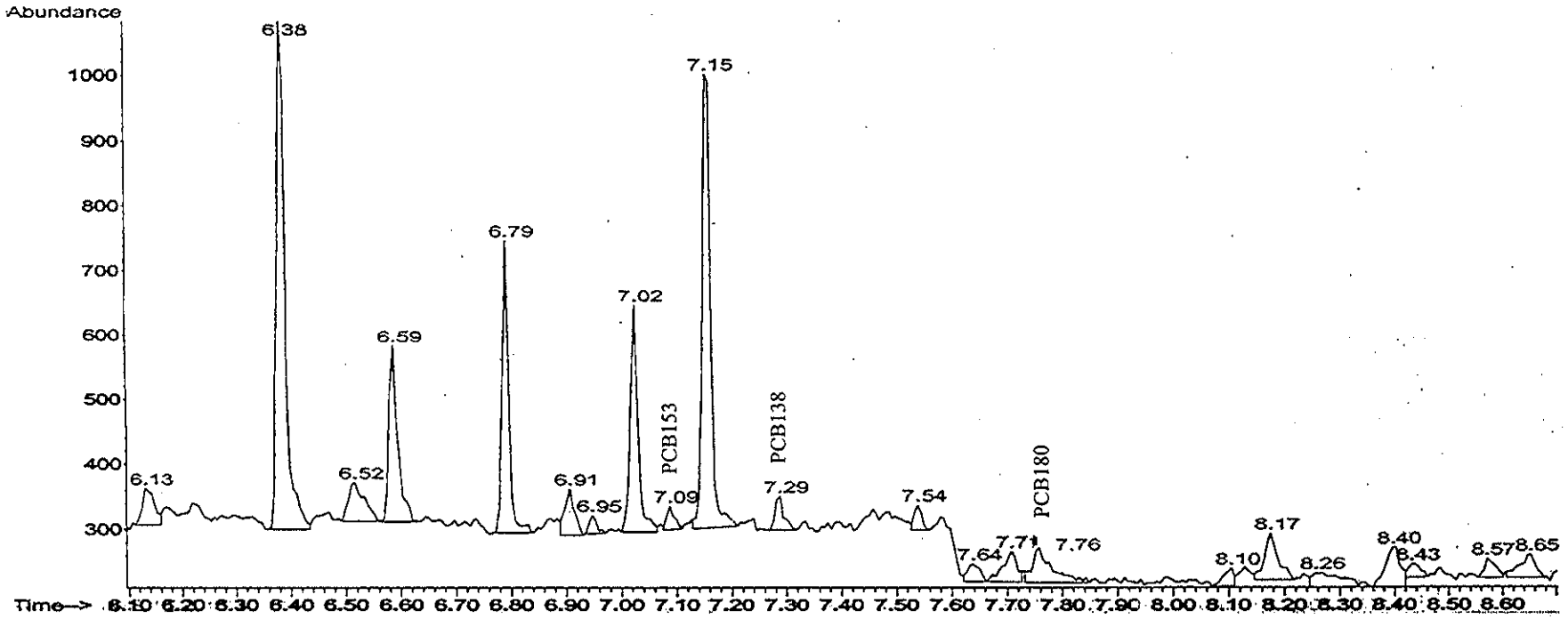


Figure 27 Total ion current chromatogram of the three PCB congeners detected in well water sample near the wastewater treatment pond and the landfill of Songkhla municipal.

Chapter 4

CONCLUSIONS

This study showed that gas chromatograph equipped with a HP-5MS capillary column and a mass selective detector together with sample preparation by solid phase extraction can be use for the qualitative and quantitative analysis of PCBs residue (PCB153, 138 and 180) in water at trace level. This system can be used to ananlyze several analytes simultaneous with high accuracy and precision. In the optimization process, the carrier gas flow rate of 0.8 ml/min provided the best resolution for the three PCBs congeners. The optimum temperature programming was obtained and performed at 130°C (hold 2 min), ramped to 250°C with 40°C/min, immediately ramped to 300°C with 25°C/min and hold at 300°C for 10 min. The optimum of the injector, transfer line, mass ion source and mass quadrupole temperatures was 230°C, 290°C, 230°C and 150°C respectively. The optimum conditions provided an analysis time at 13 minutes, limit of detection in the range of 60 – 70 ppt and a linear dynamic range in the range of 60 ppt to 1 ppm with a R^2 of more than 0.99. However, at these limit of detections the system could not be used to analyze the trace amount of PCBs residue in water as the PCBs concentration in water was normally at level between ppq to sub-ppt. Therefore, a sample preparation to extract and preconcentrate the PCBs before injecting into the GC-MS system was needed. Solid phase extraction technique using C_{18} Empore extraction disk was used for trace enrichment of very diluted PCBs residue in water, where large sample volume may have to be processed, to

yield concentrations of analyte sufficient for detection. The water sample was loaded into the extraction reservoir and vacuumed passing through the C_{18} extraction disk. Analytes were adsorbed on the media and then eluted by organic solvent. Five organic solvents were evaluated to find out an appropriate solvent for extracting PCBs in water. Dichloromethane was chosen since it could provide high percentage recovery (83-112%) with high precision, i.e. low percentage of relative standard deviation (1-3%). In addition, some interference, which could affect to the analysis were studied. Phthalate compounds, from plastic container, were found as a major interference that produced a large error in the interpretation of PCBs. Thus, sulfuric acid (1:1) solution was chosen for the cleaned up process of these compounds before the extractant was analyzed by the GC-MS system. Another interference, was the large amount of suspended particle matter content in the water sample. These could affect the extraction efficiency of the C_{18} disk since they could clogged the media if a large volume of water sample was used. Therefore, a lab built prefiltration unit was used to minimize the suspended particle content before loaded the sample to the disk. The prefiltration unit provided the advantages of reducing the quantity of suspended particle matters with particle size more than 40 micrometer and also minimizing the time of prefiltration by 30% compared to conventional method when the real samples from wells near the wastewater treatment pond and the landfill of Songkhla municipal were analyzed, it was found that water in all areas has been contaminated with the three PCBs congeners. Some congeners were closed to the contaminant level near the specification in EPA regulation, 0.79 ppt, which is the maximum level specified for PCBs in ambient water. These results are reliable since they were analyzed by following a quality assurance criteria set for such a system (gas chromatography coupled to mass selective detector with electron impact ionization was used in selected ion monitoring (SIM) mode). In addition, the

GC-MS under full scan conditions was also used for spectrum identification and analyte confirmation.

In conclusion, this single multiresidue analysis showed less analysis time by 70% campared to other methods i.e. general EPA method for analysis PCBs (approximately 40-50 minutes), less filtration time by 30% when applied a lab buit prefiltration unit together with C_{18} extraction disk compared to the work of Wolska et al., 1999, less organic waste than 90% compared to conventional technique i.e. liquid-liquid extraction, low limit of detection, high precision and reliable data which were obtained by operating SIM mode. Therefore, this analysis would improve the existing methodlogies, in terms of cost and analysis time and can be used for routine surface and drinking water monitoring. This method could provide useful information for advance analysis of polychlorinated biphenyls in water.

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Appendix

Table A Nomenclature of PCBs

BZ No.	Compound	CAS No.	BZ No.	Compound	CAS No.
	Biphenyl	92-52-4	38	3,4,5	53555-66-1
	MonoCB	27323-18-8	39	3,4',5	38444-88-1
1		2051-60-7		**TetraCB**	26914-33-0
2	2	2051-61-8	40		38444-93-8
3	3	2051-62-9	41	2,2',3,3'	52663-59-9
	4	25512-45-9	42	2,2',3,4	36559-22-5
	DiCB			2,2',3,4'	
4	2,2'	13029-08-8	43	2,2',3,5	70362-46-8
5	2,3	16605-91-7	44	2,2',3,5'	41464-39-5
6	2,3'	25569-80-6	45	2,2',3,6	70362-45-7
7	2,4	33284-50-3	46	2,2',3,6'	41464-47-5
8	2,4'	34883-43-7	47	2,2',4,4'	2437-79-8
9	2,5	34883-39-1	48	2,2',4,5	70362-47-9
10	2,6	33146-45-1	49	2,2',4,5'	41464-40-8
11	3,3'	2050-67-1	50	2,2',4,6	62796-65-8
12	3,4	2974-92-7	51	2,2',4,6'	65194-04-7
13	3,4'	2974-90-5	52	2,2',5,5'	35693-99-3
14	3,5	34883-41-5	53	2,2',5,6'	41464-41-9
15	4,4'	2050-68-2	54	2,2',6,6'	15968-05-5
	TriCB	25323-68-6	55	2,3,3',4	74338-24-2
16		38444-78-9	56	2,3,3',4'	41464-43-1
17	2,2',3	37680-66-3	57	2,3,3',5	70424-67-8
18	2,2',4	37680-65-2	58	2,3,3',5'	41464-49-7
19	2,2',5	38444-73-4	59	2,3,3',6	74472-33-6
20	2,2',6	38444-84-7	60	2,3,4,4'	33025-41-1
21	2,3,3'	55702-46-0	61	2,3,4,5	33284-53-6
22	2,3,4	38444-84-8	62	2,3,4,6	54230-23-7
23	2,3,4'	55720-44-0	63	2,3,4',5	74472-35-8
24	2,3,5	58702-45-9	64	2,3,4',6	52663-58-8
25	2,3,6	55712-37-3	65	2,3,5,6	33284-54-7
26	2,3',4	38444-81-4	66	2,3',4,4'	32598-10-0
27	2,3',5	38444-76-7	67	2,3',4,5	73575-53-8
28	2,3',6	7012-37-5	68	2,3',4,5'	73575-52-7
29	2,4,4'	15862-07-4	69	2,3',4,6	60233-24-1
30	2,4,5	35693-92-6	70	2,3',4',5	32598-11-1
31	2,4,6	16606-02-3	71	2,3',4',6	41464-46-4
32	2,4',5	38444-77-8	72	2,4',5,5'	41464-42-0
33	2,4',6	38444-86-9	73	2,3',5',6	74338-23-1
34	2',3,4	37680-68-5	74	2,4,4',5	32690-93-0
35	2',3,5	37680-69-6	75	2,4,4',6	32598-12-2
36	3,3',4	38444-87-0	76	2',3,4,5	70362-48-0
37	3,3',5	38444-90-5	77	3,3',4,4'	32598-13-3
	3,4,4'				

Table A (cont.) Nomenclature of PCBs

BZ No.	Compound	CAS No.	BZ No.	Compound	CAS No.
78	3,3',4,5	70362-49-1	126	3,3',4,4',5	57465-28-8
79	3,3',4,5'	41464-48-6	127	3,3',4,5,5'	39635-33-1
80	3,3',5,5'	33284-52-5		**HexaCB**	26601-64-9
81	3,4,4',5	70326-50-4	128		38380-07-3
	PentaCB	25429-29-2	129	2,2',3,3',4,4'	55215-18-4
82		52663-62-4	130	2,2',3,3',4,5	52663-66-8
83	2,2',3,3',4	60145-20-2	131	2,2',3,3',4,5'	61798-70-7
84	2,2',3,3',5	52663-60-2	132	2,2',3,3',4,6	38380-05-1
85	2,2',3,3',6	65510-45-4	133	2,2',3,3',4,6'	35694-04-
86	2,2',3,4,4'	55312-69-1	134	2,2',3,3',5,5'	35270-70-8
87	2,2',3,4,5	38380-02-8	135	2,2',3,3',5,6	52744-13-5
88	2,2',3,4,5'	55215-17-3	136	2,2',3,3',5,6'	38411-22-2
89	2,2',3,4,6	73575-57-2	137	2,2',3,3',6,6'	35694-06-5
90	2,2',3,4,6'	68194-07-0	138	2,2',3,4,4',5	35065-28-2
91	2,2',3,4',5	58194-05-8	139	2,2',3,4,4',5'	56060-56-9
92	2,2',3,4',6	52663-61-3	140	2,2',3,4,4',6	52591-64-4
93	2,2',3,5,5'	73575-56-1	141	2,2',3,4,4',6'	52712-04-6
94	2,2',3,5,6	73575-55-0	142	2,2',3,4,5,5'	41411-61-4
95	2,2',3,5,6'	38379-99-6	143	2,2',3,4,5,6	68194-15-0
96	2,2',3,5',6	73575-54-9	144	2,2',3,4,5,6'	68194-14-9
97	2,2',3,6,6'	41464-51-1	145	2,2',3,4,5',6	74472-40-5
98	2,2',3',4,5	60233-25-2	146	2,2',3,4,6,6'	51908-16-8
99	2,2',3',4,6	38380-01-7	147	2,2',3,4',5,5'	68194-13-8
100	2,2',4,4',5	39485-80-1	148	2,2',3,4',5,6	74472-42-7
101	2,2',4,4',6	37680-73-2	149	2,2',3,4',5,6'	38380-04-0
102	2,2',4,5,5'	68194-06-9	150	2,2',3,4',5',6'	68194-08-1
103	2,2',4,5,6'	60145-21-3	151	2,2',3,4',6,6'	52663-63-5
104	2,2',4,5',6	56558-16-8	152	2,2',3,5,5',6	68194-09-2
105	2,2',4,6,6'	32598-14-4	153	2,2',3,5,6,6'	35065-27-1
106	2,3,3',4,4'	70424-69-0	154	2,2',4,4',5,5'	60145-22-4
107	2,3,3',4,5	70424-68-9	155	2,2',4,4',5,6'	33979-03-2
108	2,3,3',4',5	70362-41-3	156	2,2',4,4',6,6'	38380-08-4
109	2,3,3',4,5'	74472-35-8	157	2,3,3',4,4',5	69782-90-7
110	2,3,3',4,6	38380-03-9	158	2,3,3',4,4',5'	74472-42-7
111	2,3,3',4',6	39635-32-0	159	2,3,3',4,4',6	39635-35-3
112	2,3,3',5,5'	74472-36-9	160	2,3,3',4,5,5'	41411-62-5
113	2,3,3',5,6	68194-10-5	161	2,3,3',4,5,6	74472-43-8
114	2,3,3',5',6	74472-37-0	162	2,3,3',4,5',6	39635-34-2
115	2,3,4,4',5	74472-38-1	163	2,3,3',4',5,5'	74472-44-9
116	2,3,4,4',6	18259-05-7	164	2,3,3',4',5,6	74472-45-0
117	2,3,4,5,6	68194-11-6	165	2,3,3',4',5',6'	74472-46-1
118	2,3,4',5,6	31508-00-6	166	2,3,3',5,5',6	41411-63-6
119	2,3',4,4',5	56558-17-9	167	2,3,4,4',5,6	52663-72-6
120	2,3',4,4',6	68194-12-7	168	2,3',4,4',5,5'	52291-65-5
121	2,3',4,5,5'	56558-18-0	169	2,3',4,4',5',6	32774-16-6
122	2,3',4,5',6	76842-07-4		3,3',4,4',5,5'	28655-71-2
123	2',3,3',4,5	65510-44-3	170	**HeptaCB**	35065-30-6
124	2',3,4,4',5	70424-70-3	171		52663-71-5
125	2',3,4,5,5'	74472-39-2	172	2,2',3,3',4,4',5	52663-74-8
	2',3,4,5,6'			2,2',3,3',4,4',6	
				2,2',3,3',4,5,5'	

Table A (cont.) Nomenclature of PCBs

BZ No.	Compound	CAS No.	BZ No.	Compound	CAS No.
173	2,2',3,3',4,5,6	68194-16-1	193	2,3,3',4,5,5',6	69782-91-8
174	2,2',3,3',4,5,6'	38411-25-5		**OctaCB**	31472-83-0
175	2,2',3,3',4,5',6	40186-70-7	194		35694-08-7
176	2,2',3,3',4,6,6'	52663-65-7	195	2,2',3,3',4,4',5,5'	52663-78-2
177	2,2',3,3',4',5,6	52663-70-4	196	2,2',3,3',4,4',5,6	42740-50-1
178	2,2',3,3',5,5',6	52663-67-9	197	2,2',3,3',4,4',5,6'	33091-17-7
179	2,2',3,3',5,6,6'	52663-64-6	198	2,2',3,3',4,4',6,6'	68194-17-2
180	2,2',3,4,4',5,5'	35065-29-3	199	2,2',3,3',4,5,5',6	52663-75-9
181	2,2',3,4,4',5,6	74742-47-2	200	2,2',3,3',4,5,5',6'	52663-73-7
182	2,2',3,4,4',5,6'	60145-23-5	201	2,2',3,3',4,5,6,6'	40186-71-8
183	2,2',3,4,4',5',6	52663-69-1	202	2,2',3,3',4,5',6,6'	2136-99-4
184	2,2',3,4,4',6,6'	74742-48-3	203	2,2',3,3',5,5',6,6'	52663-76-0
185	2,2',3,4,5,5',6	52712-05-7	204	2,2',3,4,4',5,5',6	74472-52-9
186	2,2',3,4,5,6,6'	74472-49-4	205	2,2',3,4,4',5,6,6'	74475-53-0
187	2,2',3,4',5,5',6	52663-68-0		2,3,3',4,4',5,5',6	53742-07-7
188	2,2',3,4',5,6,6'	74487-85-7	206	**NonaCB**	40186-72-9
189	2,3,3',4,4',5,5'	39635-31-9	207		52663-79-3
190	2,3,3',4,4',5,6	41411-64-7	208	2,2',3,3',4,4',5,5',6	52663-77-1
191	2,3,3',4,4',5',6	74472-50-7		2,2',3,3',4,4',5,6,6'	2051-24-3
192	2,3,3',4,5,5',6	74472-51-8	209	2,2',3,3',4,5,5',6,6'	2051-24-3
				DecaCB	
				2,2',3,3',4,4',5,5',6,6'	

Source: Analytical Chemistry of PCBs, 2nd, Lewis Publication, New York, 1997: 581-583

Table B Physical Properties of PCBs Homolog[a]

PCB isomer group	Melting point (°C)[b]	Boiling point (°C)[b,c]	Vapor pressure (Pa) at 25°C[c-e]	Water solubility at 25°C (g/m^3)[e,f]
Biphenyl	71.0	256	4.90	9.30
MonoCB	25.0-77.9	285	1.10	4.00
DiCB	24.4-149.0	312	0.24	1.60
TriCB	28.0-87.0	337	0.05	0.65
TetraCB	47.0-180.0	360	0.01	0.26
PentaCB	76.5-124.0	38i	$2.6x10^{-3}$	0.10
HexaCB	77.0-150.0	400	$5.8x10^{-4}$	0.04
HeptaCB	122.4-149.0	417	$1.3x10^{-4}$	0.01
OctaCB	159.0-162.0	432	$2.8x10^{-5}$	$5.5x10^{-3}$
NonaCB	182.8-206.0	445	$6.3x10^{-6}$	$2.0x10^{-3}$
DecaCB	305.9	456	$1.4x10^{-6}$	$7.6x10^{-4}$

Source: Analytical Chemistry of PCBs, 2nd, Lewis Publication, New York, 1997: 23

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