Field Analysis of Total PCBs in Soils by Thermal Desorption/GC and Determination of the Individual PCB Congeners by GC × GC – TOF-MS

by

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I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Environmental field analysis provides advantages that allow real-time decisions, interactive sampling and cost effective solutions to the problems faced at the time of investigation. Gas chromatography (GC), a widespread technique for the determination of organic pollutants in the environment, has also shown to be useful in environmental field analysis. Thermal desorption of solid environmental sample provides a technique for liberation of volatile analytes from the samples without the need for solvent extraction. Combining the thermal desorption technique with a field gas chromatograph (GC) thus provides the possibility of on-site determination of organic contaminants in soils. However, to better characterize trace level contaminants in complex sample matrices, laboratory analysis using analytical instrument with great separation and resolution power is required. Comprehensive two-dimensional gas chromatography (GC × GC) is such a powerful analytical tool that provides enhanced separation and resolution capacity for the task.

The project presented here involves the development and validation of a field method for the analysis of total polychlorinated biphenyls (PCBs) in soils, and determination of individual PCB congeners in the same samples by further laboratory analysis. The field analytical system developed was a field portable GC interfaced with a thermal desorber. The identification of PCB congeners was realized by a GC × GC system with a time-of-flight mass spectrometer (TOF-MS) as a detector. The field method was developed by optimizing and characterizing the method using PCB standards, followed by the application of the developed method to environmental soil samples. Finally, analyses of

PCB congeners in environmental soil samples were performed using the GC × GC system.

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1.0 Introduction

1.1 Polychlorinated Biphenyls (PCBs)

1.1.1 Nomenclature and Properties

Polychlorinated Biphenyls (PCBs) are a class of discrete organic compounds with one to ten chlorine atoms attached to biphenyl and a general chemical formula of $C_{12}H_{10-n}Cl_n$, where n = 1 ~ 10 (Figure 1-1):

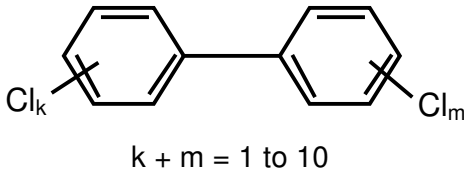


Figure 1-1: Chemical structure of PCBs

The entire set of PCBs contains 209 congeners. When the congeners are subdivided by the degree of chlorination and categorized into ten congener groups, the term "homologs" are used. PCBs of a given homolog with different chlorine substitution position are called "isomers". For example, 2,3,5-trichlorobiphenyl and 3,3′,4-trichlorobiphenyl are two isomers of trichlorobiphenyl homolog (Figure 1-2). The composition of PCBs is summarized in Table 1-1.[1]

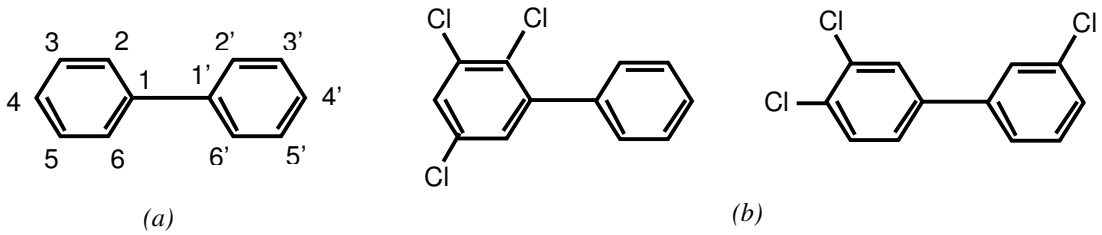


Figure 1-2: Distribution of chlorine atoms in the two rings of biphenyl: (a) possible chlorine substitution positions; (b) examples of two PCB isomers (2,3,5-trichlorobiphenyl and 3,3′,4-trichlorobiphenyl)

Table 1-1: Composition of PCBs by Homologs[1]

Homolog	Molecular formula	Chlorine (% by weight)	Number of isomers
Monochlorobiphenyl	$C_{12}H_9Cl$	19	3
Dichlorobiphenyl	$C_{12}H_8Cl_2$	32	12
Trichlorobiphenyl	$C_{12}H_7Cl_3$	41	24
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	49	42
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	54	46
Hexachlorobiphenyl	$C_{12}H_4Cl_6$	59	42
Heptachlorobiphenyl	$C_{12}H_3Cl_7$	63	24
Octachlorobiphenyl	$C_{12}H_2Cl_8$	66	12
Nonachlorobiphenyl	$C_{12}HCl_9$	69	3
Decachlorobiphenyl	$C_{12}Cl_{10}$	71	1
Total Congeners	/	/	209

Generally, the terms used to name PCB congeners fall into three categories: structural name (or chemical structure name), PCB number, and CAS (Chemical Abstracts Service) registry number.[1] The chemical structure name follows the nomenclature rules defined by the International Union of Pure and Applied Chemistry (IUPAC). The structural names are relatively complex and may easily cause confusion, as the names for distinct congeners may include long lists of substituents with only a single different digit, for example, 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl and 2,2′,3,3′,4,4′,5,6′-octachlorobiphenyl. Errors in transcription (i.e., misidentification of congeners) may result from using these long names. To reduce this type of error and for ease of use, chemists have established shorthand PCB numbering systems. Among them the BZ number, which was first proposed by Ballschmiter and Zell in 1980,[1, 2] is the most widely used. In the BZ numbering system, the 209 PCB congeners are arranged in ascending numeric order and assigned a number from 1 to 209, often prefixed with "PCB". For example, the BZ number for 2,2′,3-trichlorobiphenyl is PCB 16. The BZ system has been rectified or updated since its publication, such as the changes made by Schulte and Malisch.[1]

Subsequent updates of the BZ numbers are usually referred to as the "IUPAC" numbers, although the IUPAC has not published such a numbering system for PCBs.[2] The shorthand PCB numbers have been widely adopted and are convenient for use. However, the shorthand numbers do not reflect the chemical structures of PCBs and thus contain less information than the structural names. The CAS registry numbers are numbers assigned by the Chemical Abstracts Service and maintained in the CAS registry database.

Since PCBs occur as complex mixtures of up to 209 distinct congeners, their properties are dependent on the composition of the mixture. The properties of individual PCB congeners also vary according to the degree of chlorination and location of the chlorine atoms. As a result, the physical properties of PCBs change widely throughout the ten PCB homologs. For example, the boiling point of PCB isomer group with single chlorine atom (monochlorobiphenyl) is 285 °C, while the boiling point of PCB isomer group with 10 chlorine atoms (decachlorobiphenyl) is 456 °C.[1] Table 1-2 lists several selected physical properties of PCB homologs.

Table 1-2: Selected Physical Properties of PCB Homologs[1]

Homolog	Melting point (°C)	Boiling point (°C)	Vapor pressure at 25 °C (Pa)	Water solubility at 25 °C (g/m^3)	Partition coefficient (Log $K_{o/w}$)	Evaporation rate at 25 °C ($g/(m^2h)$)
Monochlorobiphenyl	25-77.9	285	1.1	4.0	4.7	0.25
Dichlorobiphenyl	24.4-149	312	0.24	1.6	5.1	0.065
Trichlorobiphenyl	28-87	337	0.054	0.65	5.5	0.017
Tetrachlorobiphenyl	47-180	360	0.012	0.26	5.9	4.2×10^{-3}
Pentachlorobiphenyl	76.5-124	381	2.6×10^{-3}	0.099	6.3	1.0×10^{-3}
Hexachlorobiphenyl	77-150	400	5.8×10^{-4}	0.038	6.7	2.5×10^{-4}
Heptachlorobiphenyl	122.4-149	417	1.3×10^{-4}	0.014	7.1	6.2×10^{-5}
Octachlorobiphenyl	159-162	432	2.8×10^{-5}	5.5×10^{-3}	7.5	1.5×10^{-5}
Nonachlorobiphenyl	182.8-206	445	6.3×10^{-6}	2.0×10^{-3}	7.9	3.5×10^{-6}
Decachlorobiphenyl	305.9	456	1.4×10^{-6}	7.6×10^{-4}	8.3	8.5×10^{-7}

The physical properties of PCBs bear close relationship to their environmental occurrence and are important for the understanding of their analytical properties. For example, the vapor pressure and water solubility data are useful in explaining transport and fate of PCBs in the environment. High octanol-water partition coefficients (log $K_{o/w}$) imply that PCBs are lipophillic and tend to partition away from water to most solids, especially the organic portion of the solids.[1] As can be seen in Table 1-2, the physical properties of PCBs show the trends of either increase or decrease in values as the degree of chlorination increases. Despite the fact that the physical and chemical properties of PCBs vary widely across the whole class, PCBs generally have low water solubilities, low vapor pressures, and relatively high boiling points. Most of the 209 PCB congeners are colorless and odorless crystals at room temperature. The commercial mixtures are clear viscous liquids. They are soluble in most organic solvents, oils and fats. In general, PCBs are physically and chemically stable and do not degrade easily.

1.1.2 Production and Application

PCBs do not occur naturally and were first synthesized in 1881. The commercial production of PCBs began in the United States in 1929. Industrial synthesis of PCBs was carried out by direct chlorination of biphenyl with chlorine gas. By varying the reaction conditions, products could be made with varying degrees of chlorination. In North America, the most commonly used PCB mixtures were manufactured by Monsanto under the trademark of Aroclor. PCBs were also manufactured under other commercial names by different companies, such as Bayer in Germany, Prodelec in France, Kanechlor in Japan, and Sovol in the former USSR. The commercial PCB mixtures of Aroclor are identified by a 4-digit number. The first two digits generally refer to the number of

carbon atoms in the biphenyl skeleton (for PCBs this is 12), the second two numbers indicate the percentage of chlorine by mass in the mixture. For example, Aroclor 1254 has 12 carbon atoms and contains 54% chlorine by mass.[1] Table 1-3 presents various mixtures of homologs in some Aroclor products commonly used in the past in North America. Table 1-4 provides physical properties of these products.

Table 1-3: Average Molecular Composition (wt.%) of Some Aroclors[1]

Homolog (Chlorine #)	**Aroclor**			
	1242	**1248***	**1254***	**1260**
1	1			
2	13	1		
3	45	22	1	
4	31	49	15	
5	10	27	53	12
6		2	26	42
7			4	38
8				7
9				1

* Homolog compositions for 1248 and 1254 were not 100% as provided in the reference

Table 1-4: Physical Properties of Some Common Aroclors[1]

Aroclor	Chlorine (wt.%)	Viscosity (Saybolt) at 98.9°C	Flash point (°C)	Distillation range (°C)	Dielectric constant at 20°C	Dielectric constant at 100°C	Water solubility (µg/L) at 25°C
1242	42	34 - 35	176 - 180	325 - 366	5.8	4.9	240
1248	48	36 - 36	193 - 196	340 - 375	5.6	4.6	52
1254	54	44 - 58	N/A	365 - 390	5.0	4.3	12
1260	60	72-78	N/A	385 - 420	4.3	3.7	3

PCBs are very stable compounds. They are resistant to degradation at elevated temperatures and have low volatility. Their physical and chemical stability, together with their extremely low water solubility, low flammability, and electrical resistance make them suitable for use in a wide variety of applications. These include dielectric fluids in electrical equipment, hydraulic fluids, plasticizers, additives in pesticides, carbonless

copy paper, paints and inks.[2-4] As reviewed by the World Health Organization (WHO), the applications of PCBs fell into three categories: completely closed systems (i.e., electrical equipment such as transformers and capacitors), uncontrollable closed system (i.e., hydraulic or heat transfer systems with PCBs as hydraulic fluid or heat transfer media), and open-ended applications (i.e., plasticizers, paints, inks and additives).[1] Open-ended applications resulted in widespread, low-level release to the environment. In uncontrollable closed systems, release of PCBs might result from leakage and replacement of PCBs. Although the completely closed systems were properly designed to avoid leak, environmental issues could have arisen from improper handling and disposal of large quantities of PCBs when this type of equipment was removed from service.

Large scale applications of PCBs happened during the 1940s and 1950s. As of 1980, the total worldwide production of PCBs was estimated to be 1.1×10^6 tons.[1] Production of PCBs ceased in most countries by the end of the 1970s due to increased concerns over the environmental impact of PCBs, although some production continued through at least 1983.[1]

1.1.3 Environmental Concerns and Regulatory Requirements

The same properties that led to PCBs' wide variety of applications have also resulted in PCBs becoming widely dispersed in the environment, and made them not easy to degrade. PCBs have entered the environment through both legal and illegal use and disposal. Because PCBs were commercially produced from 1929 through 1970s, they have become a widespread environmental concern due to their toxic effects on wildlife, their persistence in the environment, and their ability to bioaccumulate through the food chain.[5] PCBs are highly lipophilic, with the consequence that more than 99% of PCB

mass is found in soil.[6] However, volatilization of PCBs from spills, landfills, oils and other sources results in measurable atmospheric emissions.

Reports of hazardous effects resulting from occupational exposure to PCBs can be traced back to as early as 1936, after which a workplace threshold limit value (TLV) was subsequently set in the U.S.[1] In 1969, Jensen at al. published the initial report concerning PCBs in Swedish eagles and herring.[7] Since then, PCBs have been found in most animal and human adipose tissue samples. One of the well-known PCB contamination accidents happened in Japan when PCB-contaminated cooking oil caused 1291 so called "Yusho" patients in 1968.[1] Transport of PCBs through the environment is complex. It occurs through air, water, fish, birds and other routes. PCBs have been found in remote areas where their production never occurred. For example, PCBs were observed in the blood of Inuit infants in the remote Arctic areas in Quebec, Canada.[8] PCBs and their environmental concerns became increasingly the subject of research and a continuing topic of public discussion. Today it is commonly recognized that PCBs are one of the global environmental pollutants that include mercury, lead, and certain pesticides.[1]

Although PCBs' toxic effects on humans are still debatable, their apparent link to carcinogenesis prompted effective evaluation of their effects on human health. In order to create a reliable method for PCB toxicity assessment, the WHO has identified 12 non- and mono-ortho PCB congeners as indicators of toxicity, due to their toxin-like chemical behavior.[9, 10] Toxicity Equivalency Factors (TEFs) indicating the toxicity relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) were assigned to these selected congeners. The 12 PCB congeners and their TEFs are listed in Table 1-5.[10] Similarly, the European

Union (EU) has chosen seven PCB congeners (28, 52, 101, 118, 138, 153, and 180) to act as markers of harmful contamination.[11]

Table 1-5: Toxicity Equivalency Factors (TEFs) of 12 PCB Congeners[10]

Congener number	1997 WHO TEFs*		
	Humans/mammals	Fish	Birds
PCB-77	0.0001	0.0001	0.05
PCB-81	0.0001	0.0005	0.1
PCB-105	0.0001	<0.000005	0.0001
PCB-114	0.0005	<0.000005	0.0001
PCB-118	0.0001	<0.000005	0.00001
PCB-123	0.0001	<0.000005	0.00001
PCB-126	0.1	0.0005	0.1
PCB-156	0.0005	<0.000005	0.0001
PCB-157	0.0005	<0.000005	0.0001
PCB-167	0.00001	<0.000005	0.00001
PCB-169	0.01	0.00005	0.001
PCB-189	0.0001	<0.000005	0.00001

* The TEF of 2,3,7,8-tetrachlorodibenzo-p-dioxin is 1.0

The discovery of PCBs' widespread environmental occurrence has led to stringent regulatory control over these chemicals. In both the U.S. and Canada, PCBs must be handled, stored and transported as highly toxic substance because of the requirements that legislation has imposed. In 1976, the regulation of PCBs was enforced through the Toxic Substances Control Act (TSCA) in the U.S.[1] The TSCA has subsequently become the most important law regulating PCBs in the U.S. Under TSCA, many regulations regarding electric equipment use, spill cleanup policy, and disposal requirements have been promulgated by the U.S. Environmental Protection Agency (US EPA). There are a long list of other federal laws which address PCBs in the U.S., including acts that regulate occupational health and safety, clean water, clean air, drinking water, resource conservation, and hazardous materials transportation, etc.[1] In Canada, the first federal statute pertaining to PCBs was promulgated in 1977.[12] Now most PCB regulations in Canada fall under the Canadian Environmental Protection Act. Besides federal laws,

there are also provincial acts and regulations that regulate PCBs in Canada. In Ontario, the main regulation which defines management requirements for disposal, storage and shipping of PCB waste is Ontario Regulation 362. As required by laws, criteria and guidelines for allowable concentrations of PCBs in water, air, soil and waste, as well as concentrations for storage have been issued to restrict the risk of PCBs on humans and wildlife. For example, in the U.S., the applicable concentration of PCBs for storage and disposal purposes under TSCA is 50 ppm.[1] In Ontario, limits of PCB levels in soil for agricultural, residential, and industrial/commercial sites are 0.5, 5, and 25 ppm, respectively.[12]

1.1.4 Environmental Analysis of PCBs

Traditionally, analysis of PCBs in the environment was conducted in the laboratory by gas chromatography (GC) with electron capture detection (ECD).[13] A more selective method is coupling of GC to mass spectrometry (MS).[14] Up till now, these methods are still the gold standard for PCB analysis. For example, the US EPA Method 8000 series (Method 8080, 8081, and 8082) all address PCBs in solid waste as determined by GC/ECD. The US EPA Method 8270 determines semivolatile compounds including PCBs by GC/MS.[1] In North America, determination of PCBs in environmental samples has traditionally focused on identifying and quantifying the Aroclor(s) by GC/ECD. An overview of PCB analysis, including sampling techniques, extraction, cleanup procedures, and quantification is also reported in the US EPA Method 1668,[15] which is the current methodology used to measure specific toxic, dioxin-like PCB congeners in water, soil, sediment and tissue by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). In Canada, the corresponding method is described in

Environment Canada Method 1/RM/31.[16] In addition to laboratory analysis, field analysis provides another method for the determination of PCBs in environmental samples on site. The US EPA published a guide which contained descriptions of field analytical methods (FAMs) for PCBs.[17] Four methods for determining PCBs as Aroclors are described, including hexane/methanol extraction of water and soil samples followed by GC/ECD analysis.

Since properties of PCBs vary widely according to the composition of their mixtures, and the original commercial mixtures of PCBs can vary in their congener composition from product to product, the composition of PCBs in the environmental samples could be very complex. Therefore, laboratory analysis of PCBs is particularly challenging: in addition to qualitative and quantitative determination of the total contents of PCBs in the sample, identification of the individual PCB congeners is also important to characterize and recognize the toxicity of the sample. Tremendous amount of research has been conducted on PCB analysis because of their significant impact on the environment. One focus of this research is to provide methods for fast determination of PCBs for on-site analysis. Because PCBs are highly toxic compounds, fast determination of PCBs in environmental samples is especially useful in emergency response to environmental accidents and in PCB cleanup activities. Two methods are usually applied in on-site analysis of PCBs: one is using portable GC or GC/MS with proper sample preparation such as thermal desorption,[18] the other one is adopting immunoassay PCB test kits.[19-21] While PCB test kits are easy to carry and operate compared to GC or GC/MS methods, they provide only semi-quantitative results and are susceptible to interference from other chlorinated compounds.[22]

Due to PCBs' complex composition, many researchers have also placed emphasis on the identification of the individual PCB congeners.[23, 24] It is reported that approximately 150 of 209 PCB congeners have been found in the environment.[25] Congener-specific analysis allows for the detection of the more toxic PCB congeners and for better tracking of PCBs in the environment. Presently, all 209 PCB congeners have been commercially synthesized and available for use as standards, and because of advances in high resolution gas chromatography, it is possible to determine most of the individual PCB congeners in the environmental samples. However, separation and characterization of all 209 PCB congeners is still an extremely difficult (if not impossible) task that attracts on-going research focus in this field.[25]

1.2 Thermal Desorption

When the term "thermal desorption" is mentioned, it is more commonly referred to as a soil remediation technique. Nominally, the US EPA has recognized thermal desorption as a technology for more than 20 years, with it first being designated as the remedial technology in 1985.[26] According to a recent definition of thermal desorption contained in the US EPA Engineering Bulletin,[27] thermal desorption is based on a physical separation process where volatile or semi-volatile organics are desorbed from a solid matrix under the influence of heating (300 to 1000 °F or 90 to 540 °C). The desorbed organic components are then transferred by air, combustion gas or an inert gas such as CO_2 or N_2. Thermal desorption is usually used as a remediation technique for contaminated material such as soil, sediment, sludge or filter cake, where the organic contaminants thermally desorbed from the soil are carried to a condenser or carbon adsorption unit for further

treatment.[28, 29] In the last decade, thermal treatment of polluted soils has been developed as an alternative method for site remediation and brownfield redevelopment, especially for soils contaminated with volatile organic compounds.[30] Thermal desorption was also used for the removal of mercury from topsoil.[31]

The same concept of thermal desorption as applied in soil remediation is also used for processing samples of soil or other solid matrices for the analysis, for example, Robbat et al. reported using thermal desorption/GC-MS for in situ collection and analysis of semivolatile organics in soils.[32, 33] Davies et al. reported applying an on-line flash thermal desorption/GC-MS for determination of PCB in sewage sludge.[34] Thermal desorption can also be applied to air and water.[35, 36] There are various thermal desorbers that are commercially available. They usually take the form of a stainless steel or glass tube which may be packed with trapping materials or solid adsorbents. The sample is placed inside the tube. Desorption tubes are heated by an external or built-in heating source such as a heating coil. When heated, volatiles are released from the trapping material or from the sample itself. Inert gas flows through the tube during the heating step, and the volatiles are swept by the flow of the gas into a second trap for collection and refocusing, or to the inlet system of an analytical instrument for direct analysis. GC is most commonly coupled with thermal desorbers for direct analysis.[33-38] When thermal desorption is carried out on-line with chromatographic analysis, the volatile or semi-volatile compounds in solid or other matrices are injected and analyzed with little or no sample preparation. Also, with thermal desorption, no solvent extraction is required. Conventional technology for environmental analysis of organic contaminants in soils usually requires extraction of soils with organic solvents prior to instrumental analysis.

Organic solvents present a potential for environmental contamination and toxic risk during transportation and usage. The process of solvent extraction is also time consuming and costly. The principle of thermal desorption coupling with analytical instrument such as GC for direct analysis provides the convenience for field operations. The solvent-free extraction process also helps save on costs and sample turn-around time. With these advantages, thermal desorption provides the possibility of on-site application for real-time analysis of organic contaminants in soils.[39]

1.3 Gas Chromatography (GC)

1.3.1 GC Fundamentals

Since chromatography was invented at the turn of the previous century, gas chromatography (GC) has become the premier technique for the separation and analysis of volatile compounds. Today, gas chromatographs are probably the most widely used analytical instruments in the world.[40]

Chromatography is a separation method in which the components of a sample to be separated for subsequent analysis are distributed between two phases: the first one called a stationary phase, and the other one, continuously moving in one direction, called the mobile phase. In gas chromatography, the mobile phase is a gas, and the stationary phase could be a liquid bed which is supported on small, porous particles packed into a column, or, more often, a thin film of polymer coated on the inside wall of a narrow capillary. The separation is based on the partitioning of the components between the stationary phase and the moving gas (carrier gas), which carries the components out of the column one by one according to the time they spend associated with the stationary phase.

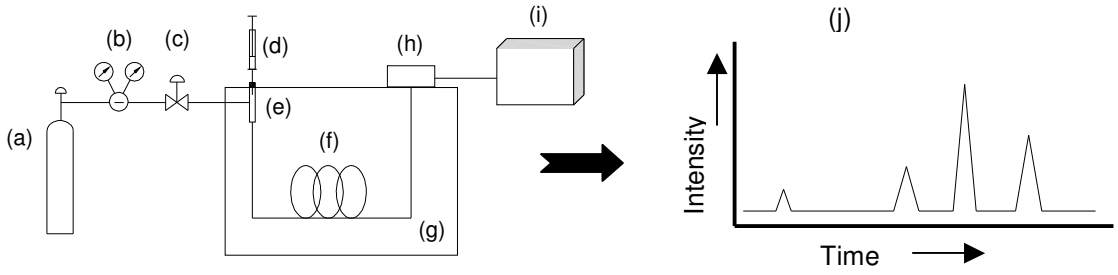


Figure 1-3: Block diagram of a GC system. (a) gas cylinder; (b) pressure regulator; (c) flow control valve; (d) syringe; (e) injection port; (f) column; (g) oven; (h) detector; (i) data system; (j) chromatogram

Figure 1-3 shows the basic components of a GC system – carrier gas supply, injector, column, oven, detector and data system. A simple GC separation can be described as follows: the sample is injected through the injector and introduced onto the head of the column, and transported through it by the carrier gas. The sample is volatilized in the injector or in the column by the heating of the oven. As the analytes are transported along the column, they partition back and forth between the stationary phase and the mobile phase, according to their partition coefficient K_c, defined as the molar concentration of the analyte in the stationary phase divided by its concentration in the mobile phase at equilibrium. When the analytes are in the mobile phase, they move along the column with its velocity, but when they partition into the stationary phase, they are held in place. The higher an analyte's K_c value, the more it will partition into the stationary phase, and the slower it will move with the carrier gas. The result is that the analytes are separated according to their partitioning into the stationary phase. The separated analytes then flow out of the column and are detected by the detector.

The instrumental output of a GC analysis is called a chromatogram. A simplified GC chromatogram is illustrated in Figure 1-3. It is a plot of detector signal vs. retention time, that is, the time from sample injection to the time when detector responds to the analyte. A GC chromatogram provides fundamental information for the analysis. For example, we can use the retention time shown on the chromatogram for identification of a particular compound, and use the peak height or peak area for quantitative determination of the analytes.

1.3.2 Field Portable GC

As with many other analytical instruments, there is a continuing effort to make GCs smaller and more portable to enable on-site applications, prompted by the increasing needs for analytical results to be obtained in the field. Nowadays, many small-size portable GCs are available commercially. These instruments contain basic GC components in a compact compartment, and perform many functions as those realized in laboratory GCs. For example, many of them provide accurate and fast temperature control and temperature programming with the capability to analyze both volatile and semivolatile compounds.[41] Some of them provide the functions of combining sample preparation to the analytical process, and the capacity for coupling mass spectrometer, so called field portable GC/MS systems.[42, 43] Field portable GCs now can be made small and compact. It is often the need for carrier gas and electrical power supply that limit the portability and application of the systems in the field.[44] Since field portable GCs are required to perform fast analysis, they are usually equipped with short capillary columns and operated at very high carrier gas velocities.[45]

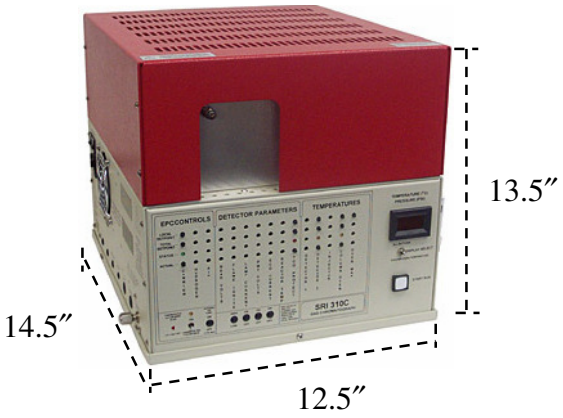


Figure 1-4: SRI model 310 gas chromatograph[46]

An example of field portable GC is SRI Instruments Model 310 GC which was selected for this research. The dimensions of this instrument are 12.5" width × 13.5" height × 14.5" depth (Figure 1-4). This small size makes it transportable and easy to use in the field. Despite its small size, the SRI 310 GC still retains the performance of a full-sized laboratory instrument. The column oven of SRI 310 GC is temperature programmable from ambient temperature to 400 ^{o}C, and the carrier gas pressure is programmable as well. Up to four detectors can be mounted simultaneously to the GC.[46]

1.3.3 GC Injectors

The GC injector is an inlet system. Its purpose is to introduce the sample into the column. There are many injection techniques used in capillary GC. The most common techniques include split injection, splitless injection and on-column injection. Split and splitless injection are both performed using the same inlet system, or the injector. The injector body contains a deactivated glass liner through which the carrier gas travels. A sample is introduced into the glass liner using a syringe. The injector is heated and the temperature is maintained at a high value. The high heat of the injector rapidly volatilizes

the sample. The carrier gas mixes with the vaporized sample and carries it into the column. In split injection, only a fraction, usually 1 – 2% of the vapor, enters the column. The rest of the vaporized sample and a large flow of carrier gas pass out through a purge valve. The fraction of the sample injected into the column can be controlled by adjusting the purge valve. On the other hand, in splitless injection, the split valve is initially closed. After a certain period of time, the split valve is opened. Thus, most of the vaporized sample (about 95%) enters the GC column. One disadvantage of split injection is that trace analysis is limited since only a fraction of the sample enters the column. Consequently, splitless injection is recommended for trace analysis. The big advantage of splitless injection is the improved sensitivity over split injection as a result of more sample entering the column. However, in splitless injection the analytes must be refocused after injection to reduce the initial band width. In both split and splitless injection, the injector temperature should be set high enough to vaporize the sample quickly, but not so high that sample components are decomposed.[47]

On-column injection means inserting a precisely aligned needle into the capillary column, usually a 0.53 mm inner diameter megabore-type, and making injections directly into the column. On-column technique allows the entire sample to be directed into a capillary column without a separate vaporization chamber. Unlike split and splitless injection, on-column injection must start with a cold injector, and the sample reaches the column as a liquid, which is then vaporized via temperature programming of the column and/or the injector. On-column injection provides best quantitative results as no analyte discrimination occurs. However, the disadvantage of placement of the entire sample directly into the column is that the column could be contaminated by the “dirty” (non-

volatile) sample material. A retention gap (described latter) can partially mitigate this problem.[47]

1.3.4 GC Columns and Retention Gap

The GC column can be considered to be the central item in a gas chromatograph. GC columns are of two types, packed and capillary. Packed columns are usually made of stainless steel or glass and are packed tightly with stationary phase in the form of an inert solid support of diatomaceous earth coated with a thin film of liquid. Because the packed column is tightly packed with small particles, its inside diameter is bigger, usually 2 to 4 mm. The packed particles cause large pressure drop along the column, thus limiting its length to 1 to 6 m.

Capillary columns were introduced later than packed columns. However, they grew quickly in popularity and became predominately used in GC analysis. In the 1990s, it was estimated that over 80% of all applications were run on capillary columns.[47] Modern capillary columns are usually open tubular columns. They are of two basic types: wall-coated open tubular (WCOT) and support-coated open tubular (SCOT). Wall-coated columns are simply capillary tubes coated inside with a thin layer of the stationary phase. In support-coated columns, the stationary phase is held by a thin film of a support material lined on the inner surface of the capillary. Open tubular columns have been historically made of metals (such as stainless steel, aluminum or copper), glass or fused-silica. Today fused-silica capillaries are most widely used because of their lower reactivity toward sample components and flexibility. Because the open tubular structure has very low resistance to gas flow, long capillary columns are possible (up to 100 m).[47] Capillary columns also have much smaller diameters than packed columns, typically

from 0.1 mm to 0.53 mm. Long lengths and small diameters of capillary columns permit much more efficient separations of complex sample mixtures then those achievable with packed columns.

One of the important factors that affect column performance is the stationary phase. It can be either a liquid or a solid. Liquids are more commonly used. For fused-silica capillary columns, the liquid is coated on the inside of the capillaries. To make it adhere better, the liquid phase is often extensively cross-linked and/or chemically bonded to the fused silica surface. Requirements for a good stationary phase are low volatility, thermal stability, chemical inertness, and low viscosity (for fast mass transfer). A large number of liquids have been used as stationary phases, among which polydimethyl siloxane with varying degrees of substitution of functional groups such as phenyl and cyanopropyl are most commonly used.

A retention gap, also called a guard column, is a section of uncoated or deactivated tubing (usually 0.5 to 5 m long) installed between the injector and the analytical column.[47] The retention gap is usually used in splitless or on-column injection. There are several reasons for using a retention gap: first, if too much solvent is injected into a column, micro-droplets of liquid solvent can spread inside the column for a certain distance; solutes dissolved in the droplets cause ragged bands to show on the chromatogram. By using a retention gap, solvent is vaporized by the end of the retention gap, avoiding sporadic portions of solutes distributing along the analytical column. Second, the retention gap is used to focus vaporized solutes on the head of the GC column, thus decreasing band broadening. The sample is injected into the retention gap where it resides and then vaporizes. The vaporized solutes travel with the carrier gas

without stationary phase retention until they reach the beginning of the analytical column, in which the analyte migration rate is retarded as analytes begin to partition into the stationary phase. In this way, analyte molecules at the rear of the moving band can catch up with the molecules that first reach the analytical column and join the partitioning process as a focused band. Third, the retention gap is used as a guard column to collect nonvolatile components and decomposition products and prevent them from accumulating at the inlet of the analytical column. As such, it preserves the lifetime of the analytical column. Proper connection of the retention gap to the analytical column is essential for the integrity of the analysis. Leaks and active sites within the connection fittings can lead to analyte loss, peak tailing and destruction of the stationary phase in extreme cases. Presently, commercially available connection fittings include metal connectors of low dead volume, press-tight connectors, and capillary Vu-Unions.[47]

1.3.5 GC Detectors

After the components of a mixture elute from the GC column, they interact with the detector. The detector provides the response signals corresponding to the amount of the components, thus the separated components can be identified and measured. The plotting of the detector signal as a function of time provides a chromatogram. Nowadays various general and selective detector types are available, among which the most widely used include flame ionization detector (FID) and electron capture detector (ECD). While FID is generally considered a universal detector responding to the presence of hydrocarbons, ECD is more selective to those compounds that "capture electrons". These compounds include halogenated molecules such as PCBs and some pesticides. Consequently, one of the primary uses for ECD is in PCB and pesticide analysis.[48] Another detector that is

selective to halogenated compounds is the dry electrolytic conductivity detector (DELCD).

FID is the most commonly used general type detector.[47] The FID consists of a small hydrogen-air burner, to which the eluted components from the column are directed with carrier gas flow. A collector electrode is located above the burner tip. The hydrogen-air burner is ignited electrically. As the organic components reach the hydrogen-air flame, they are pyrolyzed at the temperature of the flame and produce ions that can conduct electricity through the flame. A potential of a few hundred volts is applied across the burner tip and the collector electrode. As a result, a small electric current is generated between the collector electrode and the burner tip. The resulting current is then directed to an amplifier for measurement. Although the ionization of carbon compounds in the hydrogen-air flame is not well understood, it has been observed that the number of ion produced is proportional to the number of carbon atoms entering the flame. Therefore, the FID response is proportional to the number of carbon atoms, instead of the compound concentration.[47] A disadvantage of FID is that it is destructive to the sample.

ECD consists of a chamber containing two electrodes. In the chamber, there is a radioactive source (usually nickel-63) emitting β-radiation. The effluent from the GC column is passed over the radioactive source. In the absence of organic species, carrier or make-up gas (usually nitrogen) entering the detector is ionized by high-energy electrons (β-rays), inducing a burst of electrons. A constant standing current is thus generated between the two electrodes. However, in the presence of analytes with a high electron affinity, some electrons are “captured” by the analytes. As a result, the current subsequently decreases. This decrease in the standing current is recorded and converted

to the amount of analytes. The ECD is highly sensitive to molecules containing electronegative functional groups such as halogens, peroxides, and nitro groups. Based on gas-phase electron-capture reactions, the ECD is able to detect picogram and even femtogram levels of specific substances in complex matrices. This ability makes it a very useful detector for environmental and biomedical analysis.[45] The disadvantages of ECD include narrow linear range (about three orders of magnitude), strong dependence of the response factor on the structure of the molecule and degree of substitution with electron-capturing moieties, as well as the use of radioactive material, which creates difficulties when the detector is transported.

The DELCD offers somewhat worse sensitivity than ECD, but is more selective to halogens, and insensitive to oxygenated compounds. Compared to the traditional solvent-based electrolytic conductivity detector (wet ELCD), the dry ELCD does not use a solvent as the electrolyte since the reaction products are detected in the gas phase. Thus, the possible variations in sensitivity and reproducibility caused by minor changes in solvent flow can be avoided in DELCD.

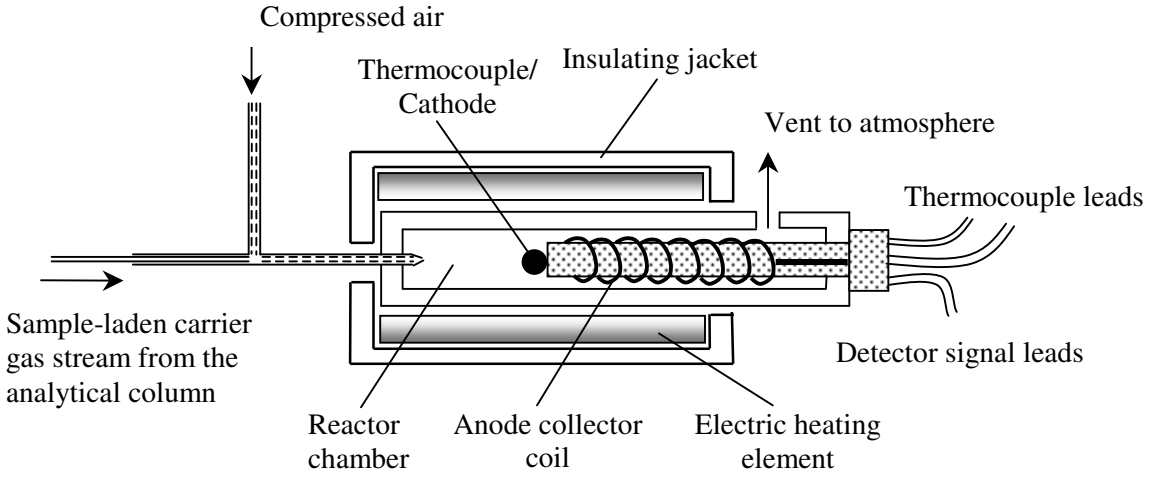


Figure 1-5: Simplified diagram of a DELCD[46]

Figure 1-5 shows a simplified diagram of a DELCD installed in the SRI model 310 GC.[46] The DELCD consists of a reactor chamber which is made of a ceramic cylinder with an inner diameter of 5 mm. The reactor chamber can be heated to 1000 °C by an electric heating element wrapped around the exterior of the ceramic cylinder. A collector electrode assembly is mounted inside the reactor chamber. A platinum thermocouple is built into the collector body. A nichrome collector electrode coil is wound around the collector body. The thermocouple permits precise temperature measurement of the site of reaction. The collector electrode is in the flow path of the carrier gas stream exiting the column and measures the conductivity of the gases flowing through the DELCD. Halogenated compounds eluting from the analytical column enter the high-temperature (1000 °C) reactor chamber. Under the high temperature, the halogenated compounds are oxidized in an oxygen-rich environment which is provided by a continuous flow of compressed air through a built-in or external compressor. Oxidation of halogenated compounds in the gaseous state generates gas phase ions, which permit the conductivity to be measured and quantified via the collector electrode connected to the detector electronics. The detector response is dependent upon its temperature. Therefore, the control circuit must maintain the temperature at 1000 °C.

1.3.6 GC in Environmental Analysis

Just as in many other areas of science, gas chromatography plays a central role in environmental analysis, especially for the determination of organic compounds of environmental concern. Because a large number of environmental pollutants are organic compounds, GC's capability to quickly and reliably detect trace levels of numerous organic contaminants in environmental samples makes it a very valuable and versatile

tool in this field. It is then not surprising that gas chromatography has been at the center of the US EPA methods for monitoring and analyzing organic compounds in the environment.[47] GC alone, or combinations of GC with other techniques such as mass spectrometry, have become standard methods for the analysis of a wide range of pollutants, such as VOCs, PAHs, pesticides, and halogenated compounds, in all kinds of matrices (air, water, sediment, soil, solid waste, animal tissue).[49] The vitality of GC in environmental analysis is also reflected by its application in fast, on-site analysis of field contaminants. Truly portable GCs are now commonly used in environmental field analysis.

In spite of the good separation power of conventional single-column GC (one-dimensional GC, or 1DGC), if the sample itself or the matrix in which it is present is very complex, the technique is usually incapable of separating all the sample components in a single chromatographic run.[50] Although resolution and separation power can be enhanced to some extent by using longer or narrower bore columns in 1DGC, the improvement is restricted by limited sample capacity and slow analysis time. For example, the determination of all individual congeners in PCBs is still one of the most difficult problems in environmental analysis. There is no single GC capillary column available that could completely separate all 209 congeners of PCBs.[51, 52] In order to overcome the separation and resolution limitations of single-column GC, one attempt is coupling GC to mass spectrometry (GC/MS), which allows for further characterization (through mass spectral information) of the eluted compounds.[53] However, even with the spectral deconvolution ability of powerful modern MS detectors, such as the time-of-flight mass spectrometer (TOF-MS), separation and identification of the components of very

complex mixtures often remains unsatisfactory.[54] Another alternative chromatographers turn to deal with the peak capacity problem in 1DGC is the implementation of comprehensive two-dimensional gas chromatography (GC × GC), which provides the greatest separation power in GC analysis so far.

1.4 Comprehensive Two-dimensional Gas Chromatography (GC × GC)

The comprehensive two-dimensional gas chromatography (GC × GC) technique arose from the need for more powerful and reliable solution to the separation and resolution problems encountered in the conventional GC. Today the GC × GC technique has become one of the most powerful analytical tools in the analysis of very complex samples.[55]

1.4.1 Principles of GC × GC

The idea of "separation dimension" was first elucidated by Giddings, who discussed many basic criteria for defining separation dimensions in his pioneering paper dating back to 1984.[56] In comprehensive two-dimensional gas chromatography, a separation dimension can be defined as a single column that separates compounds based on its particular properties, such as the stationary phase, size, length, etc. This implies that two different columns are applied in GC × GC to generate two-dimensional separations for the sample, and the separations occurring in the two columns must be independent of each other, or orthogonal. Another example of multidimensional technique is GC/MS. Coupling GC to a mass spectrometer adds the dimension of mass spectral information to the chromatographic separation. As a mass spectrometer provides mass spectrum for

every chromatographic peak eluting from the GC column, the identification of an analyte is based not only on its retention time in the GC column, but also on the second dimension of its mass spectral information, thus the separation power is enhanced by adding a second separation dimension. A comprehensive multi-dimensional separation is one in which the entire sample is subjected to separation in all dimensions, and separation accomplished in one dimension is maintained in the other. To perform a comprehensive two-dimensional separation, two orthogonal GC columns should be used, coupled by an interface (modulator) that is capable of collecting (or sampling) the effluent from the first column and periodically introducing it to the second column. A similar technique called multi-dimensional gas chromatography (MDGD), or heart-cut GC, also applies two columns with different stationary phases to realize multi-dimensional separation. However, instead of the entire sample being subjected to separation in both columns as in GC × GC, only a portion of the effluent from the first column is preserved and separated by the second column in MDGC. Therefore, the separation in MDGC is multi-dimensional but not comprehensive.[57]

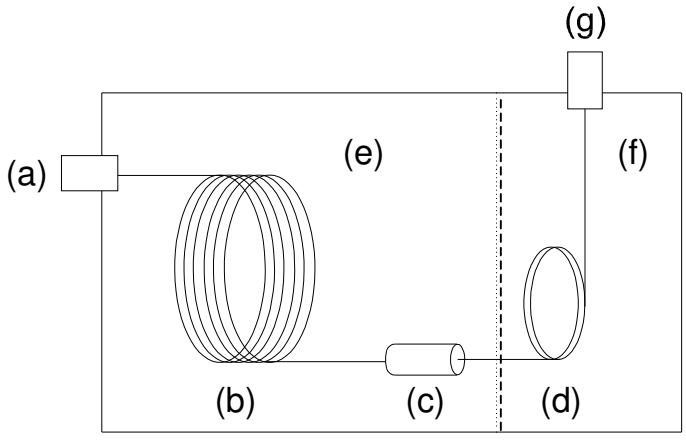


Figure 1-6: Block diagram of a GC × GC system.[58] (a) injector; (b) primary column; (c) interface/modulator; (d) secondary column; (e) oven; (f) optional secondary oven; (g) detector

A diagram of a typical GC × GC set-up is presented in Figure 1-6.[58] A long column is installed as the primary column (first dimension). Instead of connecting it to a detector, its outlet is connected through a special interface, the modulator, to the inlet of a second dimension column, coated with a stationary phase of different selectivity. A sample injected into the GC × GC system is first subjected to a chromatographic separation in the first column, identical to 1DGC. The effluent from the primary column then enters the modulator. The modulator collects the sample for a certain period of time, and then injects the entire fraction that it has collected into the second column. The separation performed in the secondary column is independent of the separation in the first dimension.[59] This process of effluent collection and injection repeats itself throughout the entire analysis.[60] Finally, the effluent from the second dimension column enters the detector to obtain a series of short second dimension chromatograms, one after another.

1.4.2 Generation and Interpretation of a GC × GC Chromatogram

The process of GC × GC chromatogram generation is illustrated in Figure 1-7.[61] First, peaks eluting from the primary dimension are sliced according to the specified modulation period ($t_2 - t_1$, $t_3 - t_2$, etc.). Primary dimension retention times are defined as the times when injection into the second column occurs (t_1, t_2, t_3, etc.; Figure 1-7a). An individual slice is then subjected to the second dimension separation, and the chromatogram from the secondary dimension is recorded by computer software (Figure 1-7b). The software then slices the entire linear chromatogram that was recorded according to the modulation period and arranges the sliced individual chromatograms side-by-side to generate a three-dimensional (3D) plot (Figure 1-7c). The 3D plot consists of the primary retention time as the x-axis, the secondary retention time as the y-axis and

the signal intensity as the z-axis. Although three-dimensional GC × GC plots are useful and straightforward when watched and manipulated on a computer screen, they are easier to interpret on paper when plotted top-down as a contour plot (Figure 1-7d). In this case, the primary and secondary dimension retention times are plotted on the x-axis and y-axis respectively, while signal intensity is either color-coded or represented with contour lines.

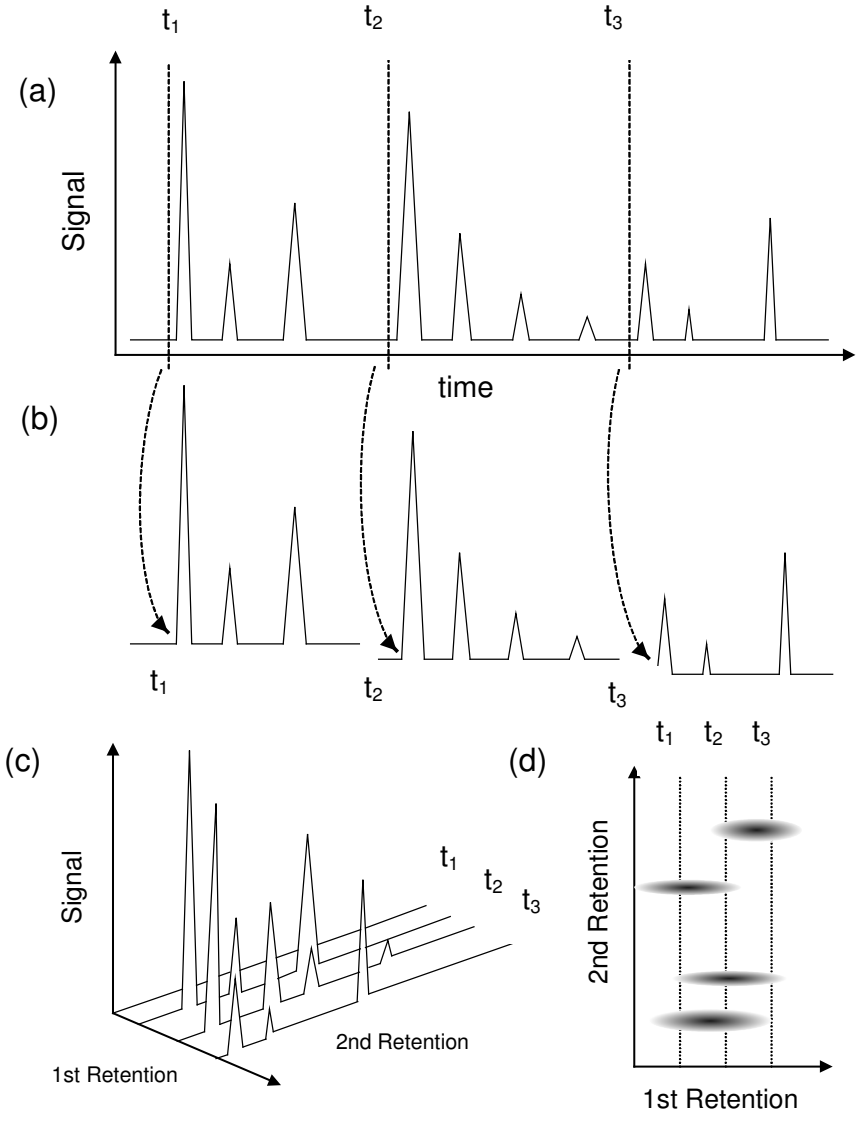


Figure 1-7: Generation and interpretation of a GC × GC chromatogram[61]

1.4.3 GC × GC Instrumentation

With the exception of the interface (modulator), most instrumental components utilized in GC × GC are in fact the same as in 1DGC. These include the carrier gas, the injector, the oven, the column and the detector. Injector types and injection techniques in GC × GC are selected according to the needs of the analysis in the same manner as they are in conventional GC analysis. It should also be pointed out that the data system for GC × GC must handle two-dimensional data, therefore data systems that are able to proceed large amount of data rapidly are required.

1.4.3.1 GC × GC Columns

The choice of the primary and secondary columns is important for successful GC × GC separation. The primary column is usually long, with typical dimensions of 15 – 30 m × 0.25 mm I.D. The stationary phase film thickness is in the range of 0.25 – 1 μm. These columns allow the generation of peaks with widths of 10 – 20 s, which allows each peak from the first column to be sampled three times with a typical modulation period of 3 – 6 seconds. The requirements for the second dimension column are that the separation is fast and must be performed on a stationary phase different from the one used in the primary column. It is desirable that each individual separation in the second dimension is finished in a time shorter than the modulation period. Consequently, short, narrow bore columns with thin films of the stationary phase are typically required to accomplish fast and efficient separations. Typical secondary column dimensions are 0.5 – 1.5 m × 0.1 – 0.25 mm I.D., coated with a thin film of the stationary phase (0.1 – 0.25 μm). Although column sets are typically non-polar (first dimension)/polar (second dimension), there are

no fixed rules to the combination of column phase types as long as they provide orthogonal separation.[62] Most commercially available GC × GC systems provide a small second oven for the second column. This allows for independent control of the second column temperature. However, most research is conducted using a single GC oven, as this prevents additional complexity.[63]

1.4.3.2 GC × GC Detectors

In principle, the detectors used in conventional GC can be applied to GC × GC systems. However, as the detector used in GC × GC system must respond very fast to the eluate from the secondary column, it is required that the detector has high data acquisition rate. For instance, peaks eluting from the secondary column usually have base widths smaller than 150 ms. Reliable and reproducible determination of a chromatographic peak area requires at least 10 data points to be collected along the peak profile. Thus, data acquisition rates of at least 70 Hz for the detector are required. This narrows the choice of suitable detectors used for GC × GC analysis. Flame ionization detectors (FID) can acquire data at a rate as high as 200 Hz,[63] therefore they remain the most popular choice for GC × GC analysis. Presently, mass spectrometry (MS) is the most powerful detection method in chromatography. In fact, using MS detector also generates another separation dimension. The most commonly used MS detector in GC × GC so far is the time-of-flight mass spectrometer (TOF-MS) due to its very fast data acquisition rates.

1.4.3.3 GC × GC Modulators

The modulator plays a core role in the success of GC × GC analysis. There are two basic types of modulators: thermal modulators and valve-based modulators. Thermal modulators are more commonly applied. They can be further subdivided into two groups: heater-based (based on an increase in temperature) and cryogenic (based on a decrease in temperature).

Heater-based modulator was introduced with the first successful implementation of GC × GC by Phillips and Liu.[64] The principle of the modulator is that a thick film-coated capillary column acting as the interface is alternately heated in two segments. The heating temperature is about 100 °C higher than oven temperature. With alternate heating of the capillary column, analytes originally trapped in it are desorbed and subsequently released. Another type of heater-based modulator, called rotating thermal modulator, was also developed by Phillips and coworkers and was the first commercially available modulator.[65, 66] The modulator also utilized a thick film capillary column as the interface. A rotating heater was used to periodically heat the column. When the heater turned to the column, the trapped analytes were desorbed and released. When the heater turned away from the column, the column cooled down and trapped next portion of the analytes eluting from the first dimension. The disadvantage of heater-based modulators is their inability to effectively trap volatile compounds at conventional oven temperatures and the requirement for high modulation temperatures for analytes with high boiling points.[55]

The idea of dual-stage modulation introduced in heater-based modulators also applies to cryogenic modulators. However, instead of trapping the effluent at oven temperature and desorbing it by increasing the temperature, cryogenic modulators trap the analytes at

temperatures significantly below that of the GC oven, and release them at oven temperature. The cryogens used for cooling are usually liquid CO_2 or liquid N_2. Presently, cryogenic modulators are most often used because of their high trapping capability for volatile compounds.[55] However, for semi-volatile compounds such as PCBs, it is difficult to modulate cryogenically. In this case heater-based modulators are desirable.

Valve-based modulators were developed based on the switching techniques applied in MDGC. Initially, valve-based modulators transferred only small portions of the effluent from the primary column to the secondary column. Recent advances in the technology largely eliminated this limitation. For example, one valve-based modulator which subjected 100% of the sample to separation in both dimensions was developed by Seeley et al.[67]

1.4.4 Applications of GC × GC

Although the idea of a GC × GC separation was first proposed as a possibility by Giddings in 1984, it was not until 1991 that the first practical implementation of this principle was demonstrated by Phillips and Liu.[64] GC × GC is a relatively young technique. However, owing to dramatically increased resolution, sensitivity, peak capacity, and selectivity of the separation, as well as highly structured, ordered chromatograms obtained by GC × GC, the years since its appearance witnessed a rapid development and implementation of this technique in many branches of industry and various research sectors.

Initially, the main application of GC × GC was the analysis of petroleum products. Typical petrochemical samples such as gasoline, diesel and kerosene contain thousands

of components. Greatly increased peak capacity and enhanced resolution of GC × GC provided the best chromatographic separations ever achieved for these types of samples, and allowed quantitative analysis of many previously undetected compounds in complex matrices.[68-70] Analyses in food and fragrance industry, as well as forensic science, have also benefited from the same advantages GC × GC offers to petrochemical analysis. Many successful applications of GC × GC techniques in these analytical sectors were reported.[71-73] In these cases, the results obtained by GC × GC were not previously achievable with 1DGC, even when coupled with the most powerful MS detectors. Since GC × GC was successfully implemented in the analytical sector, tremendous research effort has been put into its applications in environmental analysis, leading to many publications on its use in this field. A wide range of environmental pollutants such as PCBs, PCDDs, PCDFs, pesticides, fuel hydrocarbons in all kinds of sample matrices (air, water, sediment and soil) have been reported using GC × GC as the analytical method.[57, 74] Overall, GC × GC has now been accepted as a very powerful and reliable tool in environmental analysis.

2.0 Optimization and Characterization of Field GC Method

2.1 Introduction

In this research, prior to combining thermal desorption to the field GC, the field GC method must be first studied to provide fast, reproducible analysis of total PCBs. For this purpose of the field GC method, total PCBs were intended to be detected as a single elution peak. Separation of the individual PCB congeners was neither required nor desired. The use of a selective detector, DELCD, in this method eliminated the need for the separation of non-halogenated compounds from PCBs. However, other halogenated contaminants such as trichloroethylene (TCE) and pesticides could be present in the environmental samples and detected by the DELCD. In this case, the halogenated compounds must be completely separated from total PCBs so that total PCBs still be clearly identified and quantified. Therefore, the field GC conditions, such as the column setting, carrier gas flow rate, and oven temperature applied in this research should allow fast elution of total PCBs as a reproducible, non-separated single peak and should provide separation of other halogenated compounds possibly present in the sample from the PCBs. Based on the optimized filed GC conditions, analytical characteristics of the field GC method such as quantitative response and detection limit for total PCBs should also be determined. Optimization and characterization of the field GC method were done by analyzing liquid PCB standards.

2.2 Experimental

2.2.1 Instrumentation

The gas chromatograph used for the separation and detection of total PCBs in this research was SRI Instruments Model 310 ultra compact field portable GC (SRI 310 GC).

The SRI 310 GC was equipped with a direct injection-type injection port made of Swagelok stainless steel fitting. This injection port allowed on-column manual injections with regular chromatographic syringes. Injection of 1 μL liquid standards was performed using a 10 μL standard syringe. The SRI 310 GC can mount up to 4 detectors. For detection of total PCBs, a dry electrolytic conductivity detector (DELCD) was used. The SRI 310 GC oven was temperature programmable from ambient to 400 °C, with unlimited holding times.[1]

The on-column injection required that a megabore, or 0.53 mm I.D. column (or retention gap) be connected to the injector. Because fast elution of total PCBs as a single peak was expected in this research, the column used should not be long. Using megabore column also made up for the reduced column capacity due to a short column length. For these reasons, 0.53 mm I.D. Silcosteel tubing and 0.53 mm I.D. MXT-1 analytical column were selected for the separation of total PCBs. The MXT-1 column selected was coated with 0.5 μm 100% polydimethylsiloxane (PDMS) stationary phase that was recommended for the separation of PCBs.[2] When using the MXT-1 column, a section of 0.5 m long deactivated 0.53 mm I.D. Silcosteel tubing was used to connect the MXT-1 column and the detector for protection of the MXT-1 column from the high temperature (1000 °C) of the detector. A 0.5 m long deactivated 0.53 mm I.D. Silcosteel tubing was installed in front of the MXT-1 column as the retention gap. To compare total PCBs separation, a 0.5 m long and a 4 m long MXT-1 column were tested respectively.

Dry compressed nitrogen was used as the carrier gas for the SRI 310 GC. Make-up air was supplied by a compressor built into the SRI 310 GC to provide oxygen for the oxidation of halogenated compounds under high temperature. Both carrier gas and make-

up air flow rates were controlled by electronic pressure controllers (EPCs). An Agilent ADM2000 flow meter was also used to verify carrier gas and make-up air flow rates. The compressed air (make-up air) flow rate and reactor temperatures were set unchanged at 10 mL/min and 1000 °C respectively according to manufacturer specifications.[1] The temperature of the detector base heater was maintained at 300 °C to prevent condensation of the effluents coming out from the column.

The control of the SRI 310 GC operation and data processing was performed by PeakSimple Chromatography Data System software (SRI Instruments) run on a personal computer connected to the GC. Since no extra hardware is required for the computer, a portable laptop computer can be easily connected to the GC for on-site applications. The PeakSimple software required manual initiation of a GC run by pressing space bar of the computer after injection. Integration of elution peaks was conducted automatically by the software or using "manual integration" function of the software.

2.2.2 Liquid Standards

Optimization study of the SRI 310 GC conditions and determination of the calibration curve and detection limit for total PCBs, which were represented by Aroclor 1254 in this research, were conducted using liquid total PCBs standards. Liquid decachlorinated biphenyl (DCB) congener standards were prepared to test the sensitivity of the DELCD. In order to investigate the separation of trichloroethylene (TCE) from total PCBs, liquid TCE standards and mixtures of liquid TCE and total PCB standards were also prepared.

Table 2-1: Liquid Standard Series Prepared by Dilution

Name	Concentration of standard used for dilution (µg/mL)	Volume of standard used for dilution (µL)	Volume of hexane added (µL)	Total dilution volume (µL)	Concentration of diluted standard series (µg/mL)
Total PCBs (Stock standard: 1000 µg/mL Aroclor 1254 in hexane)	1000	110	1000	1110	99.1
	1000	50	1000	1050	47.6
	1000	25	1000	1025	24.4
	1000	10	1000	1010	9.9
	1000	5	1000	1005	5.0
	1000	2.5	1000	1002.5	2.5
	1000	1	1000	1001	1.0
	1000	0.5	1000	1000.5	0.5
	0.5	500	500	1000	0.25
	1.0	100	900	1000	0.1
	1.0	50	950	1000	0.05
	1.0	10	990	1000	0.01
DCB (Stock standard: 1382 µg/mL DCB in hexane)	1382	80	1000	1080	102.4
	1382	40	1000	1040	53.2
	1382	19	1000	1019	25.8
	1382	8	1000	1008	11.0
	1382	4	1000	1004	5.5
	1382	1.5	1000	1001.5	2.1
	1382	1	1000	1001	1.4
	1382	0.5	1000	1000.5	0.7
	1.4	70	930	1000	0.1
	1.4	35	970	1005	0.05
TCE (Stock standard: 16.27 mg/mL TCE in hexane)	16270	0.6	1000	1000.6	9.8
Mixture of TCE and PCB	TCE: 16270 PCB: 1000	TCE: 0.6 PCB: 10	990	1000.6	TCE: 9.8 PCB: 10

Preparation of liquid total PCBs standards was performed through the following procedure: a solution of 1 mg/mL Aroclor 1254 in hexane stock standard was used for preparation of diluted PCB standard series. The standard series were prepared by dilution of an aliquot of the stock standard with an aliquot of hexane in a 1.5 mL vial using size appropriate syringes. The solution in the vial was then thoroughly mixed for 1 to 2 minutes using a vortex type mixer. For the determination of the limit of detection, low concentration PCB standards must be prepared. This was conducted by further diluting an

intermediate standard through the same procedure. For example, a 0.05 µg/mL standard was prepared by adding 50 µL of 1.0 µg/mL standard to 1.5 mL vial, and diluting it with 950 µL hexane. All liquid standards were stored at 4 °C for future use.

Likewise, liquid DCB standards, TCE standards and mixtures of TCE and total PCBs standards were prepared following the same procedure. Liquid standard series prepared by dilution are summarized in Table 2-1.

2.3 Results and Discussion

2.3.1 Optimization of Field GC Conditions

2.3.1.1 Injector Temperature

In the SRI 310 GC, the on-column injector was mounted on the inside wall of the GC oven. Swagelok stainless steel hardware was used in the assembly of the injection port. The heating source for the injection port was the GC oven. The effect of changing oven temperature on the injector temperature was investigated by placing a K-type thermocouple at the injector position that the syringe tip reaches. The oven temperature was set at initial temperature of 50 °C, ramping at a rate of 100 °C/min. When the final temperature reached 300 °C, it was held for 3 minutes. The results of the actual temperature change for the GC oven and the injector are presented in Figure 2-1.

This experiment confirmed that the actual injector temperature was lower than the oven temperature for most of the run. For example, starting from 50 °C, the oven took about 4 minutes to reach 300 °C and then needed 6.5 minutes to cool down to 50 °C, while the time for the injector to complete the process were 4.5 minutes and 12 minutes respectively. From this result, we can conclude that the injector needed more time to

return to the initial temperature than that of the oven. Increasing the initial temperature could narrow the time difference. For example, if initial temperature was 125 °C, the oven would take 5.5 minutes to finish the cycle and the injector would need 6.5 minutes. The difference was shortened to 1 minute. Therefore, if the initial oven temperature was set at 125 °C, there should be 1 minute waiting time for another injection after each run to make sure that the starting temperatures for the injection port and the oven were identical. It was also observed that the actual oven temperature did not rise as rapidly as the programmed setting. With the oven temperature ramp setting at 100 °C/min, the oven temperature should have reached the desired final temperature (300 °C) in 2.5 minutes. However, the oven took approximately 4 minutes to reach the final temperature setting. That meant that the actual oven temperature ramp was 75 °C/min. Consequently, the maximum temperature ramp rate setting should be no higher than 75 °C/min.

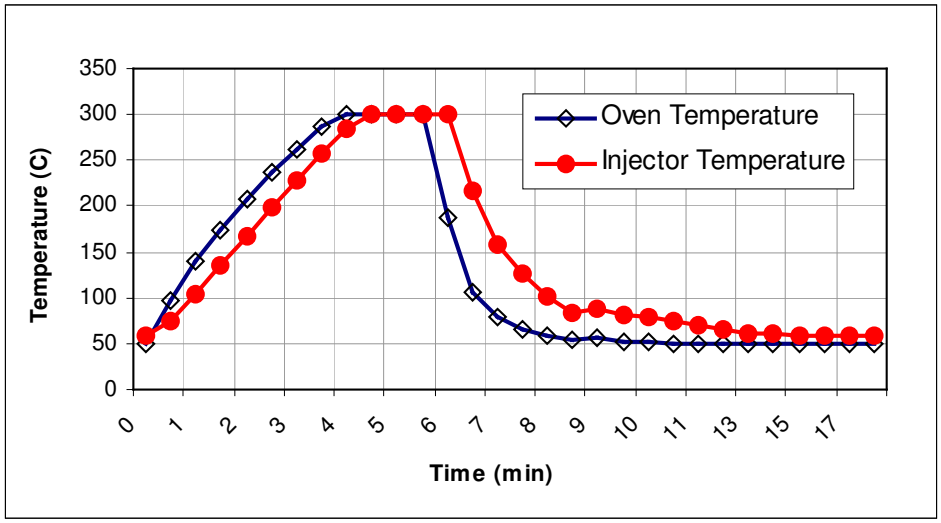
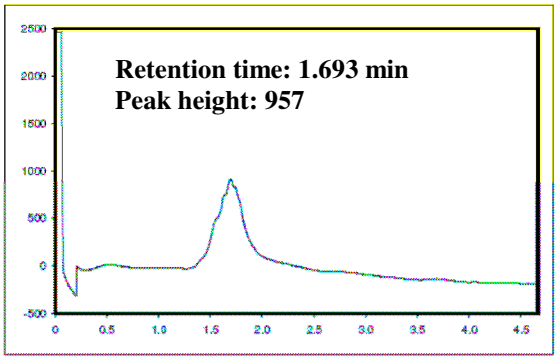


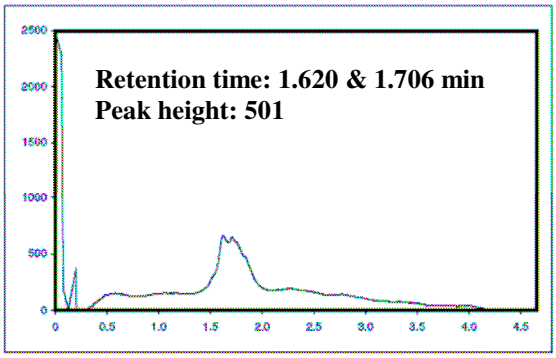
Figure 2-1: Comparison of oven and injector temperature change

2.3.1.2 Column Selection for the Separation of Total PCBs

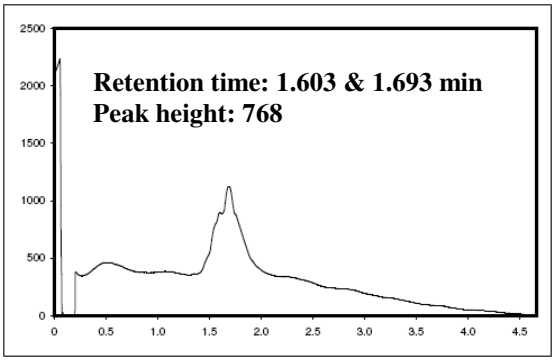
Initially, introduction and transfer of PCBs to the detector were done using a 1.5 m long, 0.53 mm I.D. deactivated Silcosteel tubing. As no stationary phase was in the tubing, this tubing simply acted as a transfer line. PCBs injected into the tubing volatilized with the increased oven temperature and were driven to the detector by the flow of carrier gas. Partial separation of the PCBs was due to the different boiling points of the individual PCB congeners contained in the sample. Figure 2-2 shows the chromatograms for 3 repeat injections of 1 µL of 10 µg/mL Aroclor 1254 standard in hexane.



Injection 1



Injection 2

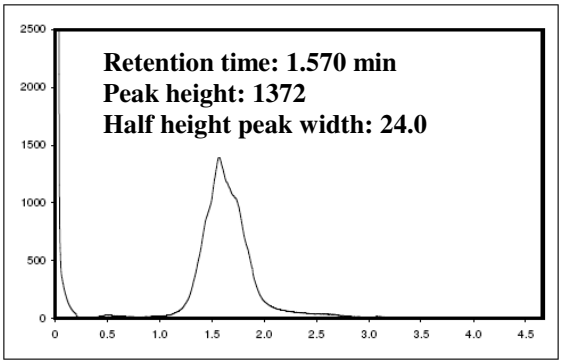


Injection 3

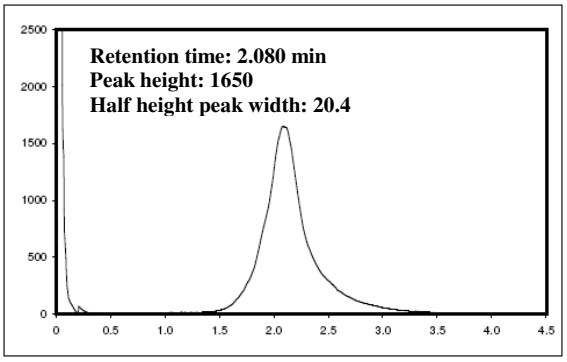
Figure 2-2: Chromatograms of three injections of 10 ng total PCBs separated using a 1.5 m long, 0.53 mm I.D. deactivated Silcosteel tubing. Oven temperature: 125 °C initial temperature held for 0.5 min, ramping to 250 °C at a rate of 75 °C/min. Carrier gas flow rate: 20 mL/min. Make-up air flow rate: 10 mL/min. Detector heater temperature: 300 °C. Detector reactor temperature: 1000 °C. Detector attenuation: medium.

As can be seen in Figure 2-2, total PCBs were detected as a broad peak containing small, partially separated peaks. Distributions of the minor peaks in the major peak were

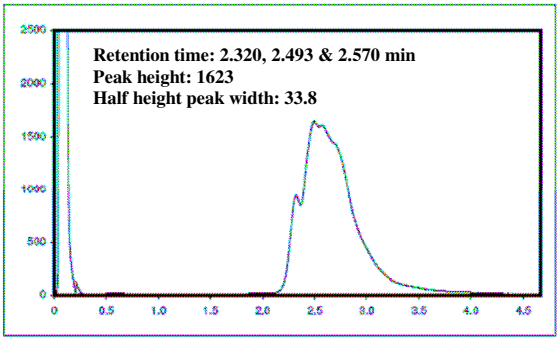
different in the three chromatograms. Peak shapes and peak heights in these chromatograms were also different, indicating poor reproducibility of the separation. Another problem with the separation of total PCBs using a deactivated tubing was that if other halogenated compounds with boiling points close to that of PCBs would be present in the sample, separation of these compounds from total PCBs would be impossible.



(a) 0.5 m × 0.53 mm × 0.5 µm MXT-1 without retention gap



(b) 0.5 m × 0.53 mm × 0.5 µm MXT-1 with 0.5m retention gap



(c) 4 m × 0.53 mm × 0.5 µm MXT-1 with 0.5m retention gap

Figure 2-3: Chromatograms of 10 ng total PCBs separated using different column settings (other GC conditions same as Figure 2-2).

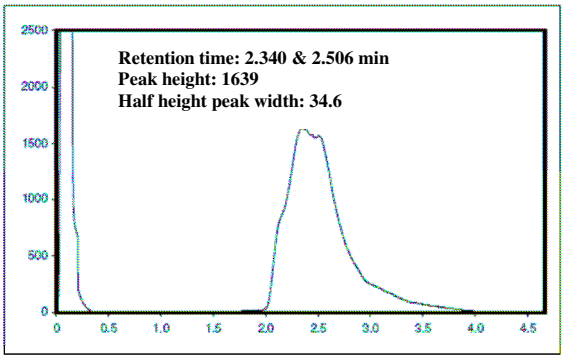
Separation of total PCBs was then tested using MXT-1 column with different settings (column length, with or without retention gap). The column that would generate sharp, non-separated single peak with faster total PCBs elution time would be selected for this research. Injections were conducted using 1 µL injections of 10 µg/mL Aroclor 1254 standard in hexane. Chromatograms of total PCBs using different MXT-1 column settings are presented in Figure 2-3. A long column (4 m) generated partly separated

peaks. According to plate theory[3], resolution of the GC column is proportional to the square root of the column length. Therefore, long column provides better separation of the analytes. However, separated peaks were not desirable in this research because peak separation was usually not reproducible, which increased the uncertainty of total PCBs measurements. The retention time of total PCBs in a long column was also longer. As a comparison, total PCBs eluted as a non-separated single peak when using 0.5 m long columns. We can also see that the peak shape was improved when using a retention gap with 0.5 m long MXT-1 column: the half height peak width was reduced from 24.0 to 20.4 s, and the peak height increased from 1372 to 1650 units. As a result, the 0.5 m × 0.53 mm I.D. × 0.5 μm d_f MXT-1 column with a 0.5 m retention gap gave the best performance for total PCBs analysis, with fast elution of PCBs as a sharp single peak.

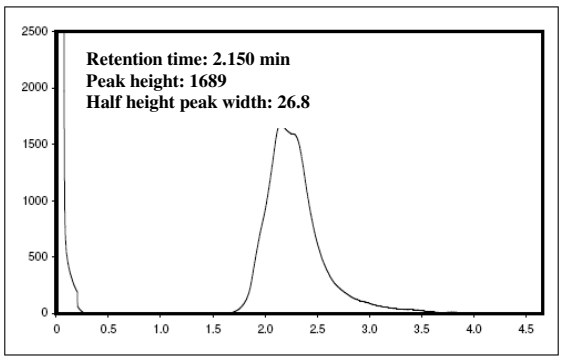
2.3.1.3 Carrier Gas Flow Rate

According to the van Deemter's plot,[4] which illustrates the effect of mobile phase flow rate on plate height in chromatographic analysis, there is a minimum plate height in the curve corresponding to the velocity that provides the highest efficiency of separation in the column. On the other hand, the velocity of the mobile phase also affects the elution time of the analyte. In this research, total PCBs were expected to elute as a single peak, and separation of PCB congeners was not desired. Therefore, the selected carrier gas flow rate was not intended to provide high separation efficiency. This carrier gas flow rate was desired to generate a sharp total PCBs peak in a reasonable total PCBs elution time, leading to fast analysis. In this investigation, different carrier gas flow rates were tested to obtain the optimum flow rate that provided the least peak broadening in a relatively short analysis time. The tests were carried out using the optimized column setting in the

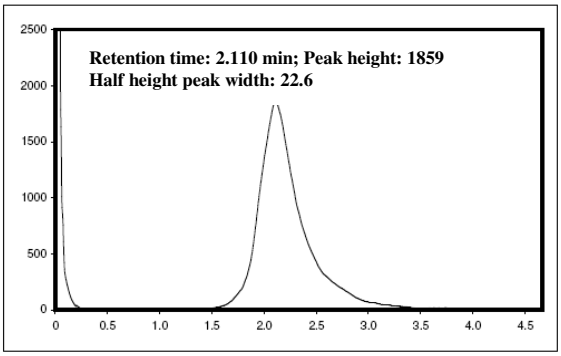
previous section. Injections were performed using 10 µg/mL Aroclor 1254 in hexane (1 µL injection). The results are shown in Figure 2-4.



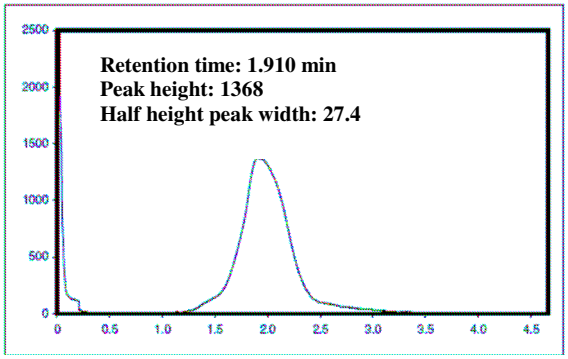
(a) Carrier gas flow rate: 5 mL/min



(b) Carrier gas flow rate: 10 mL/min



(c) Carrier gas flow rate: 20 mL/min



(d) Carrier gas flow rate: 40 mL/min

Figure 2-4: Chromatograms of 10 ng total PCBs analyzed under different carrier gas flow rates (other GC conditions same as Figure 2-2).

As expected, the retention time of total PCBs decreased with the increase of carrier gas flow rate (retention time decreased from 2.506 to 1.910 minutes when flow rate increased from 5 mL/min to 40 mL/min). Figure 2-4 also shows that when the carrier gas flow rates were 5 mL/min and 10 mL/min, partial separation of the PCBs was observed. Sharper, single peaks formed when the carrier gas flow rates were greater than 20

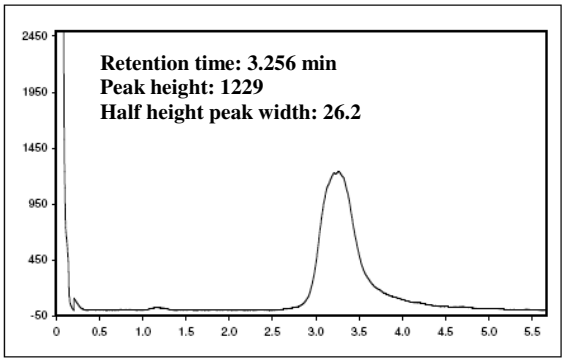
mL/min. The narrowest peak was generated with the flow rate of 20 mL/min. Therefore, the carrier gas flow rate was selected to be 20 mL/min.

2.3.1.4 Oven Temperature

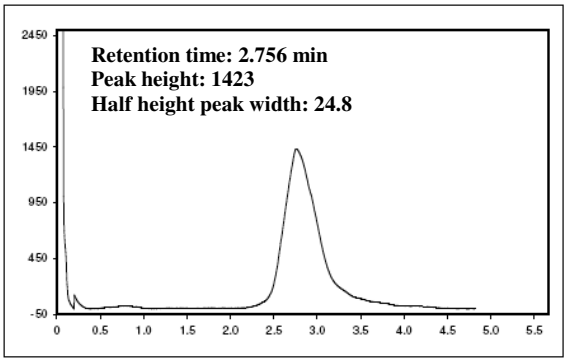
To find out how the initial oven temperature affects retention time and peak width, 1 µL aliquots of Aroclor 1254 in hexane (10 µg/mL) were injected under different initial oven temperature conditions. Using the optimized column setting, the flow rate of the carrier gas was 20 mL/min. The initial oven temperatures tested included 50, 75, 100, 125, and 150 °C. Each initial oven temperature was held for 0.5 minutes. The temperature was then ramped at a rate of 75° C/min to a final temperature of 250 °C and held for 2 minutes. Chromatograms of total PCBs under different column temperature conditions are provided in Figure 2-5.

As the initial oven temperature increased from 50 to 75, 100, 125 and 150 °C, the retention time for the total PCBs peak decreased from 3.256 to 2.756, 2.510, 2.110 and 1.690 minutes, respectively. This decrease in retention time was foreseeable because the partition coefficient between the stationary phase and the mobile phase (K) is temperature dependent. Partition coefficients of PCBs decreased with increasing temperature, which means PCBs migrated faster through the column at higher temperatures. Accordingly, the peak widths decreased with the increasing initial oven temperature as a result of reduced retention. Higher temperatures provided shorter retention times and narrower half-height peak widths that were more preferable for the purposes of this research. However, if the initial oven temperature was too high, for example 150 °C, the retention time for the total PCBs peak was very short, which could lead to co-elution of total PCBs and lower

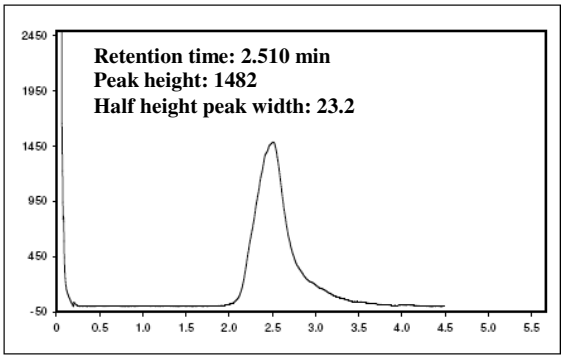
boiling point halogenated compounds in the sample. Therefore, the initial oven temperature should not be too high.



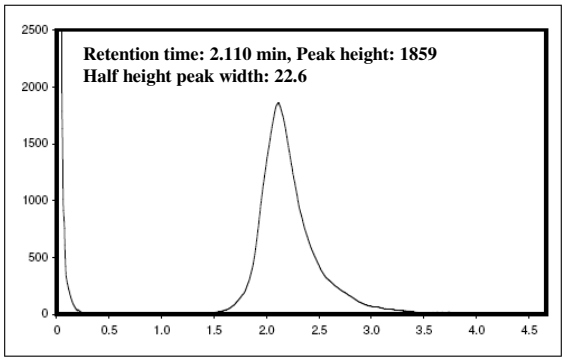
(a) Initial oven temperature: 50 °C



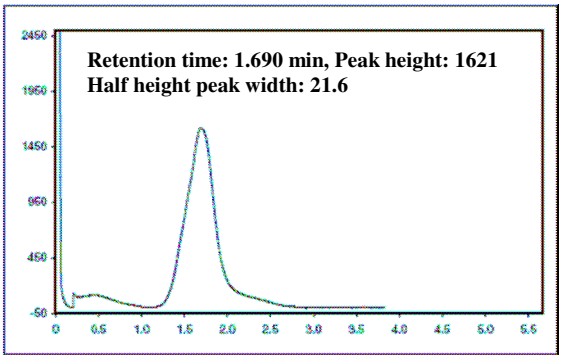
(b) Initial oven temperature: 75 °C



(c) Initial oven temperature: 100 °C



(d) Initial oven temperature: 125 °C



(e) Initial oven temperature: 150 °C

Figure 2-5: Chromatograms of 10 ng total PCBs separated under different initial oven temperature conditions (other GC conditions same as Figure 2-2).

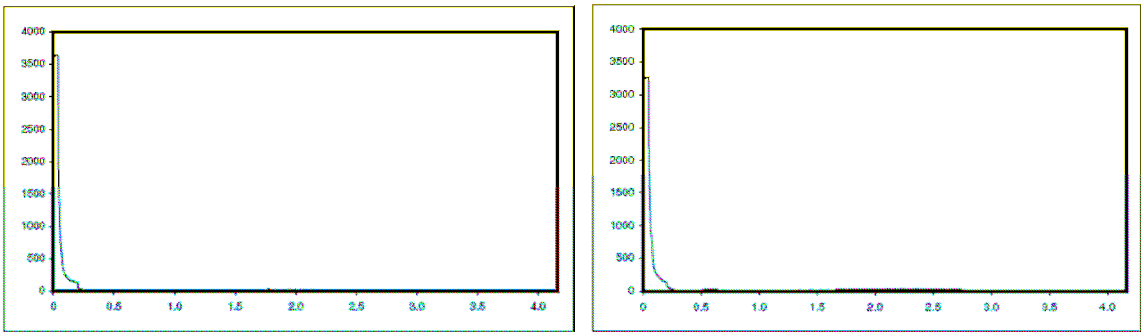
2.3.1.5 Separation of Trichloroethylene (TCE) from Total PCBs

TCE belongs to halogenated volatile organic compounds (VOCs). It does not occur naturally in the environment but is released from man-made sources.[4] TCE has a boiling

point of 87.2 °C. It is poorly soluble in water but is miscible with most organic solvents. TCE is a good solvent and is used in the degreasing of metals, in extraction processes, dry-cleaning and in insecticides. TCE is released into the environment as a result of human activities such as degreasing operations, household and industrial dry-cleaning. Water treatment facilities and landfills also release TCE. If released to soil, TCE is expected to have high mobility. Both TCE and PCBs are common in some contaminated sites and are among the top hazardous substances found at the Superfund sites.[5] Therefore, TCE and PCBs could coexist in environmental soil samples, and separation of them is thus necessary.

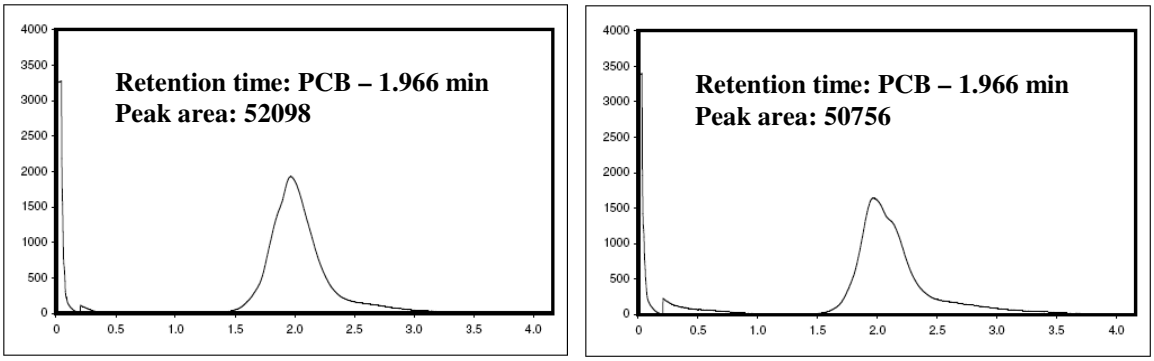
(1) Separation of TCE from Total PCBs Using a 0.5 m Long MXT-1 Column

Separation of TCE from total PCBs was first investigated using the optimized 0.5 m long MXT-1 column setting. Tests were first done under the initial oven temperature of 125 °C. Other GC conditions previously optimized were also applied. Injections of 1 μL solvent blank, 1 μL 10 μg/mL TCE in hexane, 1 μL 10 μg/mL Aroclor 1254 in hexane, and 1 μL mixture of 10 μg/mL TCE and 10 μg/mL Aroclor 1254 in hexane were carried out to compare their chromatograms. The results are presented in Figure 2-6. No TCE peak was found in the chromatogram of 1 μL of 10 μg/mL TCE standard (the disturbance of the base line at the beginning was the detector response to overloading of the solvent rather than a real peak signal, just as that of the solvent blank chromatogram). With the injection of the mixture of TCE and total PCBs, only the total PCBs peak showed in the chromatogram (this can be seen from the single peaks with very close peak areas in the two chromatograms). Therefore, under the selected optimum GC conditions, TCE could be eluted at the dead time and thus was completely separated from total PCBs.



(a) Injection: blank (hexane)

(b) Injection: 1 µL 10 µg/mL TCE in hexane



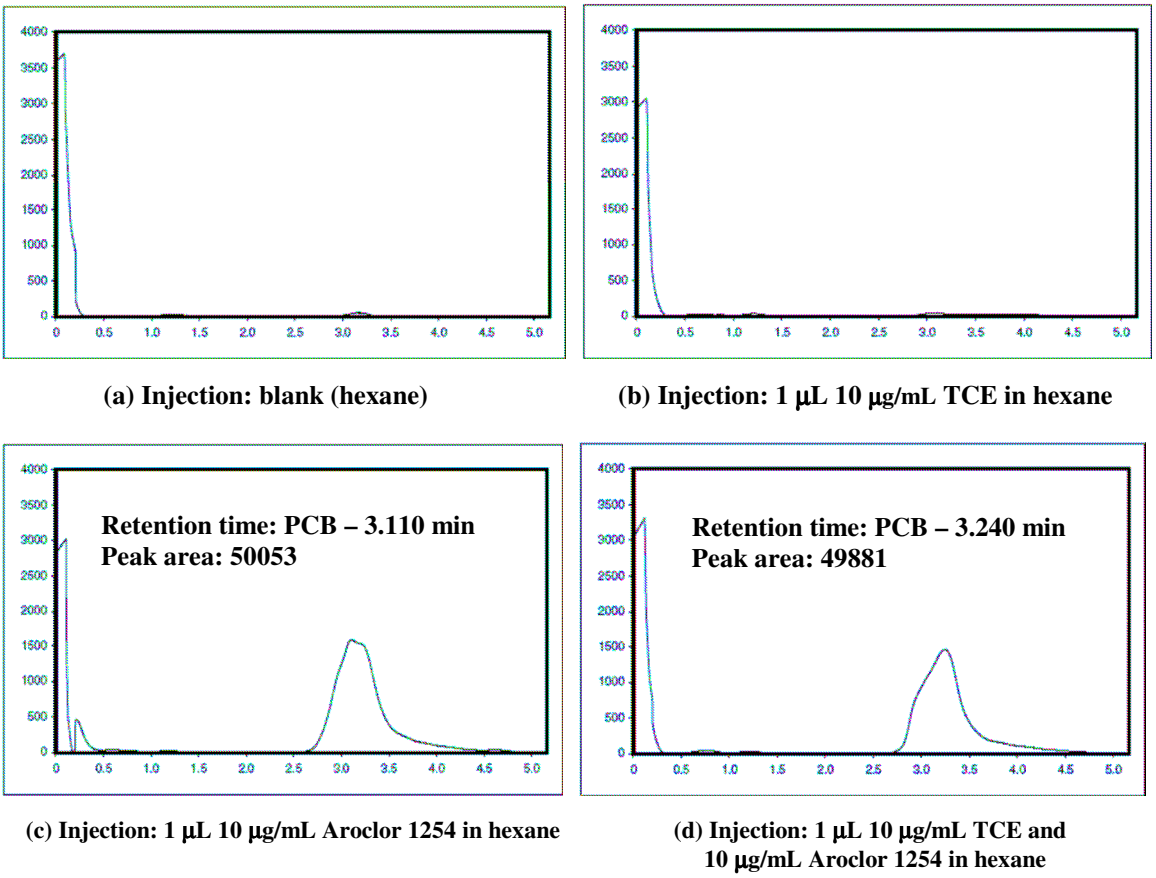
(c) Injection: 1 µL 10 µg/mL Aroclor 1254 in hexane

(d) Injection: 1 µL 10 µg/mL TCE and 10 µg/mL Aroclor 1254 in hexane

Figure 2-6: Chromatograms of TCE and total PCBs using a 0.5 m MXT-1 column setting with an initial oven temperature of 125 °C (other GC conditions as optimized in previous tests)

The separation of TCE from total PCBs was also examined at lower initial oven temperature with the same 0.5 m long MXT-1 column setting. Tests were conducted under the initial oven temperature of 50 °C, with other GC conditions kept unchanged. The results for the injections of 1 µL solvent blank, 1 µL 10 µg/mL TCE in hexane, 1 µL 10 µg/mL Aroclor 1254 in hexane, and 1 µL mixture of 10 µg/mL TCE and 10 µg/mL Aroclor 1254 in hexane are presented in Figure 2-7. The results showed that when using a short MXT-1 column (0.5 m long) with a relatively high carrier gas flow rate (20 mL/min), TCE was not detected even under a low initial oven temperature of 50 °C.

Therefore, the presence of TCE in the sample would not affect the detection of total PCBs. On the other hand, under the conditions used, the presence of TCE could not be established.



(a) Injection: blank (hexane)

(b) Injection: 1 µL 10 µg/mL TCE in hexane

(c) Injection: 1 µL 10 µg/mL Aroclor 1254 in hexane

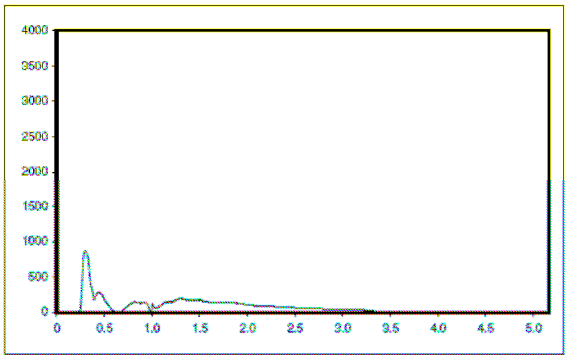
(d) Injection: 1 µL 10 µg/mL TCE and 10 µg/mL Aroclor 1254 in hexane

Figure 2-7: Chromatograms of TCE and total PCBs using a 0.5 m MXT-1 column setting with an initial oven temperature of 50 °C (other GC conditions as optimized in previous tests).

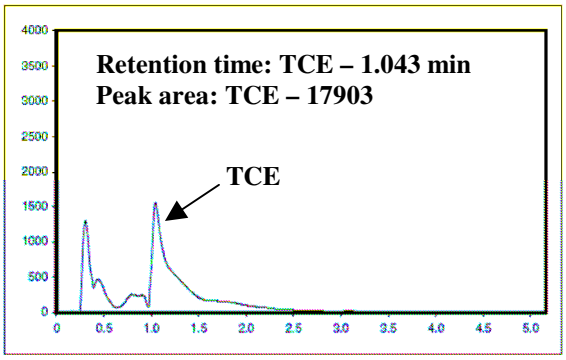
(2) Separation of TCE from Total PCBs Using a 4 m Long MXT-1 Column

Even though the detection of TCE was not the purpose of this research, and complete separation of TCE from total PCBs was achieved under the selected optimum GC conditions, some more investigations were still conducted to check the DELCD response to TCE and to test the separation of TCE and total PCBs under possible conditions

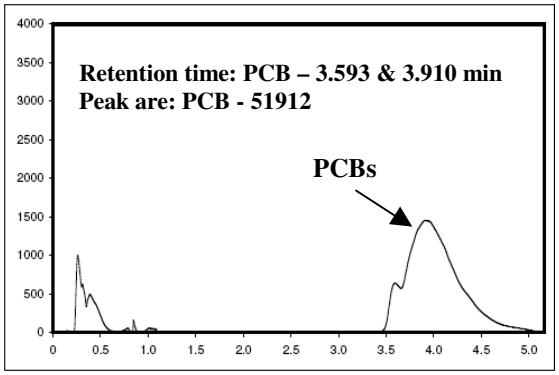
involved in a field method. From the results of previous investigations it was concluded that the separation was better with a longer column and lower carrier gas flow rate. The investigation was thus first conducted using a 4 m long MXT-1 column setting (with 0.5 m retention gap) and a carrier gas flow rate of 2 mL/min. Because the boiling point of TCE is relatively low (87.2 °C), the initial oven temperature was set at 50 °C to avoid immediate evaporation of TCE upon injection. 1 µL solvent blank (hexane), 1 µL 10 µg/mL TCE in hexane, and 1 µL 10 µg/mL Aroclor 1254 in hexane were injected respectively to get their individual chromatograms. Separation of TCE from total PCBs was then characterized by injecting 1 µL mixture of 10 µg/mL TCE and 10 µg/mL Aroclor 1254 in hexane. The chromatograms are shown in Figure 2-8.



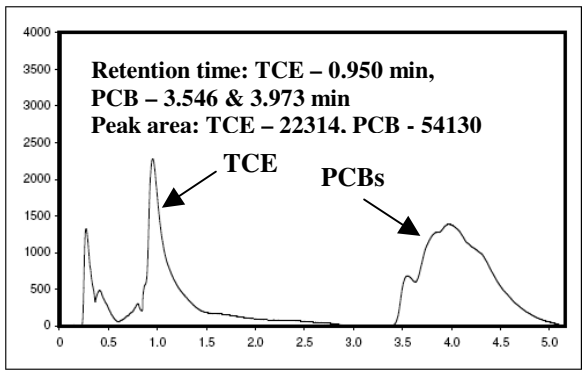
(a) Injection: blank (hexane)



(b) Injection: 1 µL 10 µg/mL TCE in hexane



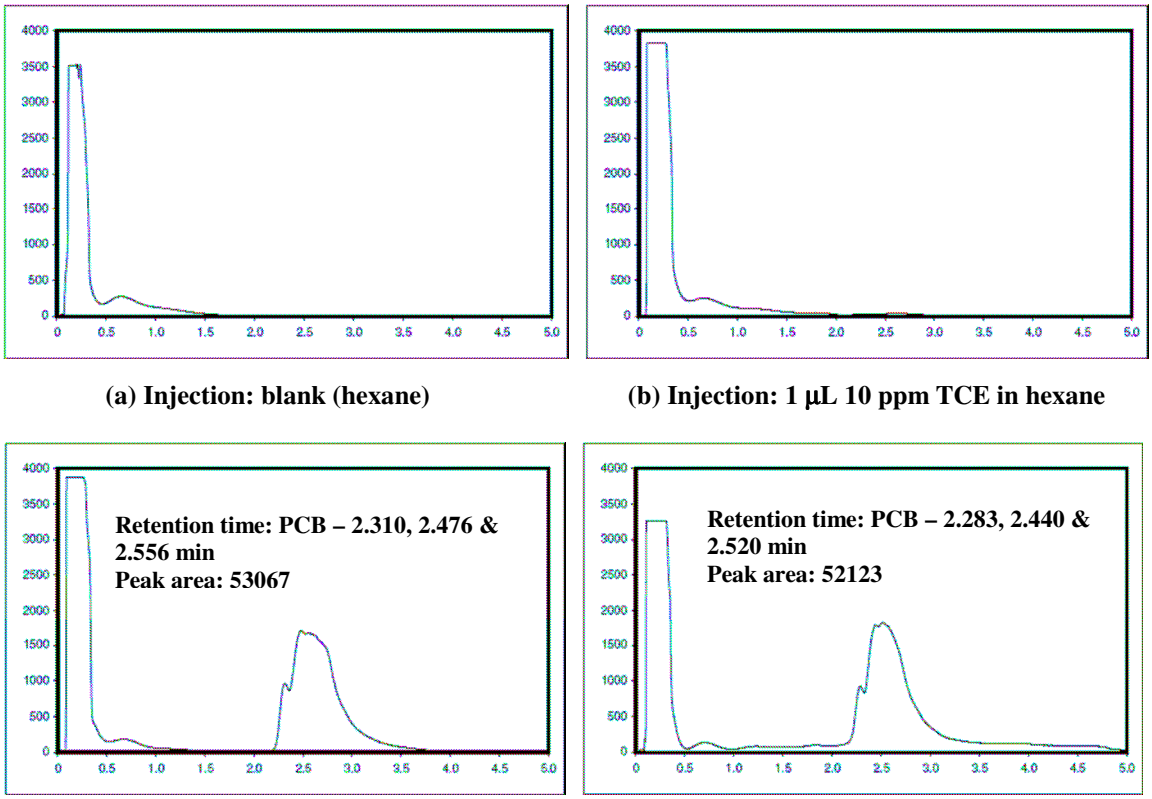
(c) Injection: 1 µL 10 µg/mL Aroclor 1254 in hexane



(d) Injection: 1 µL 10 µg/mL TCE and 10 µg/mL Aroclor 1254 in hexane

Figure 2-8: Chromatograms of TCE and PCBs using a 4 m MXT-1 column setting with an initial oven temperature of 50 °C and a carrier gas flow rate of 2 mL/min (other GC conditions kept unchanged as previous tests).

Figure 2-8 (b) shows that when using a 4 m long column with a low carrier gas flow rate (2 mL/min) and a low initial oven temperature (50 °C), TCE was detected by DELCD and its retention time (about 1 minute) was much shorter than that of total PCBs (about 3.5 to 4 minutes). Therefore, a complete separation and detection of TCE and total PCBs under these particular conditions were possible. As expected, when the mixture of TCE and total PCBs went through the column, TCE and total PCBs were completely separated and detected as shown in Figure 2-8 (d).



(a) Injection: blank (hexane)

(b) Injection: 1 µL 10 ppm TCE in hexane

(c) Injection: 1 µL 10 µg/mL Aroclor 1254 in hexane

(d) Injection: 1 µL 10 µg/mL TCE and 10 µg/mL Aroclor 1254 in hexane

Figure 2-9: Chromatograms of TCE and total PCBs using a 4 m MXT-1 column setting with an initial oven temperature of 125 °C and a carrier gas flow rate of 2 mL/min (other GC conditions kept unchanged as previous tests)

Using the same 4 m long MXT-1 column setting, the initial oven temperature was then set at 125 °C to investigate the separation of TCE and total PCBs. Other GC conditions were maintained the same. The chromatograms of 1 μL solvent blank (hexane), 1 μL of 10 μg/mL TCE in hexane, 1 μL 10 of μg/mL Aroclor 1254 in hexane, and 1 μL mixture of 10 μg/mL TCE and 10 μg/mL Aroclor 1254 in hexane are presented in Figure 2-9. It can be seen from Figure 2-9 that when initial oven temperature was 125 °C, no TCE peak was found. The chromatogram of 1 μL 10 μg/mL TCE looked like the chromatogram of the solvent blank. The chromatogram of TCE and total PCBs mixture was similar to the one of total PCBs with the PCBs peak only showing in the chromatogram. As a conclusion, TCE was not detectable with an initial oven temperature of 125 °C even when a relatively long column (4 m) and a low carrier gas flow rate (2 mL/min) were applied. This was because the initial oven temperature was higher than the boiling point of TCE so that TCE evaporated at the moment of injection and was not separated from the solvent band.

2.3.2 Characterization of the Optimized Field GC Method

Once the field GC method was optimized, it was characterized through the determination of detector sensitivity, limit of detection (LOD), reproducibility, and detector response for total PCBs using liquid PCB standards.

2.3.2.1 Detector Sensitivity

The original design of the DELCD electrode probe used in SRI 310 GC is shown in Figure 2-10 (a). The electrode probe included a platinum thermocouple mounted in a tiny

glass rod. The thermocouple also acted as the cathode of the probe. A nichrome wire coil wound around the glass rod was used as the anode. The electrical conductivity of the gas phase was measured by applying a voltage between the cathode and the anode.

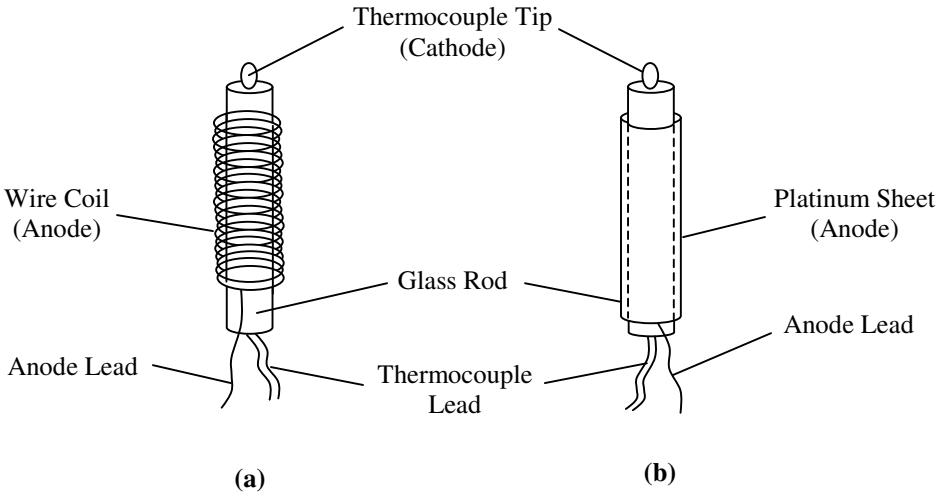
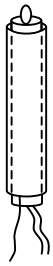
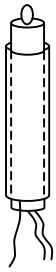
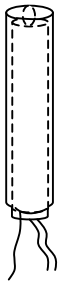


Figure 2-10: Schematic diagram of the DELCD detection probe: (a) original design; (b) modified design

By using such a DELCD detection probe, a detection limit of 0.5 μg/mL for total PCBs was obtained in a previous project completed in Dr. Górecki's group.[6] The problem with such a design was that oxidation products tended to build up around the anode coil over time, and the sensitivity of the detection probe deteriorated. In order to overcome the drawback of this design, the original DELCD electrode probe was replaced with a modified probe made in the laboratory. As indicated in Figure 2-10 (b), a thin platinum sheet was used in the modified design instead of the wire coil to act as the anode.

Table 2-2: DELCD Response to DCB for Different Anode-Cathode Positions of the Detection Probe*

DCB concentration (μg/mL)	Chromatogram peak area		
0.05	775	/	/
0.1	1410	/	/
0.7	3743	2287	1610
1.4	7348	3027	2252
2.1	10630	5666	3367
5.5	16851	12930	6085
11.0	26786	19223	8922
25.8	42874	37430	13502
53.2	53977	50469	17855
102.4	60674	64958	23066
Detection limit (ng)**	0.016	0.03	0.09
Anode-cathode position of DELCD detection probe	Position 1 	Position 2 	Position 3 

* Carrier gas flow rate: 20 mL/min; make up air flow rate: 10 mL/min; temperature program: 125 °C (0.5 min) → 250 °C (2 min) with 75 °C/min ramp; detector attenuation: medium

** Method detection limit for 8 repeat measurements of 1 μL 0.1 μg/mL for position 1, 1 μL 0.2 μg/mL for position 2, and 1 μL 0.7 μg/mL for position 3

/ Not detected

When the electrical conductivity of the gas phase was measured by the detection probe in the DELCD, the sensitivity of the measurement would change with the change of the distance between the cathode and the anode of the detection probe. This could be easily done by changing the relative position of the thermocouple tip and the platinum sheet in the modified DELCD detection probe. Three different electrode relative positions were tested to investigate their effect on the sensitivity of the measurement: in position 1, the distance between the thermocouple tip and the edge of the platinum sheet was 2 mm; in position 2, this distance was 5 mm; in position 3, the edge of the platinum sheet was

even with the thermocouple tip (Table 2-2). By applying the GC conditions optimized for the analysis of total PCBs, 1 μL DCB standards (from 0.05 to 102.4 μg/mL) were injected into the selected GC column (0.5 m × 0.53 mm I.D. × 0.5 μm d_f MXT-1 column with a 0.5 m × 0.53 mm I.D. deactivated Silcosteel retention gap). Peak areas for each injection were recorded. The method detection limit (MDL, see Section 2.3.2.3) for DCB measurement with each different electrode position was also calculated. The results are listed in Table 2-2. By comparing peak area measurements and method detection limits for each electrode position, it was established that the highest peak area readings for each DCB concentration (except for 102.4 μg/mL) and the lowest detection limit (0.016 ng) were obtained for position 1. Therefore, position 1 gave the most sensitive response and this electrode position setup was thus chosen to detect total PCBs in this research.

2.3.2.2 Detector Response to Total PCBs in Liquid Standards

The detector response to total PCBs was characterized by establishing the calibration curve for the total PCB measurement and exploring the reproducibility of the measurement. The response of the detector (DELCD) to total PCBs in liquid standards was determined using the optimized GC conditions as determined in previous tests. 1 μL aliquots of each liquid PCB standard (Aroclor 1254 in hexane) were injected a minimum of three times from the lowest to the highest concentration. The peak areas for each injection were determined by PeakSimple software and recorded. The peak areas of total PCBs for each concentration were averaged. Intraday standard deviations (STD) and relative standard deviations (RSD) for repeat measurements were calculated. Day-to-day

reproducibility of the measurements was also determined over 3 days. Table 2-3 provides the measurement data for repeat injections of each concentration in each individual day.

Table 2-3: Measurement Data of Liquid Total PCBs Standard Series

Injection quantity (ng)	Day 1			Day 2			Day 3		
	Average peak area	STD	RSD (%)	Average peak area	STD	RSD	Average peak area	STD	RSD
0.05	523	39.7	7.6	537	39.7	7.4	532	31.0	5.8
0.1	921	13.5	1.5	927	23.7	2.6	907	34.0	3.7
0.25	2326	107.4	4.6	2240	88.1	4.0	2236	94.9	4.2
0.5	4439	244.2	5.5	4355	872.6	20.0	4462	181.5	4.1
1.0	8878	512.1	5.8	8732	750.1	8.6	8760	327.7	3.7
2.5	21122	1044.4	4.9	21297	1348.7	6.3	20892	1121.0	5.4
5.0	33372	196.8	0.6	33699	469.9	1.4	33545	271.8	0.8
9.9	51059	920.8	1.8	53197	405.0	0.8	52940	1891.3	3.6
24.4	82941	973.9	1.2	83932	1531.9	1.8	82329	862.7	1.0
47.6	111311	4751.1	4.3	110643	4963.8	4.5	113851	2182.4	1.9
99.1	158222	1890.8	1.2	151534	/	/	157826	3183.0	2.0

Table 2-4: 3-Day Reproducibility – Peak Area vs. Total PCBs Quantity

Injection quantity (ng)	Day 1 average peak area	Day 2 average peak area	Day 3 average peak area	3-Day average peak area	3-Day STD	3-Day RSD (%)
0.05	523	537	532	531	7.1	1.3
0.1	921	927	907	918	10.3	1.1
0.25	2326	2240	2236	2267	50.8	2.2
0.5	4439	4355	4462	4419	56.3	1.3
1.0	8878	8732	8760	8790	77.5	0.9
2.5	21122	21297	20892	21104	203.1	1.0
5.0	33372	33699	33545	33539	163.6	0.5
9.9	51059	53197	52940	52399	1167.3	2.2
24.4	82941	83932	82329	83067	808.9	1.0
47.6	111311	110643	113851	111935	1692.6	1.5
99.1	158222	151534	157826	152962	8769.9	5.7

Data in Table 2-3 showed average peak areas and deviations of the measurements for repeat injections of each concentration. To show the reproducibility of total PCBs measurement on 3 different days, data in Table 2-3 were rearranged and the results are listed in Table 2-4. Based on the data provided in Table 2-4, calibration curves of peak area vs. quantity for the measurements in 3 days were constructed and presented in Figure 2-11.

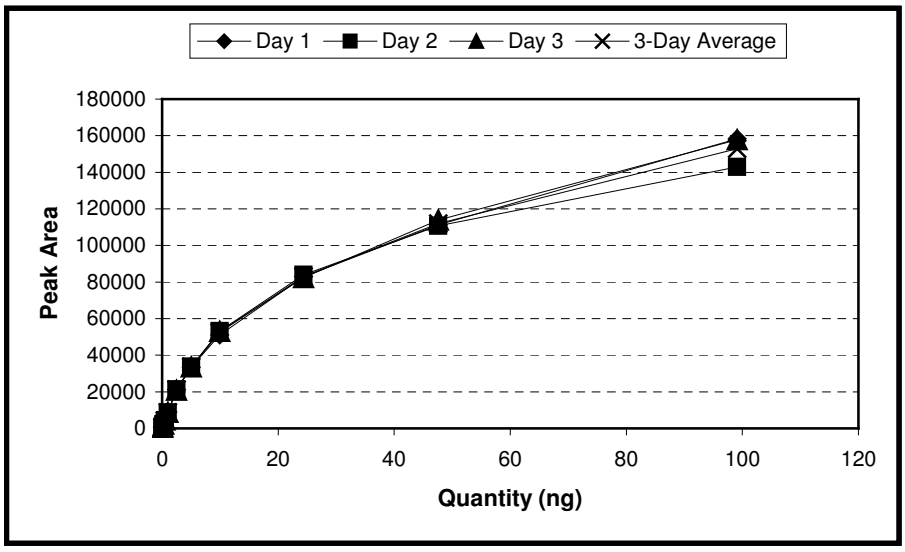


Figure 2-11: Calibration curves for total PCB measurements

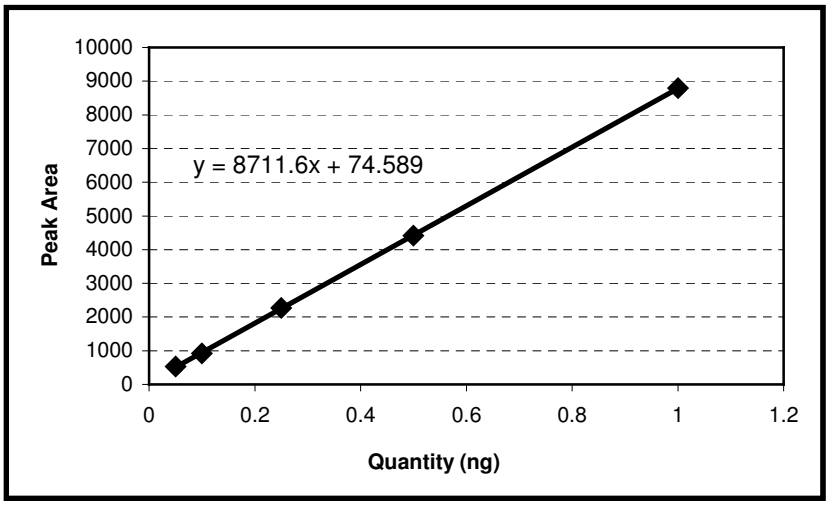


Figure 2-12: Linear Response of DELCD to Total PCBs (0.05 to 1.0 ng)

Table 2-3 and Table 2-4 show intraday RSDs of 0.6~20% for repeat measurements of total PCBs and day-to-day RSDs of 0.5~5.7%, indicating good reproducibility of the measurements with the GC method. Figure 2-11 illustrates good reproducibility of the calibration curves for total PCB measurements obtained on different days. Figure 2-11 also shows that the DELCD did not produce a linear response to total PCBs with

concentrations ranging from 0.05 to 99.1 μg/mL (or quantities of 0.05 to 99.1 ng with 1 μL injection). However, a linear response was obtained with the concentration in the range of 0.05 to 1.0 μg/mL (or quantity of 0.05 to 1.0 ng with 1 μL injection), as indicated in Figure 2-12.

2.3.2.3 Limit of Detection

The determination of the method detection limit (MDL) was conducted following the procedure in the Code of Regulations Title 40 (40 CFR) defined by the US EPA.[7] According to this definition, MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero in a given matrix containing the analyte. Briefly, the MDL is determined by taking a minimum of seven repeat measurements of a standard or sample with the concentration in the range of one to five times the estimated detection limit (for GC method, the estimated detection limit is the concentration value corresponding to an instrument's signal/noise ratio in the range of 2.5 to 5). Once the measurements according to the defined method with final results in the method reporting units are obtained, the standard deviation (STD) of the measurements is computed and the MDL is calculated as below:

$$MDL = t(n-1,\ 1-\alpha=0.99) \times (S) \qquad \text{Equation (1)}$$

where,

$t(n-1,\ 1-\alpha=0.99)$ = the students t value appropriate for a 99% confidence level and a standard deviation estimate with n–1 degrees of freedom

S = standard deviation of the replicate peak height measurements

Applying the same GC conditions used for the determination of the calibration curve as described earlier, the detection limits for total PCBs with the selected method were estimated by injecting low concentrations of liquid total PCB standards (Aroclor 1254 in hexane) until a signal/noise ratio of about 3 was found. The corresponding concentration was 0.05 µg/mL, or 0.05 ng with 1 µL injection. The chromatogram of 0.05 ng total PCBs measurement is presented in Figure 2-13.

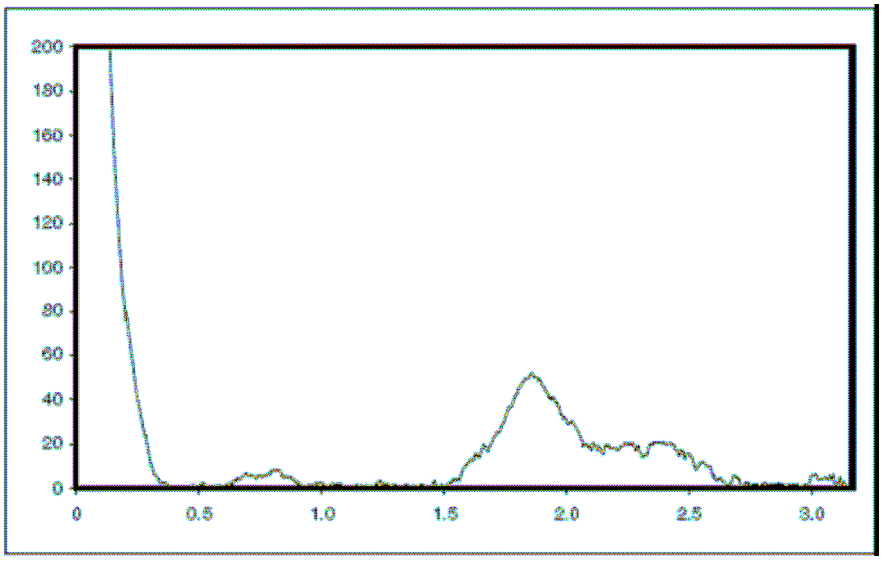


Figure 2-13: Chromatogram of 0.05 ng total PCBs

Once the estimated detection limit of 0.05 µg/mL was found, a concentration of 0.1 µg/mL, two times the estimated detection limit, was selected for the determination of method detection limit. Peak heights for eight repeat measurements of 0.1 µg/mL total PCBs in hexane were recorded. The MDL was determined by equation (1). The results are presented in Table 2-5. The computation result of MDL for peak height measurement was 18.4. The calibration curve of peak height vs. injection quantity in the range of 0.1 to

1.0 ng was established and presented in Figure 2-14. A linear relationship of peak height and quantity of total PCBs was described by the equation $y = 471.13x + 13.371$, with y representing the peak height and x representing the quantity. Accordingly, the peak height of 18.4 corresponded to the quantity of 0.01 ng total PCBs in the liquid standard, or the method detection limit for total PCBs measurement was 0.01 ng.

Table 2-5: Determination of MDL for total PCBs Measurement

n	Peak height	MDL Calculation
1	65	
2	62	
3	69	Standard deviation (S) = 6.14
4	76	
5	78	MDL = $t\,(n-1,\ 1-\alpha=0.99) \times (S)$*
6	63	$= 6.14 \times 2.998 = 18.4$
7	73	
8	74	
Average	70	

* For n = 8, t value is 2.998.[6]

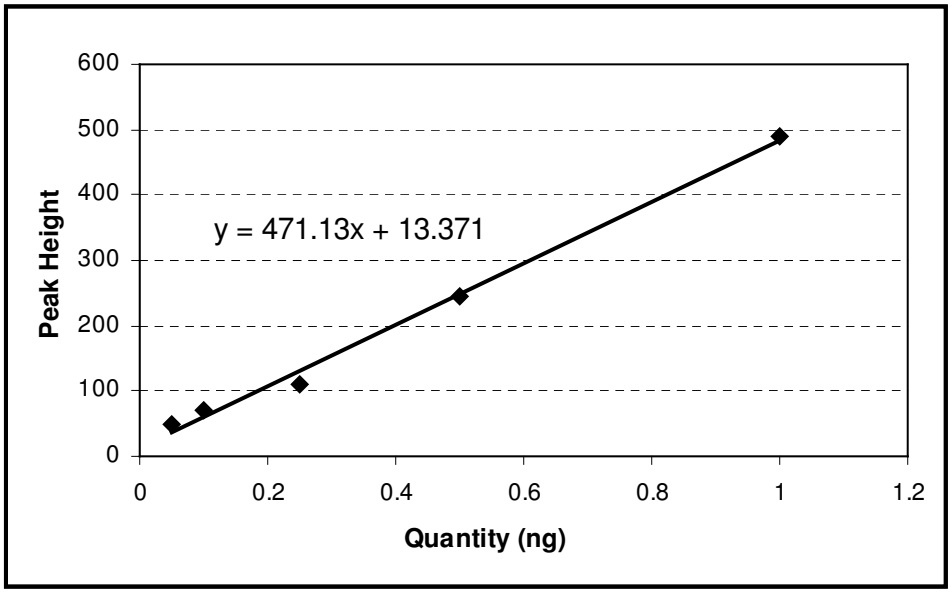


Figure 2-14: Calibration curve of peak height vs. quantity for total PCBs measurement

The optimized and characterized SRI 310 GC method for the analysis of total PCBs in liquid standard is summarized in Table 2-6. It should be pointed out that the detector attenuation was selected to be "medium" because under the "high" setting the upper limit of the detector dynamic range would decrease. If the concentration of the sample would be too high, the detector response would be out of the detection range. Even though a "high" setting would provide higher detection sensitivity, the detection sensitivity with a detection limit of 0.01 ng total PCBs obtained from the "medium" gain was satisfactory for the purpose of this research.

Table 2-6: Summary of the Optimized GC Method for the Measurement of total PCBs in Liquid Standards and its Analytical Characteristics

GC column	0.5 m × 0.53 mm I.D. × 0.5 μm MXT-1 Silcosteel column with 0.5 m × 0.53 mm I.D. deactivated Silcosteel retention gap
Carrier gas (N_2) flow rate	20 mL/min
GC make-up air flow rate	10 mL/min
GC oven temperature program	125 °C (0.5 min) → 250 °C (2 min), with a ramp of 75 °C/min
Detector heater temperature	300 °C
Detector reactor temperature	1000 °C
Detector attenuation	Medium
Method detection limit	0.01 ng
Linear detection range for total PCBs	0.05 ~ 1.0 ng
3-Day RSD	0.5 ~ 5.7%
Sample turnaround time	5.5 minutes

2.4 Conclusions

Before combining thermal desorption method to the field GC to analyze total PCBs in soils, the GC method was first optimized and characterized by injections of liquid PCB standards (Aroclor 1254 in hexane). The following considerations with respect to the optimization and characterization of the field GC method were taken into account: total

PCBs should be separated as a single peak from other chlorinated compounds; separation of the individual PCB congeners was not necessary; the method should provide reproducible analysis results and a low detection limit; and the sample turnaround time should be short enough to satisfy field application of the method. The optimum conditions for total PCB separation were determined by testing GC operating parameters, such as column type and size, GC mobile phase flow rate, temperature program, and detector setting. Reproducibility and limit of detection of the method under the selected optimum conditions were investigated and proved to be satisfactory for the purposes of this method.

Total PCBs were separated as a single peak in a 0.5 m long, 0.53 mm I.D. MXT-1 column with 0.5 μm stationary phase thickness. Peak shape was improved with the use of a 0.5 m long, 0.53 mm I.D. deactivated Silcosteel retention gap. The optimum results (narrow peak and short analysis time) were obtained under the carrier gas flow rate of 20 mL/min with an initial oven temperature of 125 °C. When applying the conditions mentioned above, total PCBs were completely separated from TCE, a chlorinated contaminant that could be present in the sample and detected by DELCD. When using a temperature program with initial temperature of 125 °C (0.5 min) ramping at a rate of 75 °C/min to reach 300 °C (2 min), the oven needed 1 minute to cool down from 300 °C to 125 °C. Given the selected optimum carrier gas flow rate and temperature program, the sample turnaround time was 5.5 minutes, with 4.5 minutes of analysis time followed by 1 minute of cooling time for the oven to return to the initial temperature. The DELCD with the modified detection probe was very sensitive to PCBs when a proper anode-cathode position in the detection probe was selected, with a method detection limit of 0.01 μg/mL

(or 0.01 ng with 1 μL injection) for total PCBs. Measurements of liquid total PCB standards under optimized GC conditions repeated over 3 days gave the RSDs in the range of 0.5 to 5.7%, indicating good reproducibility of the method. The calibration curve for the total PCBs measurement using liquid standards was established with a linear response in the range of 0.05 to 1.0 μg/mL (or 0.05 to 1.0 ng with 1 μL injection). With the GC method being effectively optimized and characterized, the next stage of combining thermal desorption to the GC method was possible.

3.0 Analysis Using Thermal Desorption/GC Method

3.1 Introduction

Thermal desorption in GC analysis can be described as akin to using temperature as a syringe.[1] In desorption techniques, the sample is swept into the GC using the heating and the flow of carrier gas. Although it is important that analytes should be desorbed and removed from the solid sample as thoroughly as possible, the introduction of the sample as a narrow chromatographic band is also critical. GC conditions optimized for liquid injection might be applied for separation and detection of samples introduced by thermal desorption; however, experimental conditions for thermal desorption need to be optimized so that gas phase analytes are desorbed from the sample matrix sufficiently and quickly and the analytes are re-condensed and trapped at the beginning of the column as a narrow band. Therefore, in this stage of research, tests were first done to obtain optimal conditions for sample desorption and introduction using sand standards. Based on the optimized conditions, the method was characterized using sand and soil standards. Finally, analyses of total PCBs in environmental soil samples were conducted using the developed method. Analytical results with the developed method were compared with the results from conventional laboratory methods.

3.2 Experimental

3.2.1 Instrumentation and Setup

A laboratory-made thermal desorber as illustrated in Figure 3-1 was used for this project. The desorption tube was a 1/4" I.D. × 4" long glass tube with a narrow neck 1" from the outlet end. A small amount of fiberglass wool was put in front of the neck to

prevent solid sample from moving to the outlet end. A ring-shape electric block heater with a Eurotherm 847 temperature controller (Eurotherm Controls Inc., VA, USA) was used as the heating source. The heating temperature was monitored and controlled by the controller. The desorption tube was put through the block heater. Heating a desired portion of the desorption tube was accomplished by moving the block heater along the tube.

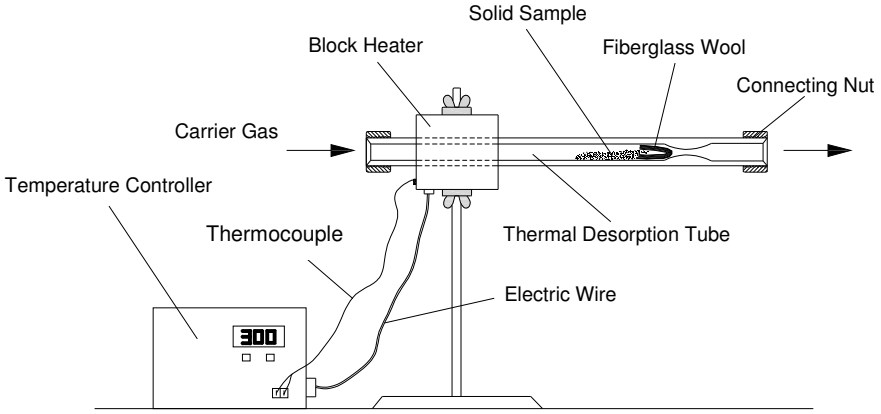


Figure 3-1: Schematic diagram of a laboratory made thermal desorber

The thermal desorber was mounted directly onto the injection port of the SRI 310 GC. The connection of the thermal desorber to the GC is shown in Figure 3-2. Solid samples were placed in the desorption tube close to the end that contained glass wool. The block heater could generate a highest temperature of about 400 °C. The heating block was first placed at the empty end of the desorption tube and then moved to the end containing the sample to rapidly heat the sample. Gas phase analytes desorbed from the sample were swept into the column of the GC by the flow of the carrier gas, which was directed using

a three-way valve. GC conditions were first set based on the optimized conditions for the measurement of total PCBs in liquid standards.

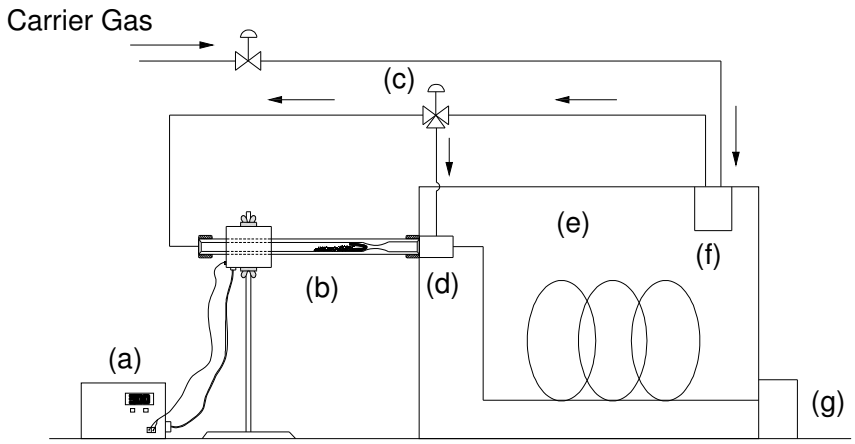


Figure 3-2: Schematic diagram of the connection of the thermal desorber to the GC system. (a) temperature controller; (b) thermal desorber; (c) three way-valve; (d) GC injector; (e) GC oven; (f) carrier gas flow regulator; (g) GC detector

3.2.2 Preparation of Sand and Soil Standards

Sand and soil standard series were prepared to optimize thermal desorption conditions and to characterize the thermal desorption/GC method prior to field soil sample analysis. In order to find out the desorption efficiency of total PCBs from different sample matrices, two types of sand, coarse and fine sand, as well as one sandy soil sample were used to prepare the standard series. The coarse sand was silica sand with the size between 425 to 850 μm (supplied by Barnes Environmental International, Hamilton, Ontario). The fine sand was olivine sand (silicate of iron and magnesium) with the size ranging from 75 to 180 μm (supplied by Bell & Mackenzie Co., Ltd., Waterdown, Ontario). The soil

sample was a sandy soil taken from a residential house construction site in Guelph, Ontario.

Table 3-1: Preparation of Sand and Soil PCB Standard Series

Weight of sand/soil sample (g)	Concentration of stock PCB solution – Aroclor 1254 in hexane (µg/mL)	Stock solution added into sample (µL)	Final concentration in sand and soil standard	
			µg/g or ppm	ng/100 mg
10.00	1	1.0	0.0001	0.01
10.00	10	0.5	0.0005	0.05
10.00	10	1.0	0.001	0.1
10.00	10	2.5	0.0025	0.25
10.00	100	0.5	0.005	0.5
10.00	100	1.0	0.01	1.0
10.00	100	2.5	0.025	2.5
10.00	1000	0.5	0.05	5.0
10.00	1000	1.0	0.1	10
10.00	1000	2.4	0.24	24
10.00	1000	4.8	0.48	48
10.00	1000	9.9	0.99	99

The procedure for the preparation of sand and soil PCB standard series was as below: a certain amount of sand or soil sample was conditioned by baking for 24 hours at 150 °C in an oven, then cooling to room temperature. Soil samples were sieved using a U.S.A standard No. 20 (850 µm) sieve to remove large size pebbles. 10 g baked samples were then weighed into tared, labeled 20 mL vials fitted with aluminum lined screw caps. Approximately 5 mL aliquots of HPLC grade (99.9+ % pure) hexane were added to each vial using a dispenser pipette. Hexane was added to improve analyte mixing and contact with the sand/soil matrix, therefore addition of accurate volumes of hexane was not required. Aliquots of stock solutions of Aroclor 1254 in hexane were added into each vial as listed in Table 3-1, using an appropriate size glass syringe. The vials were then capped with aluminum-lined screw caps and shaken vigorously using a vortex type mixer. Any sample clung to the top portion of the vial was washed down using a small amount of

hexane. The vials were then placed in an ultrasonic water bath (CREST Model 275D, Crest Ultrasonics Corp., NJ, USA) and sonicated for 5 minutes. The vials were taken out from the water bath. Each cap was labeled and removed from the vials. The open vials were placed in a fume hood to allow the solvent to evaporate overnight. Caps were then replaced on the vials. The vials were then shaken for 1 minute by hand to mix the spiked sample thoroughly.

3.3 Results and Discussion

3.3.1 Optimization of Thermal Desorption/GC Method

To achieve appropriate conditions that give optimal desorption and analysis results, several factors were considered, such as sample size, heating temperature, and duration of heating. Too much sample put in the desorption tube would require longer heating time to release PCBs. Small size samples could be heated rapidly, but they contained less analytes, thus decreased the sensitivity. The heating temperature should be high enough to desorb as much PCBs from the sample matrix as possible, but not too high so as not to cause pyrolysis of PCBs.[2] Heating duration was an important factor that affected the efficiency of desorption and the analysis time. Too short heating time would cause insufficient desorption; on the other hand, a long sample turnaround time occurred if heating time was too long. Another factor that should be considered to enhance the efficiency of thermal desorption was relevant to extraction kinetics. There were reports demonstrating that moisture[3] and subcritical water[4,5] facilitated extraction of PCBs and other organic compounds from soils. In addition, although the field portable GC conditions had been optimized by injection of liquid PCB standards, some operating

parameters of the GC might still need to be adjusted to satisfy the condition for the introduction of gas phase sample from thermal desorption. All factors mentioned above were tested using spiked sand standards to obtain optimum conditions for the thermal desorption/GC method.

3.3.1.1 GC Conditions

In the optimization study of the GC method, the SRI 310 GC operating conditions were set to generate optimal peak shape and sample turnaround time for on-column injection of liquid total PCBs standards. These operating conditions included column dimensions, carrier gas flow rate, make-up air flow rate and oven temperature program. These conditions decided the peak shape and retention time for total PCBs separated in the column. It was expected that the conditions optimized for on-column liquid injection would provide similar performance for gas phase total PCBs that were introduced into the column through thermal desorption. Therefore, these conditions were adopted for the initial study of thermal desorption/GC method. However, it should be noted that introduction of gas phase analytes into the GC column by thermal desorption was indeed a different sample introduction technique from on-column liquid injection. The process of thermal desorption itself would affect the efficiency of sample introduction and sample turnaround time. This would be otherwise tested and investigated.

Separation and detection of gas phase total PCBs were initially tested with 1 μL 10 μg/mL liquid total PCBs standard (Aroclor 1254 in hexane) directly injected into the desorption tube. The desorption tube was then connected to the SRI 310 GC and heated to desorb total PCBs for analysis. The heating temperature was set at 350 °C according to a report by M. Aresta et al., where 100% release of PCBs from spiked soil was observed.[2]

The desorption tube was heated at 350 °C for 1 minute, following which the GC separation was started. The desorption tube was kept under heating until the end of the GC run to remove as much PCBs from the desorption tube as possible. The carrier gas kept running through the desorption tube during the entire cycle. Optimized GC conditions listed in Table 2-6 were applied. The results were then compared to the results from on-column injection of 1 µL 10 µg/mL PCB standard with the same GC operating settings. Comparison of the chromatograms is shown in Figure 3-3 (a) and (b).

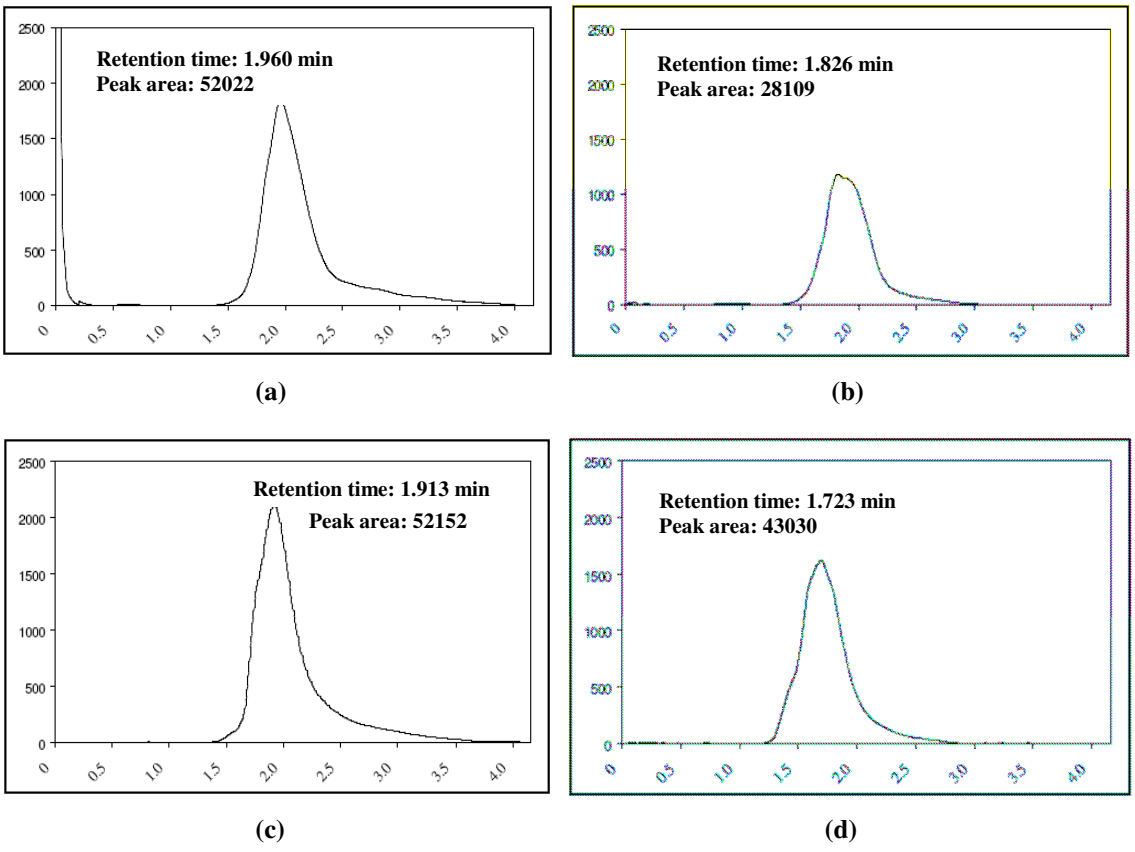


Figure 3-3: Chromatograms of 10 ng total PCBs: (a) on-column injection of 1 µL 10 µg/mL total PCBs standard; (b) thermal desorption of 1 µL 10 µg/mL total PCBs standard with 10 mL/min make-up air flow rate; (c) thermal desorption of 1 µL 10 µg/mL total PCBs standard with 5 mL/min make-up air flow rate; (d) thermal desorption of 100 mg 0.1 µg/g total PCBs coarse sand standard with 5 mL/min make-up air flow rate.

The results showed that retention times of total PCBs for the two processes were 1.960 and 1.826 minutes respectively, with peak areas of 52022 and 28109. The peak area of total PCBs from thermal desorption process was just about 50% of that obtained with on-column injection of the same amount of the analyte. The process of thermal desorption and analysis under the same conditions was then repeated with the desorption tube from the last run. No PCB peak was found for the second run, indicating a complete release of the PCBs in the first desorption. It was speculated therefore that the smaller peak area from the thermal desorption process could be related to GC operating conditions. Among the GC operating parameters, make-up air flow rate decided the rate at which the PCBs were oxidized, hence affected the amount of PCBs being detected, or the sensitivity of detection. By changing the make-up air flow rate to 5 mL/min with other conditions kept unchanged, thermal desorption of 1 μL 10 μg/mL total PCBs standard in the desorption tube generated a total PCBs peak area of 52152 (Figure 3-3 (c)), greatly increased from that of 10 mL/min make-up air flow rate. As a conclusion, the GC conditions optimized for on-column liquid injection also worked effectively for the analysis of gas phase total PCBs introduced by thermal desorption, with an exception of the make-up air flow rate, which caused different detection sensitivity from two different sample introduction techniques. In order to increase detection sensitivity for samples introduced by thermal desorption, the make-up air flow rate was decided to be 5 mL/min, with other GC conditions optimized for on-column injection maintained unchanged. By applying these conditions, 100 mg spiked coarse sand standard with the concentration of 0.1 μg/g total PCBs (10 ng total PCBs in the sample) was analyzed by thermal desorption. The result is shown in Figure 3-3 (d). The total PCBs peak had similar peak shape to that

from the direct liquid standard injection into the desorption tube, with an 80% peak area of that from direct liquid standard injection. This indicated that the selected conditions worked effectively for coarse sand standards.

3.3.1.2 Heating Temperature and Heating Time of Thermal Desorption

The boiling points of PCBs range from 256 to 456 °C.[6] For fast release of PCBs from solid matrices, higher temperatures were preferred. However, higher temperatures required longer time for the block heater to heat up. High temperature might also cause degradation of PCBs. The effect of heating temperature on the analysis was investigated using 100 mg spiked coarse and fine sand standards with a concentration of 0.1 μg/g total PCBs. By applying the selected GC conditions, measurements of total PCBs under each selected desorption temperature at a constant heating time were conducted in triplicate. Peak areas were used to calculate recoveries of total PCBs from the samples, with peak area of the same amount of direct injection of total PCBs into the empty desorption tube as 100% recovery. Results are listed in Table 3-2.

Table 3-2: Effect of Desorption Temperature at Constant Heating Time*

Temperature (°C)	Average peak area for 3 repeat measurements	Total PCBs recovery (%)**	Time for block heater heating up (min)
(a) Spiked coarse sand standard			
250	31213	60	25
300	42850	82	35
350	43878	84	45
400	43605	84	55
(b) Spiked fine sand standard			
250	2604	5	25
300	3769	7	35
350	3648	7	45
400	3701	7	55

* Heating time: heating for 1 minute then starting GC analysis; heating until the end of the run
** 100% recovery with direct injection of same amount of total PCBs into empty desorption tube

The results showed that the release of PCBs from both coarse and fine sand samples reached maximum at about 350 °C. A higher temperature (400 °C) did not assure better recovery. In addition, 10 minutes were required to increase the temperature by 50 °C. The optimal heating temperature for thermal desorption was thus established to be 350 °C.

Heating time for the thermal desorption was another factor that affected the recovery rate from the sample and the sample turnaround time. Heating time was determined by temperature and sample size. Tests were conducted by heating and analyzing 100 mg spiked coarse sand and fine sand standards of 0.1 μg/g total PCBs concentration under a constant temperature of 350 °C for different heating times. Triplicate measurements were conducted for each selected time. The results are shown in Table 3-3.

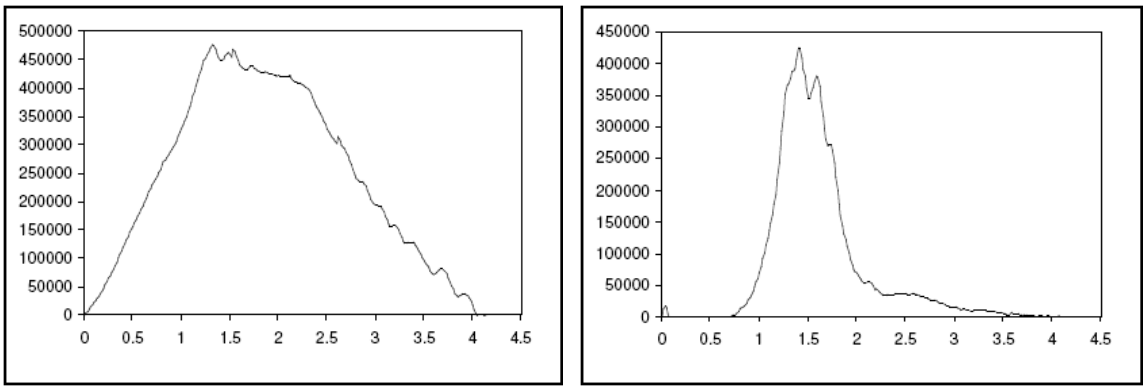
Table 3-3: Effect of Heating Time at Constant Heating Temperature*

Heating time	Average peak area for 3 repeat measurements	Total PCBs recovery (%)**	Sample turnaround time (min)
(a) Spiked coarse sand standard			
30 s, start GC and stop heating	5844	11	5.6
1 min, start GC and stop heating	31381	60	6.6
2 min, start GC and stop heating	43451	84	7.6
1 min, start GC and keep heating	43878	84	6.6
(b) Spiked fine sand standard			
30 s, start GC and stop heating	/	/	5.6
1 min, start GC and stop heating	/	/	6.6
2 min, start GC and stop heating	2597	5	7.6
1 min, start GC and keep heating	3648	7	6.6

* Heating Temperature: 350 °C
** 100% recovery with direct injection of same amount of total PCBs into empty desorption tube
/ Not detected

As shown in Table 3-3, recovery of total PCBs from thermal desorption increased with the increase of the heating time under a constant temperature of 350 °C. Short

heating times led to very low recoveries of the PCBs from coarse sand. The highest recovery rate was obtained after heating for over 2 minutes. If 2 minute heating was applied before starting the GC run, the total analysis time was 7.6 minutes. A shorter analysis time was available if the GC run was started after 1 minute preheating, and the heating continued until the end of the GC run (1-minute preheating procedure). In this case the total heating time exceeded 2 minutes, while the analysis time was reduced to 6.6 minutes. This heating procedure yielded the highest PCB recoveries and the best total PCBs peak shape. However, it produced poor results when applied to the spiked sandy soil standard. The PCBs were not properly focused, with the peak being very broad and difficult to distinguish from the base line (Figure 3-4 (a)). With 2-minute preheating time followed by start of the GC run and stopping the heating (2-minute preheating procedure), a better total PCBs peak was obtained (Figure 3-4 (b)). Therefore, for sandy soil samples, 2-minute preheating procedure was applied, in spite of the analysis time being 1 minute longer.



(a) **(b)**

Figure 3-4: Chromatograms of total PCBs from thermal desorption of 100 mg 0.1 µg/g total PCBs sandy soil standards. (a) heating time: 1-minute heating followed by start of the GC run and continuous heating; (b) 2-minute heating followed by start of the GC run and stopping the heating

3.3.1.3 Sample Size

The size of the desorption tube (about 1.25 mL volume) determined the maximum amount of sample required for the analysis. Two sample sizes, 50 mg and 100 mg, were tested using the coarse sand standard of 0.1 μg/g total PCBs concentration. Seven repeat measurements of total PCBs for samples of both sizes were conducted under the selected thermal desorption/GC conditions as mentioned in previous sections. Standard deviation (STD) and relative standard deviation (RSD) for 7 measurements of the total PCB peak areas were calculated. The results are shown in Table 3-4.

Table 3-4: STDs and RSDs for the Analysis of 50 mg and 100 mg Coarse Sand Standards

Sample Size	No.	Peak Area	Average Peak Area	STD	RSD (%)
50 mg	1	15870	17232	3057	17.7
	2	13082			
	3	14908			
	4	17116			
	5	22401			
	6	19331			
	7	17914			
100 mg	1	32313	39444	4235	10.7
	2	38652			
	3	39809			
	4	40621			
	5	37549			
	6	40681			
	7	46480			

The results showed that the RSD for 50 mg size samples was higher than that for the 100 mg size samples, which meant that the reproducibility of the analysis for 100 mg size samples was better than that for 50 mg size samples. One possible reason was that the bigger sample size led to better homogeneity of the sample. For samples with low concentration analytes, small sample sizes also reduced the sensitivity of the method. On the other hand, with the analyte concentration in the sample very high, the bigger sample

size might lead to exceeding the limits of the calibration curve. Since sample "dilution" is not possible with direct thermal desorption, the sample size needs to be reduced in such cases.

3.3.1.4 Effects of Water/Solvent Addition into the Samples

With the conditions for thermal desorption (heating time and temperature, sample size) and the GC conditions determined, 100 mg coarse sand and fine sand standard of 0.1 μg/g total PCBs concentration were analyzed. Results were compared to that of direct injection of same amount of total PCBs into the empty desorption tube. Average peak areas of triplicate measurements for coarse sand and fine sand standard were 42609 and 3667 respectively. Under the same operating conditions, the peak area for the same amount of total PCBs directly injected into the empty desorption tube was 52152. Given 100% PCB recovery was with direct injection of total PCBs into the empty desorption tube, PCB recoveries from coarse sand and fine sand standard were 80% and 7% respectively. Thus, it was deemed necessary to improve the PCB recovery rates from thermal desorption of the samples, especially for fine sand. Previous tests showed that upon reaching a particular heating temperature (350 °C) and heating time (2 minutes), raising the temperature or increasing the thermal desorption time did not lead to better total PCBs recovery. Therefore, other factors related to desorption kinetics should be considered to facilitate the release of total PCBs by thermal desorption.

In thermal desorption process, soil moisture content plays a critical role in the effectiveness of thermal desorption. At levels below 20%, soil moisture plays a beneficial role by removing contaminants through steam distillation. When the soil is heated, the

water in the soil undergoes a phase change to steam. During the phase change, contaminants boil with the water and partition into the gas phase where they are removed from the soil with the steam. While steam distillation is beneficial at lower moisture contents, higher soil moisture contents inhibit thermal desorption as additional energy is required to volatize the water.[7] The use of water or cosolvents to enhance the desorption process were reported in some studies.[3-5] As indicated in these reports, adding water or solvents into the sample could be an easy way to improve sample recovery from the desorption process.

Table 3-5: Effect of Water/Solvent Addition on Sample Recovery

Water/Solvents added	Sample					
	Coarse sand		Fine sand		Sandy soil	
	Peak area*	Total PCBs recovery (%)**	Peak area	Total PCBs recovery (%)**	Peak area	Total PCBs recovery (%)**
No water/solvents added	41808	80	3832	7	6152	12
2 µL water	47382	91	3500	7	6405	12
5 µL water	51724	99	7336	14	7366	14
10 µL water	50448	97	13107	25	7418	14
15 µL water	51447	99	13901	27	10545	20
20 µL water	12320	24	7033	14	4484	9
2 µL methanol	/	/	3912	8	6650	13
5 µL methanol	/	/	5983	12	7641	15
10 µL methanol	/	/	10415	20	9474	18
15 µL methanol	/	/	14535	28	9485	18
20 µL methanol	/	/	18154	35	2055	4
2 µL 50% water and 50% methanol	/	/	3125	6	5892	11
5 µL 50% water and 50% methanol	/	/	6389	12	6208	12
10 µL 50% water and 50% methanol	/	/	13852	27	9378	18
15 µL 50% water and 50% methanol	/	/	23200	45	8250	16
20 µL 50% water and 50% methanol	/	/	20955	40	3166	6

* Average peak area of 3 repeat measurements
** Peak area obtained for direct injection of the same amount of liquid PCB standard into the empty desorption tube was taken as 100% recovery
/ Test not conducted

Deionized water, methanol, as well as a mixture of 50% deionized water and 50% methanol were added to coarse sand, fine sand and sandy soil standards to investigate their effect on the PCB recovery by thermal desorption. 100 mg spiked coarse sand, fine sand and sandy soil standards containing 0.1 μg/g total PCBs were placed in the desorption tube, with selected volumes of water or solvent injected onto the sample using an appropriate syringe. The samples were tested in triplicate under optimized thermal desorption/GC conditions. The results are listed in Table 3-5. When no water or solvent were added into the sample, the recovery rates (taking the result from direct injection of the same amount of total PCBs into the empty desorption tube as 100% recovery) for spiked coarse sand, fine sand and sandy soil standards were 80, 7 and 12%, respectively. Adding 5, 10, or 15 μL of deionized water into the coarse sand standard increased the recovery rate to almost 100%. On the other hand, adding 20 μL of water to the standard reduced the recovery rate to 24%. This might be related to the DELCD's loss sensitivity in the presence of water,[8] or it might be higher soil moisture contents leading to additional energy required to volatize the water, thus inhibiting thermal desorption.[7] The minimum volume of water needed to reach the highest recovery rate for coarse sand was 5 μL. Since almost 100% recovery rate was available by adding water only, the tests with methanol or the mixture of water and methanol were not necessary for coarse sand. For the fine sand standard, the recovery rates improved with the addition of an appropriate amounts of deionized water, methanol, or the methanol/water mixture. The highest recovery rate of 45%, which was over 6 times higher than the one without adding any solvent, was obtained when 15 μL of 50% water and 50% methanol mixture were added. Recovery improvement was also found for sandy soil samples with the addition of water

or solvent into the samples, but the effect was not as significant as that for the fine sand. The highest recovery rate of 20%, almost double the one without water or solvent addition, was obtained with the addition of 15 μL deionized water. In all cases, addition of an appropriate amount of water or organic solvent into solid samples facilitated thermal desorption of the PCBs from the sample matrix. The recovery improved to different extent for different types of samples. Recovery improvement also depended on the type and volume of the solvent added.

The optimized conditions for the analysis of total PCBs in sand and soil samples are summarized in Table 3-6.

Table 3-6: Operating Conditions for Thermal Desorption/GC Analysis

Sample	100 mg with addition of deionized water or solvents (coarse sand: 5 μL deionized water; fine sand: 15 μL mixture of 50% water and 50% methanol; sandy soil: 15 μL deionized water)
Heating temperature	350 °C
Heating time	1-minute heating followed by start of the GC run, with heating until the end of the run (for sand samples); alternatively, 2-minute heating followed by start of the GC run and stopping the heating (for sandy soil samples)
GC column	0.5 m × 0.53 mm I.D. × 0.5 μm d_f MXT-1 Silcosteel column with 0.5 m × 0.53 mm I.D. deactivated Silcosteel retention gap
Carrier gas (N_2) flow rate	20 mL/min
GC make-up air flow rate	5 mL/min
GC oven temperature program	125 °C (0.5 min) → 250 °C (2 min), with a ramp of 75 °C/min
Detector heater temperature	300 °C
Detector reactor temperature	1000 °C
Detector attenuation	Medium or low
Sample turnaround time	6.6 minutes (1-minute preheating) and 7.6 minutes (2-minute preheating)

3.3.2 Characterization of the Thermal Desorption/GC Method

Once the optimal operating conditions for the thermal desorption/GC method were determined, analytical characteristics of the method were determined for sand and soil

samples. It must be pointed out that in reality total PCB recoveries from thermal desorption of different types of sample matrices were not known. Thus, there was no general calibration curve that was applicable to soil samples of all types. Establishing calibration curves for individual types of soil samples could be troublesome and time-consuming: clean soil samples of the same kind must be obtained and made into standards, analyses of the standards would then have to be carried out to produce the calibration curve. The process would be impractical in the case of field analysis. Therefore, the standard addition method[9] was necessary to obtain quantitative analysis results without the need for external calibration. Investigations of the standard addition method for the analysis of total PCBs in the fine sand and sandy soil standards were conducted.

3.3.2.1 Coarse Sand

As almost 100% recoveries of total PCBs (given the recovery from the injection of total PCBs into the empty desorption tube was 100%, although this might not be completely true as glass surfaces might retain PCBs)[7] from the spiked coarse sand standards were obtained in the previous tests, it was possible to establish a calibration curve with 100% total PCBs recovery. The limit of detection for total PCBs in coarse sand could thus be determined. Using the conditions listed in Table 3-6, 100 mg each spiked coarse sand standards (from 0.05 μg/g to 99 μg/g) were analyzed in triplicate. Peak areas for each measurement were recorded and relative standard deviations were calculated. Tests of the entire standard series were also repeated on different days to check the day-to-day reproducibility of the analysis. The results are listed in Table 3-7. The calibration curve is shown in Figure 3-5.

Table 3-7: Analysis Results of Total PCBs in Coarse Sand Standards

Quantity (ng)	Average peak area of triplicate analysis*			3-Day average peak area	3-Day RSD (%)
	Day 1	Day 2	Day 3		
0.05	541	509	515	522	3.3
0.1	946	995	995	979	2.9
0.25	2102	2221	2278	2200	4.1
0.5	4393	4462	4363	4406	1.2
1.0	8733	8816	8708	8752	0.6
2.5	20205	19427	19618	19750	2.1
5.0	31533	31986	29542	31020	4.2
10	51541	54080	52358	52660	2.5
24	81143	80809	81433	81128	0.4
48	107109	111410	109886	109468	2.0
99	150226	149962	146108	148765	1.5

* RSDs for triplicate analyses were from 0.8 to 10.9%

It follows from the results that after adding 5 µL deionized water into the coarse sand samples, the RSDs for triplicate measurements were from 0.8 to 10.9%, and the RSDs for three-day repeat measurements were 0.4 ~ 4.2%. The results confirmed good reproducibility of the analysis, which are illustrated in Figure 3-5. The calibration curves for 3-day repeat measurements were nearly perfectly superimposed.

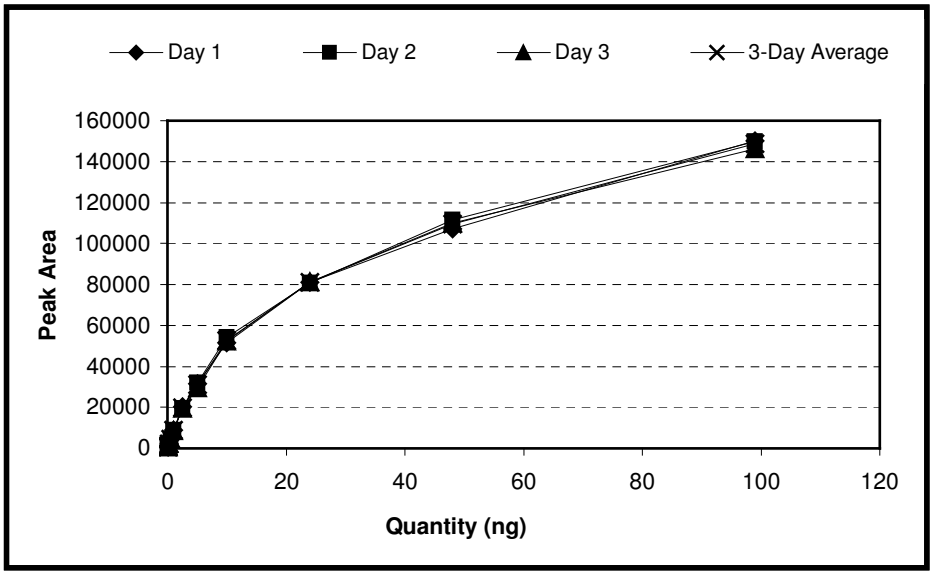


Figure 3-5: Calibration curves of total PCBs for spiked coarse sand

The method detection limit for total PCBs was determined by 8 repeat measurements of 100 mg spiked coarse sand standard with a concentration of 0.001 μg/g (0.1 ng in 100 mg) total PCBs, which was 2 times the estimated detection limit of 5×10^{-4} μg/g (0.05 ng in 100mg) total PCBs. Peak heights of the measurements were recorded and the MDL was determined according to Equation (1). The MDL was found to be 0.01 ng.

3.3.2.2 Fine Sand

Standard addition method was used to characterize the thermal desorption/GC method for the analysis of spiked fine sand samples. Standard addition method is especially useful when the sample matrices are complicated and their effects on the analytical process are unknown. In standard addition method, known quantities of the analyte (standard) are added to the sample. From the increase in the analytical signal, the original amount of the analyte in the sample can be determined. The prerequisite for this method is that the response to the analyte is linear. It is also assumed that the sample matrix imposes the same effects on the original analyte as on the analyte added to the sample, thus the effect of the sample matrix is offset. If the quantities of the analyte added and the signals corresponding to the analyte in the original sample and in the spiked sample are known, the quantities of the analyte in the original sample can be calculated by the following equation:[9]

$$A_o/(A_o + A_{st}) = S_o/S_{o+st} \qquad \text{Equation (2)}$$

where,

A_o = original quantity of the analyte in the sample
A_{st} = quantity of the analyte (standard) added to the sample
S_o = signal due to the analyte in the original sample
S_{o+st} = signal due to the analyte in the spiked sample

Another way to carry out standard addition is by adding the standard at different levels[9]. Each sample with different standard addition level is analyzed. A graph with *x*-axis as the quantities of added standard and *y*-axis as the analytical signal is constructed. The intersection of the extrapolated line with the *x*-axis points to the original quantity of the analyte in the sample.

Table 3-8: Analysis Results of Standard Addition Method for Fine Sand Standards

Quantity of standard addition (ng)	Average peak area of triplicate analyses			3-Day average peak area	3-Day RSD (%)	Quantity of original analyte calculated using Equation (2)	% Difference from theoretical true value*
	Day 1	Day 2	Day 3				
0	18578	17750	18248	18192	2.3	/	/
1.0	19945	19972	20568	20162	1.7	9.2	8.3
2.5	22210	22496	22559	22422	0.8	10.8	7.7
5.0	28020	27618	27562	27733	0.9	9.5	5.1
10	36065	35738	35370	35724	1.0	10.4	3.9

* The theoretical true value was 10 ng (100 mg fine sand with a concentration of 0.1 μg/g total PCBs)

The standard addition method for the analysis of fine sand sample was conducted using 100 mg spiked fine sand standards containing 0.1 μg/g total PCBs. Using an appropriate syringe, aliquots of liquid total PCBs standards (Aroclor 1254 in hexane) were added into the spiked fine sand standard. Liquid PCB standards were added at 4 levels: 1 ng, 2.5 ng, 5 ng, and 10 ng. Each fine sand sample with standard added was then analyzed in triplicate by applying the conditions listed in Table 3-6. Repeat analyses of the samples under the same operating conditions were conducted over three days to investigate the reproducibility. Peak areas for each measurement were recorded and their 3-day RSDs were calculated. The results are listed in Table 3-8. The total PCBs concentrations calculated from Equation (2) for the original fine sand standard ranged

from 9.2 to 10.8 ng, and the percent difference from the theoretical true value (10 ng) ranged from 3.9 to 8.3%. The 3-day RSDs were in the range of 0.8 to 2.3 %, indicating good reproducibility. The graphic treatment of the standard addition data is illustrated in Figure 3-6:

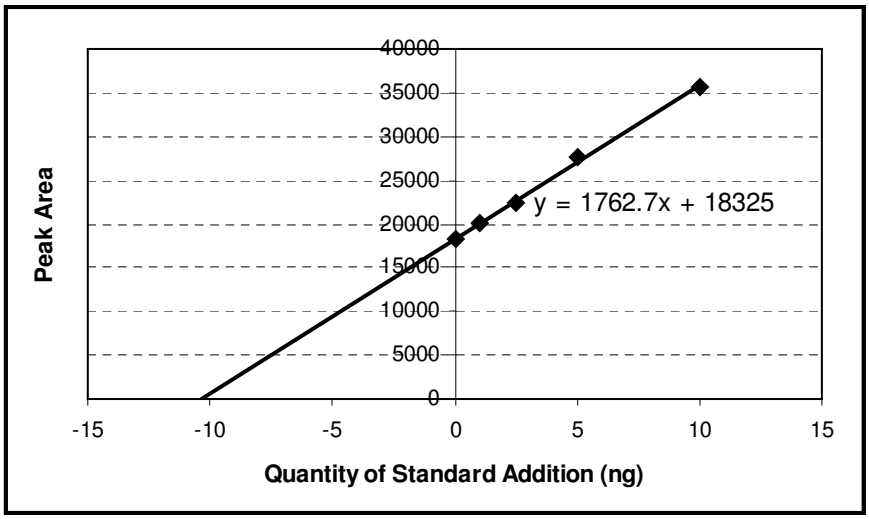


Figure 3-6: Graphical treatment of the standard addition data for fine sand standards

The absolute value of the *x*-intercept of the extrapolated line shown in Figure 3-6 was 10.4 ng. This was the value of total PCBs in the original fine sand standard. The percent difference of the result from the theoretical value (10 ng) was 3.9%.

3.3.2.3 Sandy Soil

The same procedure of standard addition used for fine sand standards was applied to spiked sandy soil standards using the 2-minute sample preheating procedure instead of the 1-minute preheating procedure. 100 mg of spiked sandy soil standard with the concentration of 0.1 μg/g total PCBs was used as the original sandy soil sample. Liquid PCB standards (Aroclor 1254 in hexane) were added at 4 different levels: 5, 7.5, 10 and

15 ng. Analyses of each sample were conducted in triplicate and measurements were repeated over three days. The data and their graphic treatment are shown in Table 3-9 and Figure 3-7, respectively.

Table 3-9: Analysis Results of Standard Addition Method for Sandy Soil Standards

Quantity of standard addition (ng)	Average peak area of triplicate analyses			3-Day average peak area	3-Day RSD (%)	Quantity of original analyte calculated using Equation (3)	% Difference from theoretical true value*
	Day 1	Day 2	Day 3				
0	15939	15041	15063	15348	3.3	/	/
5.0	23590	23222	24111	23641	1.9	9.3	7.3
7.5	25848	26102	25603	25851	1.0	11.0	9.5
10	29389	29364	31373	30042	3.8	10.4	3.9
15	36431	37092	36359	36627	1.1	10.8	7.7

* The theoretical true value was 10 ng (100 mg fine sand with a concentration of 0.1 μg/g total PCBs)

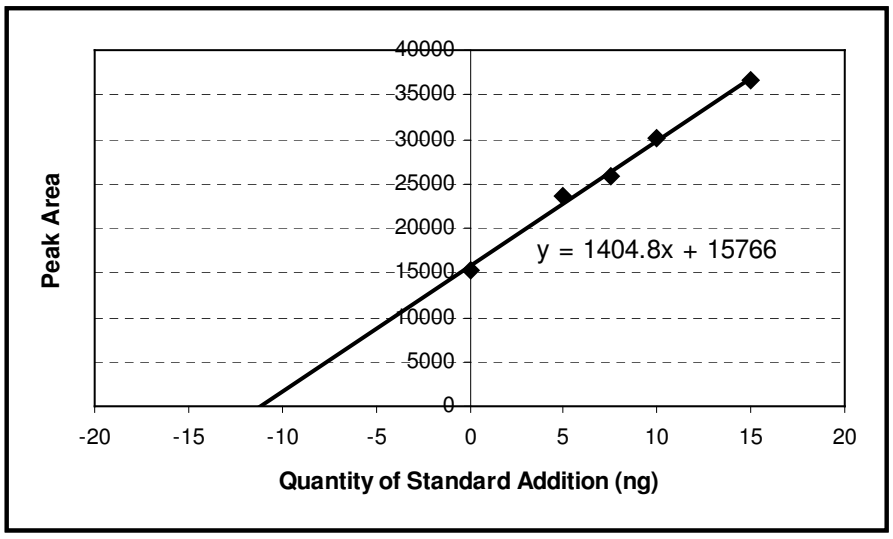


Figure 3-7: Graphical treatment of standard addition data for sandy soil samples

The values of the total PCBs in the original sandy soil samples calculated from Equation (2) ranged from 9.3 to 11.0 ng. The percent differences from the theoretical true value (10 ng) were from 3.9 to 9.5%. Graphic treatment of the standard addition data

showed a value of 11.2 ng total PCBs in the original sandy soil sample, with a percent difference of 11.3% from the theoretical true value.

3.3.3 Analysis of Real Soil Samples

3.3.3.1 Environmental Field Soil Samples

After the thermal desorption/GC method was optimized and characterized using sand and soil standards, it was validated by testing environmental field soil samples. Four soil samples labeled #46, ML Profile 4 Red Kai, S677-04, and BH 18-1 were tested. Among these samples #46 and ML Profile 4 Red Kai were taken from a contaminated landfill in Norway during remediation of the landfill site. The landfill had been used for disposal of both household waste and industrial waste since 1930's. It is now closed and undergoing remediation. The industrial waste disposed in the landfill included transformer oil, which resulted in spreading of PCBs in the soil of the landfill site. Soil sample BH 18-1 was obtained from a decommissioned radar site in central Ontario. The site was contaminated with PCBs from transformer oil previously stored at the site. Sample S677-04 was from a privately owned site in Southern Ontario that has PCB contamination.

The appearance of the 4 soil samples was different: samples #46, ML Profile 4 Red Kai, and BH 18-1 were dry and stored in plastic bags at room temperature. There was gravel, pebbles, wood debris, coarse sand and sandy soil mixed together in sample BH 18-1. Sample #46 was the mix of coarse sand, fine sand and sandy soil. Sample ML Profile 4 Red Kai was similar to sandy soil. Both sample #46 and ML Profile 4 Red Kai contained some humus from the decomposition of vegetation and grass roots.

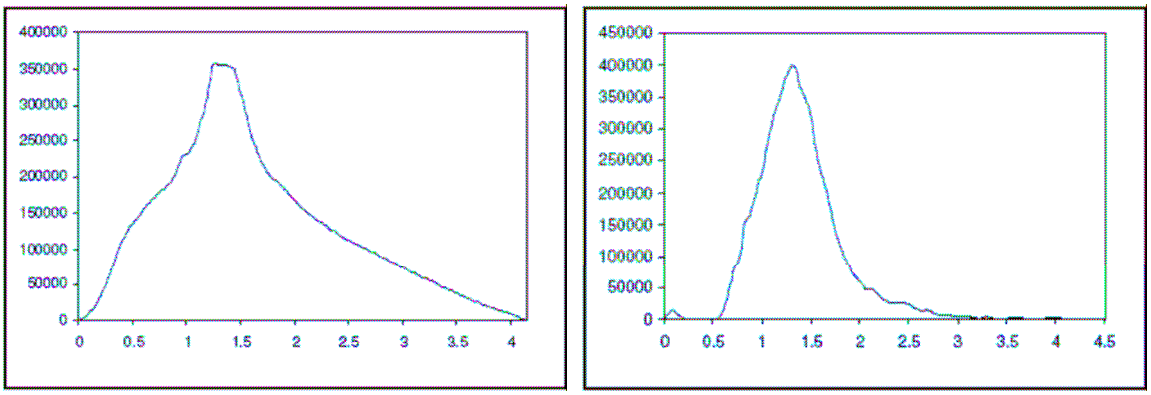
Sample S677-04 was a moist black soil with rich source of humus from the decomposition of vegetation. The sample was placed in a glass flask with waterproof lid, sealed and stored in a freezer to preserve the moisture in the sample. Samples S677-04 and BH 18-1 were previously tested in the laboratory using standard GC/ECD method for the analysis of solvent extracts.[10] Sample #46 and ML Profile 4 Red Kai were tested in a previous project by Dr. Gorecki's group in which extracts of the samples were analyzed using the same SRI 310 GC.[11] The analytical results from these tests were used to compare with the results obtained using the thermal desorption/GC method in this research.

3.3.3.2 Analytical Procedure and Results

Dry samples #46, ML Profile 4 Red Kai and BH 18-1 in plastic bags were shaken thoroughly by hand prior to loading them into the desorption tube. After being taken out from the freezer, sample S677-04 was brought to room temperature before loading. All samples were loaded into the desorption tube using a spatula. Large gravel and pebbles were removed from the sample before loading. The samples were weighted using an ACB 600H balance (Adam Equipment Co. Ltd., CT, USA) for 50 and 100 mg sample size or an analytical balance for 20 mg sample size.

The operating conditions for thermal desorption and the GC analysis were selected as specified in Table 3-6. Two different heating settings (1-minute preheating procedure and 2-minute preheating procedure) were first tested for each kind of samples to choose the heating procedure that produced optimal peak shape. It was found that 2-minute preheating procedure gave the best results for all of the samples, with a clear,

distinguishable peak generated. Figure 3-8 shows an example of the results obtained for sample #46. The 2-minute preheating procedure was thus selected for all 4 soil samples.



(a) **(b)**

Figure 3-8: Chromatograms of total PCBs from thermal desorption of 100mg soil sample #46. (a) heating time: 1-minute heating followed by start of GC and continuous heating; (b) 2-minute heating followed by start of GC analysis and stopping the heating

Standard addition approach was applied to determine the content of total PCBs in the 4 field soil samples. A series of Aroclor 1254 standards in hexane prepared according to Table 2-1 were used as analyte standards. Both single standard addition procedure (as defined by Equation (2)) and multiple standard addition procedure were used to compare the efficiency of two procedures. Appropriate amounts of the standard (Aroclor 1254 in hexane) were injected into the soil sample in the desorption tube using a 10 µL syringe. The standard addition procedure was performed as below: first, 100 mg of the soil samples were analyzed in triplicate using the selected thermal desorption/GC method to obtain information on the total PCBs in the original sample. The next step was to decide the appropriate amount of standard that should be added to the original sample. Because the content of total PCBs in the original sample was unknown, standard addition should

start from a small amount. The standard was added to 100 mg of the original sample and the spiked sample was then analyzed under the same conditions. The added standard would increase the signal so that the peak area of total PCBs for the spiked sample would increase. In order to discriminate this increase in peak area from the change due to random error or heterogeneity of the sample, the standard should be added until an increase of at least 20% in peak area was observed. After the appropriate amount of standard that should be added was decided, the measurements of the spiked sample were repeated at least three times. The average of the peak areas were then used to calculate the amount of the total PCBs in the original sample according to Equation (2). For the multiple standard addition procedure, measurements of spiked samples with at least three different levels of standard additions were required to get enough data points for the construction of the standard addition graph.

Table 3-10: Analysis Results of Standard Addition for 100 mg ML Profile 4 Red Kai

Sample	Average peak area of total PCBs for triplicate measurements	Calculation result of total PCBs in the original sample using Equation (2)
100 mg ML Profile 4 Red Kai (original sample)	39132	/
100 mg ML Profile 4 Red Kai with addition of 1 µL 10 µg/mL Aroclor 1254 in hexane (10 ng total PCBs added)	48200	43.1 ng
100 mg ML Profile 4 Red Kai with addition of 1.5 µL 10 µg/mL Aroclor 1254 in hexane (15 ng total PCBs added)	49232	58.1 ng
100 mg ML Profile 4 Red Kai with addition of 2 µL 10 µg/mL Aroclor 1254 in hexane (20 ng total PCBs added)	49905	72.6 ng

When applying the standard addition procedure, a linear response from the standard addition is required.[9] If the concentration of total PCBs in the original sample was too

high, adding in extra standard could have led to exceeding the linear range of the detector (0.05 ~ 1.0 ng). In such cases, a smaller sample size had to be used. One example was soil sample ML Profile 4 Red Kai. When applying 100 mg sample size, addition of the standards did not provide a linear response (Table 3-10 and Figure 3-9).

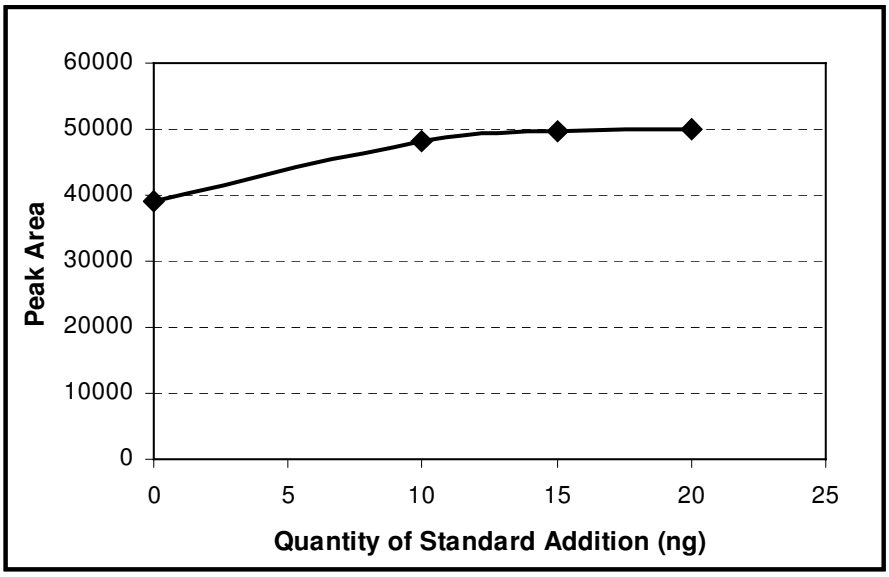


Figure 3-9: Graphical treatment of standard addition data for 100 mg ML Profile 4 Red Kai

Table 3-10 shows that with a non-linear response, different levels of standard addition gave very different calculation results from Equation (2) for total PCBs in the original sample (the highest value was 1.7 times of the lowest value). In addition, it was practically impossible to deduce the result from the multiple standard addition graph (Figure 3-9) because the response line was not linear. The sample size of ML Profile 4 Red Kai was then reduced to 50 mg for the analysis. The results are presented in Table 3-11 and Figure 3-10.

Table 3-11: Analysis Results of Standard Addition for 50 mg ML Profile 4 Red Kai

Sample	Average peak area of total PCBs for 4 repeat measurements	Calculation result of total PCBs in the original sample using Equation (2)
50 mg ML Profile 4 Red Kai (original sample)	19365	/
50 mg ML Profile 4 Red Kai with addition of 1 µL 5 µg/mL Aroclor 1254 in hexane (5 ng total PCBs added)	23323	24.5 ng
50 mg ML Profile 4 Red Kai with addition of 1 µL 10 µg/mL Aroclor 1254 in hexane (10 ng total PCBs added)	28969	20.2 ng
50 mg ML Profile 4 Red Kai with addition of 2 µL 10 µg/mL Aroclor 1254 in hexane (20 ng total PCBs added)	34389	25.8 ng

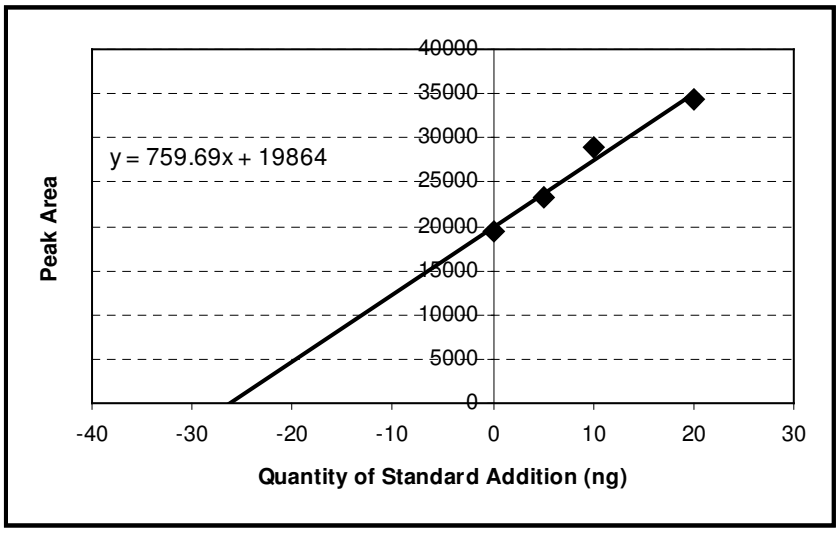


Figure 3-10: Graphical treatment of standard addition data for 50 mg ML Profile 4 Red Kai

It can be seen that when using 50 mg sample size, a linear detection response for total PCBs was obtained, indicated both by close calculation results from Equation (2) for three different levels of standard additions and the linear correlation shown in the standard addition graph. Thus, the proper sample size for ML Profile 4 Red Kai sample was 50 mg. Likewise, a 20 mg sample size was found to be appropriate for soil sample BH 18-1.

Following the procedures described above, measurements of total PCBs in 4 soil samples using both single standard addition and multiple standard addition procedures were conducted. Measurements for the original sample and each standard addition were repeated 3 to 5 times. Results of total PCBs analysis in the 4 soil samples are listed in Table 3-12.

Table 3-12: Analysis Results of Total PCBs in 4 Soil Samples by Thermal Desorption/GC Method

Analytical item		Soil sample			
		S677-04	**#46**	**ML Profile 4**	**BH 18-1**
Graphical procedure	**Sample size (mg)**	100	100	50	20
	Standard addition (ng)	0, 1, 2, 3	0, 5, 10, 20	0, 5, 10, 20	0, 10, 15, 20
	No. of measurements for each standard addition	3	3	4	5
	RSD (%) for repeat measurements of multiple additions in time	4.9 ~ 12.1	3.3 ~ 7.4	3.9 ~ 6.3	5.1 ~ 8.0
	Average calculated total PCBs concentration (μg/g)	0.009	0.34	0.52	1.58
Single addition procedure	**Sample size (mg)**	100	100	50	20
	Standard addition (ng)	0, 1.5	0, 15	0, 15	0, 15
	No. of measurements for each standard addition	3	3	4	5
	RSD (%) for repeat measurements of single addition in time	9.5	11.7	7.9	9.4
	Average calculated total PCBs concentration (μg/g)	0.012	0.31	0.53	1.76

Results showed that RSDs of peak areas for repeat measurements were from 3.3 to 12.1%. The percent differences between the total PCBs concentrations determined by the graphical procedure and the single standard addition procedure ranged from 0 to 10.8%, indicating close analytical results from these two procedures. Since a good linear response was obtained from the standard addition graph, the graph could be rearranged to establish a calibration curve for direct measurement of total PCBs in the sample without

standard addition. This was done by moving the whole linear line along the *y*-axis down to the origin with the slope kept unchanged. The result of such rearrangement from the standard addition graph for soil sample ML Profile 4 Red Kai (Figure 3-10) is presented in Figure 3-11. We can see in Figure 3-11 that the peak area of 19365 from the original sample corresponds to a quantity of total PCBs of 24.8 ng. While in standard addition graph (Figure 3-10), the quantity of total PCBs corresponding to the original sample was 26.1 ng, very close to the one from calibration curve. Therefore, the calibration curve also worked effectively in determination of total PCBs in the original sample. Since direct measurement of the soil sample would be available with the calibration curve established, it would provide great convenience in analyzing large batches of soil samples in the field.

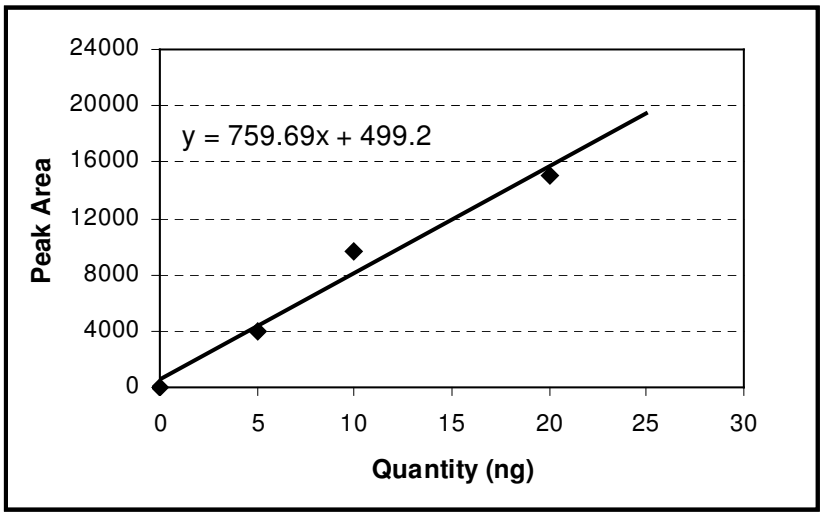


Figure 3-11: Calibration curve of ML Profile 4 Red Kai by rearrangement of the standard addition graph

The results from the thermal desorption/GC method with standard addition for 4 soil samples were then compared with the results from previous tests (analyses of the solvent extract by GC/ECD and SRI 310 GC).[10, 11] The comparison is summarized in Table 3-13.

Table 3-13: Comparison of Total PCBs in 4 Soil Samples by Different Methods

Soil sample	Total PCBs concentration (μg/g)				% Difference		
	Thermal desorption/ GC method (graphical procedure)	Thermal desorption/ GC method (single addition procedure)	Solvent extraction –GC/ECD method[10]	Solvent extraction/ SRI 310 GC method[11]	Graphical procedure to single addition procedure	Graphical procedure to other methods	Single addition procedure to other methods
S677-04	0.01	0.01	< 0.05	/	0	/	/
#46	0.34	0.31	/	0.21	9.2	47.3	38.5
ML Profile 4	0.52	0.53	/	0.08*	1.9	146.7	147.5
BH 18-1	1.58	1.76	1.72	/	10.8	8.5	2.3

* Extract contained fine particles that would affect the GC analysis[11]
/ Sample not tested by this method

Comparison of the results between the thermal desorption/GC method and GC/ECD method showed good matches of total PCBs concentration for soil sample S677-04 and BH 18-1, with less than 10% difference for BH 18-1 and 0.01 μg/g compared to <0.05 μg/g for S677-04. Differences of the results between the thermal desorption/GC method and solvent extraction/SRI 310 GC method for sample #46 and ML Profile 4 Red Kai were about 50% and 150% respectively. The relatively large difference was probably due to the fact that fine particles in the extract affected the GC analysis.[11]

3.4 Conclusions

For the analysis of total PCBs in soils using thermal desorption/GC, the conditions for the thermal desorption/GC method were first investigated using spiked sand and soil standards. A laboratory made thermal desorber was connected to the SRI 310 GC. Tests were initially conducted based on the GC conditions previously optimized using liquid total PCBs standards. It was found that those optimal GC conditions worked effectively

for the analysis using thermal desorption/GC method, with a change to the make-up air flow rate from 10 mL/min to 5 mL/min.

Operating conditions for the thermal desorption were investigated by testing different heating temperatures, heating times, and sample sizes to find the optimal total PCBs peak shape, sample recovery, and reproducibility of the analysis. The results indicated that the total PCB recovery from thermal desorption reached its highest when the heating temperature was about 350 °C. Temperature higher than 350 °C did not improve the sample recovery any further. The heating time for the desorption should be at least 2 minutes to obtain the highest sample recovery. 2-minute desorption could be performed by either 2-minute preheating procedure or 1-minute preheating procedure. The 1-minute preheating procedure worked effectively for coarse and fine sand samples. However, 1-minute preheating procedure could not focus total PCBs sufficiently for sandy soil samples. In this case, 2-minute preheating procedure was applied. Both 100 mg and 50 mg sample sizes were tested with better reproducibility for the 100 mg sample size. However, for real samples, when the total PCBs concentration in the sample was too high, smaller sample sizes had to be used to ensure that the linear range of the method was not exceeded.

The recovery of total PCBs from thermal desorption improved with the addition of appropriate amounts of water or an organic solvent into sand and soil standards: total PCBs recoveries increased from 80%, 7%, 12% to 100%, 45%, and 20% for coarse sand, fine sand and sandy soil, respectively. Under the optimized thermal desorption/GC conditions, a calibration curve was established for coarse sand standards because of ~100% total PCBs recovery from the sample. The method detection limit for coarse sand

was found to be 0.01 ng, the same as for liquid injection of PCB standards. Determination of total PCBs in fine sand and sandy soil was tested using the standard addition method. Both single standard addition and multiple standard addition procedures proved to be effective for the determination of total PCBs in fine sand and sandy soil standards, with less than 10% difference from the theoretical true value. The thermal desorption/GC method also provided good reproducibility for the analysis, with the RSDs ranging from 0.8 to 4.2% for 3-day repeat measurements. Sample turnaround time with the optimized method was 6.6 minutes for the 1-minute preheating procedure and 7.6 minutes for the 2-minute procedure, respectively.

The thermal desorption/GC method developed was validated by testing 4 environmental soil samples. Standard addition graphs for the samples showed good linear response. Thus the calibration curve for the measurement of total PCBs in the soil sample without the need for standard addition would be established by rearranging the available standard addition graph. Analysis results with standard addition showed a good match with the results from a standard GC/ECD method. As a conclusion, the developed thermal desorption/GC method provided a fast and effective analysis of total PCBs in soils, with a sample turnaround time of about 7.6 minutes without the need for solvent extraction of the sample. Practically, the method can be applied by first establishing a standard addition graph with several levels of standard additions to the soil samples, then developing the calibration curve based on the standard addition graph. With the calibration curve established, fast and direct measurement of large batches of soil samples is possible. The method providing sensitive, quantitative analytical results and fast sample turnaround time is thus suitable for screening applications in the field.

4.0 PCB Analysis Using GC × GC – TOF-MS Method

4.1 Introduction

In order to fully characterize the PCBs in the soil samples, a GC × GC – TOF-MS method was applied to identify selected individual PCB congeners in the samples and to verify the contents of total PCBs. Twelve PCB congeners (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) defined as indicators of toxicity by WHO[1] were selected as target PCB congeners to be identified and quantified in the environmental soil samples. Based on the selected GC × GC – TOF-MS conditions, PCB standards were first analyzed to get chromatographic retention indices and mass spectra for the selected twelve PCB congeners. Calibration curves for the individual PCB congeners and total PCBs were also established. Solvent extraction of the environmental soil sample was conducted to obtain extract of the sample for PCB analysis. With the same operating conditions, solvent extracts of four environmental soil samples were then analyzed. Identification of the selected PCB congeners in the environmental soil samples was implemented according to both retention index and mass spectrum information found for the PCB standards. If selected PCB congeners were identified, they were to be quantitated using the corresponding congener calibration curve. By summing up individual PCB congener peaks showed on the chromatogram, total PCBs in the environmental soil samples were also quantitated according to the calibration curve of total PCBs standards. The results of total PCBs in the environmental soil samples were compared to that from the thermal desorption/GC method.

4.2 Experimental

4.2.1 PCB Standards

The selected 12 PCB congener standards were purchased from AccuStandard Inc. (CT, USA) as neat compounds (99 – 100% purity) packed in vials. To prepare stock solutions from the neat compounds, the following procedure was followed: a vial containing the neat compound was weighed on an analytical balance and the weight was recorded to the nearest 0.1 mg. The contents of the vial were then carefully transferred to an appropriate volumetric flask using hexane. The vial and the cap of the vial were rinsed several times to assure complete transfer. The vial and the cap were then dried with a gentle stream of air. The empty dry vial with the cap was weighed again on the same analytical balance to the nearest 0.1 mg. The amount of the neat material recovered from the vial was calculated from the difference in masses. The recovered material was finally diluted with hexane to the mark of the volumetric flask and stored as the stock solution. Data for the preparation of stock PCB congener standards are presented in Table 4-1.

Table 4-1: Data for Preparation of Stock PCB Congener Standards

PCB No.	Contents transferred (mg)	Dilution volume (mL)	Concentration of stock solution (μg/mL in hexane)
77	26.4	25	1056
81	5.0	5	1000
105	5.5	5	1100
114	5.6	5	1120
118	5.2	5	1040
123	5.5	5	1100
126	5.2	5	1040
156	5.6	5	1120
157	7.5	5	1500
167	6.4	5	1280
169	7.2	25	288
189	5.1	5	1020

Table 4-2: Data for Preparation of Diluted PCB Congener Standards

PCB No.	Concentration of stock standard (µg/mL)	10 µg/mL individual congener solution		Mixture of 12 PCB congeners with each concentration of 1 µg/mL		Mixture of 12 PCB congeners with each concentration of 5 µg/mL		Mixture of 12 PCB congeners with each concentration of 10 µg/mL		Mixture of 12 PCB congeners with each concentration of 20 µg/mL	
		Vol. of stock standard (µL)	Vol. of hexane (mL)	Vol. of stock standard (µL)	Vol. of hexane (mL)	Vol. of stock standard (µL)	Vol. of hexane (mL)	Vol. of stock standard (µL)	Vol. of hexane (mL)	Vol. of stock standard (µL)	Vol. of hexane (mL)
77	1056	9.5	0.99	1		4.7		9.5		19	
81	1000	10	0.99	1		5		10		20	
105	1100	9	0.99	0.9		4.5		9		18	
114	1120	9	0.99	0.9		4.5		9		18	
118	1040	9.5	0.99	1		4.8		9.5		19	
123	1100	9	0.99	0.9	0.99	4.5	0.95	9	0.87	18	0.73
126	1040	9.5	0.99	1		4.8		9.5		19	
156	1120	9	0.99	0.9		4.5		9		18	
157	1500	6.5	0.99	0.7		3.3		6.6		13	
167	1280	8	0.99	0.8		3.9		7.8		16	
169	288	35	0.97	3.5		1.7		35		70	
189	1020	10	0.99	1		4.9		9.8		20	

Diluted individual PCB congener standards (individual PCB congener standards) and standards of the mixture of the 12 PCB congeners (PCB congener mixtures) were then prepared from the stock congener standards (Table 4-2): each standard series was prepared by the dilution of an appropriate amount of each stock congener standard with an aliquot of hexane in a 1.5 mL vial. Size appropriate syringes were used for the measurements. The content in the vial was then thoroughly mixed using a vortex type mixer. A PCB congener mixture with each congener concentration of 0.5 µg/mL was prepared by 10 times dilution of a PCB congener mixture with each congener concentration of 5 µg/mL. Standards containing 10, 50, 100 and 200 µg/mL Aroclor 1254 in hexane were prepared according to the procedure described in section 2.2.2. The Aroclor 1254 solutions were used as total PCB standards.

4.2.2 Sample Preparation

Solvent extraction of soil samples was applied to prepare liquid phase extracts for GC × GC – TOF-MS analysis of PCBs. Solvent extraction was performed using Soxhlet apparatus. Hexane was used as the extracting solvent. Soxhlet extraction has been a standard extraction technique and widely used for over a century.[2] At present, it is still a standard sample preparation step involved in many official procedures and methods, such as US EPA method 8100 and method 3540.[3,4]

In this research, a 46 mm diameter Soxhlet apparatus (ACE Glass Inc.) with a 250 mL round bottom flask and a water-cooled condenser was used. Soil samples S677-04, #46, ML Profile 4 Red Kai and BH 18-1 were extracted using hexane. The procedure of sample preparation was as follows: 50 g of a soil sample were weighed into the Soxhlet extraction thimble. About 250 mL of hexane were added into the round bottom flask and heated to 80 °C using a hotplate/stirrer. The extraction was carried out for 24 hours. After completion of the extraction, the extract collected in the flask was concentrated to a volume of about 10 mL by evaporating extra solvent with heating. The concentrated extract was then transferred to a 25 mL volumetric flask and diluted to 25 mL. To make higher concentration extract, 15 mL of the extract were transferred from the 25 mL volumetric flask to a labeled 20 mL vial using a 15 mL transfer pipette. The 20 mL vial was then placed in the fume hood to evaporate all the solvent from the extract. After all the solvent evaporated, the dry extract was reconstituted with 1 mL hexane delivered by a syringe. After being thoroughly mixed in the 20 mL vial using a vortex type mixer, the reconstituted extract was finally transferred to a labeled 1.5 mL vial and stored at 4 °C for future analysis.

4.2.3 Instrumentation and Operating Conditions

The GC × GC – TOF-MS instrument was an Agilent 6890A GC coupled to a Leco Pegasus III time-of-flight mass spectrometer as the detector. The first dimension column was a 30 m long ZB-50 column (0.25 mm I.D. × 0.25 μm df), and the second dimension column was a 1.1 m long Rt-LC350 column (0.15 mm I.D. × 0.1 μm d_f) with a liquid crystal stationary phase. Liquid crystal stationary phases exhibit particularly strong retention of planar compounds.[5] Therefore, the second column should separate the PCBs according to their planarity. The use of liquid crystal stationary phase column to successfully separate toxic planar PCBs including PCB 77, 105, 118, 126, 156, and 169 in GC × GC was reported.[5,6] In this research, both columns were mounted in the same Agilent 6890A GC oven. A heater-based interface previously developed in Dr. Gorecki's laboratory was used as the modulator between the first and the second dimension column.[7] The trapping capillary was a 15 cm long, 0.28 mm I.D. segment of deactivated Silcosteel tubing. Two electrical contacts were mounted at two ends of the trapping capillary and one electrical contact was mounted at the middle. The electrical contacts were connected to a custom-designed capacitive discharge power supply, in which two capacitors were periodically and alternately discharged, causing resistive heating of the two segments of the trapping capillary. Thus, dual-stage modulation was possible. Cooling of the trapping capillary was implemented using an electric blower (a hair dryer).

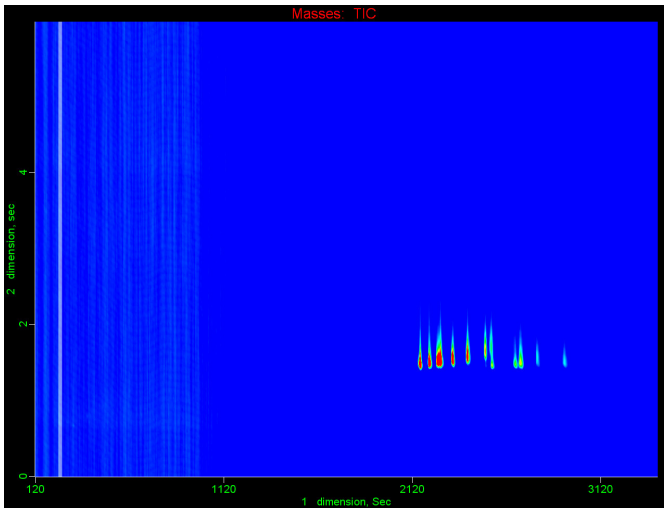
Operating conditions for the modulator were determined in previous studies.[7] The discharge voltage of the capacitive discharge power supply was 36.6 V, which generated a temperature of ~275 °C for the trapping capillary. The modulation period was set at 6 seconds, with 3 seconds alternate discharging of the two capacitors in the power supply.

Initial GC and TOF-MS conditions were set based on published reports where analysis of PCBs with instruments of the same kind was involved.[8, 9] Helium was used as the carrier gas at a constant flow of 1 mL/min. One microlitre of the standard or sample extract were injected into the split/splitless GC injector held at 250 °C in splitless mode. A solvent delay setting of 120 s was applied. The MS transfer line was kept at 290 °C . The ion source temperature was 250 °C with EI energy of 70 eV. The mass spectra were collected with a start mass of 100 u and an end mass of 550 u. The mass spectra were acquired at a rate of 50 spectra/second. The detector voltage was 1770 V. Data processing and display of the GC × GC chromatograms and mass spectra were achieved using the Leco ChromaTOF software.

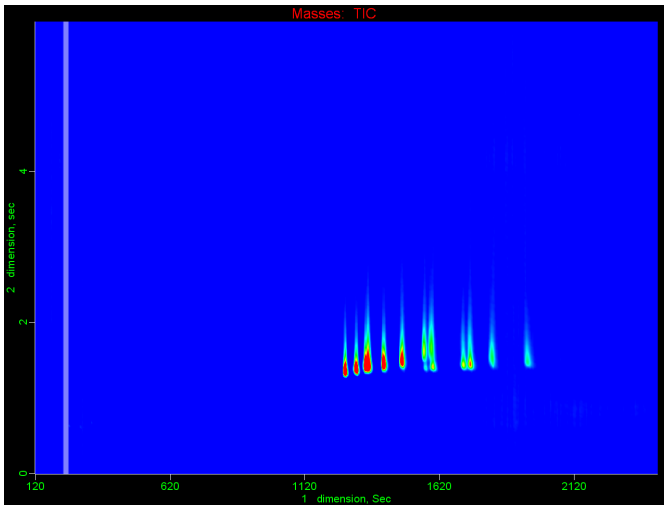
Table 4-3: Retention Times of 12 PCB Congeners with Different Temperature Programs

Peak order	Program 1		Program 2		Program 3	
	1st Retention time (s)	2nd Retention time (s)	1st Retention time (s)	2nd Retention time (s)	1st Retention time (s)	2nd Retention time (s)
1	2160	1.50	1272	1.36	1254	1.54
2	2208	1.50	1308	1.40	1302	1.56
3	2256	1.52	1344	1.44	1344	1.62
4	2268	1.52	1356	1.44	1356	1.62
5	2334	1.54	1410	1.46	1428	1.64
6	2412	1.60	1482	1.50	1512	1.72
7	2508	1.64	1560	1.62	1620	1.80
8	2538	1.70	1596	1.66	1656	1.88
9	2664	1.48	1710	1.44	1800	1.89
10	2694	1.50	1734	1.46	1836	1.82
11	2778	1.56	1818	1.52	1944	1.85
12	2928	1.50	1944	1.50	2118	1.82
Analysis time (min)	58		41		51	

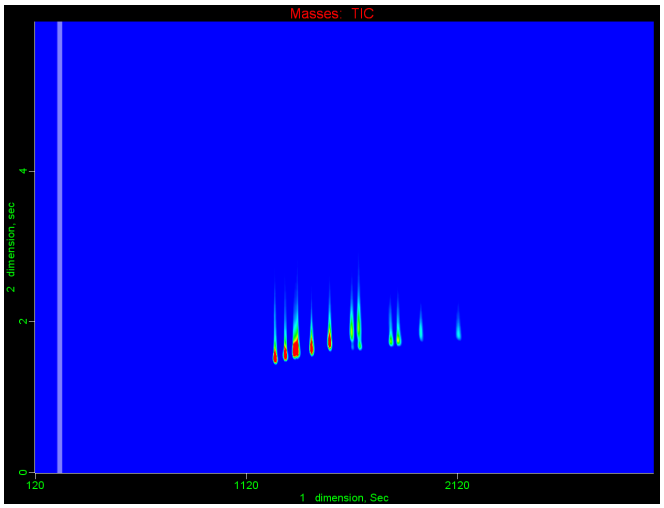
GC × GC separation of the selected PCB congeners was optimized with testing of 3 GC oven temperature program settings. The first one was 60 °C for 1 min, at 20 °C/min to 150 °C, then at 3 °C/min to 290 °C for 5 min. The second one was 60 °C for 1 min, at 30 °C/min to 200 °C, then at 3 °C/min to 290 °C for 5 min. The last one was 60 °C for 1



(a)



(b)



(c)

Figure 4-1: GC × GC chromatograms for the separation of 12 PCB congeners under different temperature programs: (a) program 1; (b) program 2; (c) program 3

min, at 30 °C/min to 210 °C, then at 2 °C/min to 290 °C for 5 min. An aliquot of 1 μL of the PCB congener mixture with 10 μg/mL concentration of each congener was injected. The GC × GC chromatograms obtained with each temperature program are presented in Figure 4-1. All three temperature programs provided good separation of the 12 PCB congeners, with only two congener peaks overlapping. However, the extent of separation between each congener peak was different with different temperature programs. Retention times for twelve PCB congeners and total analysis time under the three temperature programs are listed in Table 4-3. The total analysis times under program 1, 2 and 3 were 58, 41, and 51 minutes, respectively. Program 3 provided the greatest separation between the congener peaks, indicating optimum separation. Temperature program 3 was thus selected for the separation of the PCB congeners, in which a 2 °C/min secondary temperature ramp was applied instead of 3 °C/min in programs 1 and 2.

4.3 Results and Discussion

4.3.1 Analysis Using PCB Standards

4.3.1.1 Identification of Selected PCB Congeners

Identification of 12 PCB congener peaks in the GC × GC chromatogram was carried out using 1 μL of each 10 μg/mL individual PCB congener standard and the PCB congener mixture (10 μg/mL concentration of each congener). The 12 individual PCB congener standards were injected and analyzed one by one under the selected operating conditions as described in section 4.2.3. Retention times in both 1^{st} and 2^{nd} dimension, as well as the mass spectra for the individual congener were recorded. Afterwards, 1 μL of the PCB congener mixture was analyzed in triplicate under the same conditions.

Retention times and mass spectra for each individual congener in the mixture were also recorded. Table 4-4 shows retention times for 12 individual congeners detected in both the individual PCB congener standards and the PCB congener mixture.

Table 4-4: Retention Times for the Selected 12 PCB Congeners

Elution order	Individual PCB congener standards			PCB congener mixture	
	PCB No.	1st Dimension retention time (s)	2nd Dimension retention time (s)	Average 1st dimension retention time (s)*	Average 2nd dimension retention time (s)
1	81	1254	1.56	1254	1.54
2	77	1302	1.68	1304	1.56
3	123	1344	1.74	1350	1.62
4	118	1356	1.68	1360	1.62
5	114	1428	1.74	1430	1.64
6	105	1512	1.76	1514	1.72
7	126	1620	1.78	1618	1.80
8	167	1656	1.72	1652	1.88
9	156	1800	1.78	1802	1.89
10	157	1836	1.80	1840	1.82
11	169	1944	1.82	1940	1.85
12	189	2118	1.86	2124	1.82

* Average for 3 repeat measurements

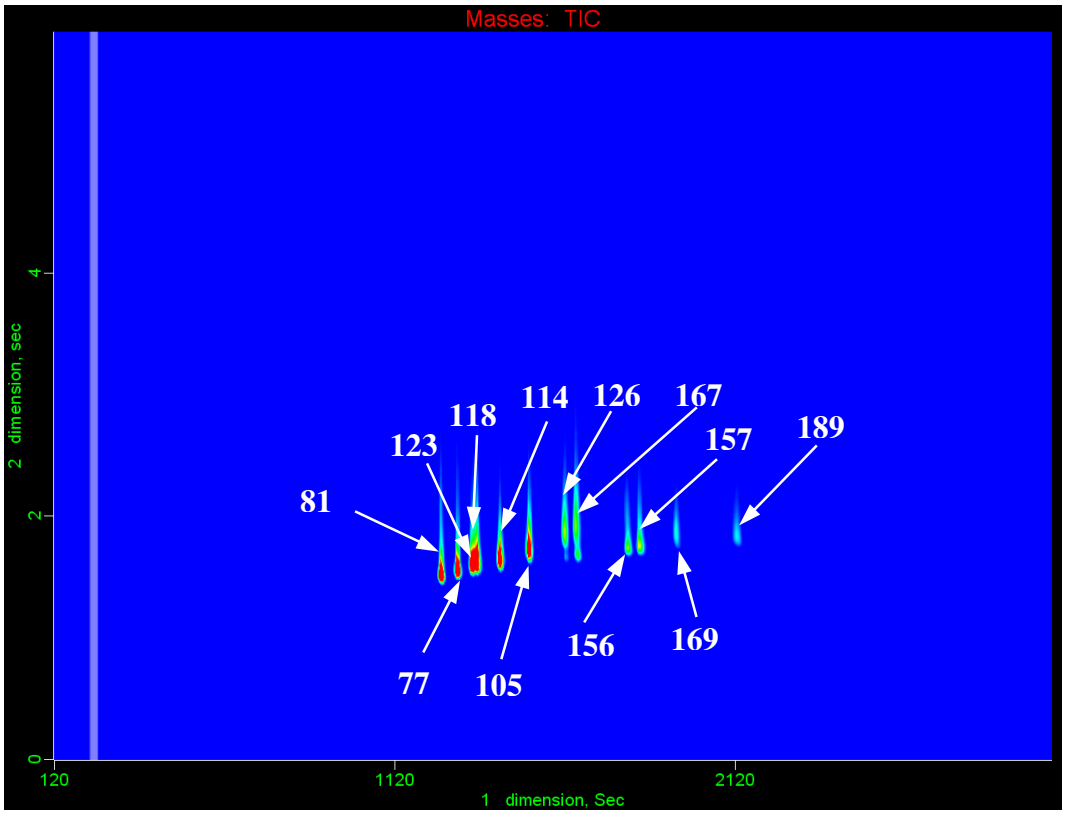


Figure 4-2: Identification of 12 PCB congeners in the PCB congener mixture

By comparing retention times and mass spectra from each PCB congener standard and PCB congener mixture, the PCB congeners that had close retention times and mass spectra were thus identified. The identified 12 PCB congeners in the chromatogram of the PCB congener mixture are presented in Figure 4-2.

1 µL of 100 µg/mL Aroclor 1254 in hexane was also injected to identify the selected 12 PCB congeners in the Aroclor. GC × GC chromatogram of Aroclor 1254 is shown in Figure 4-3. The selected PCB congeners were then identified by comparing both retention times and mass spectra of the congener peaks in Aroclor 1254 to those of the PCB congener standards. Only those congener peaks with both retention times and mass spectra closely matching were identified as peaks of identical congeners.

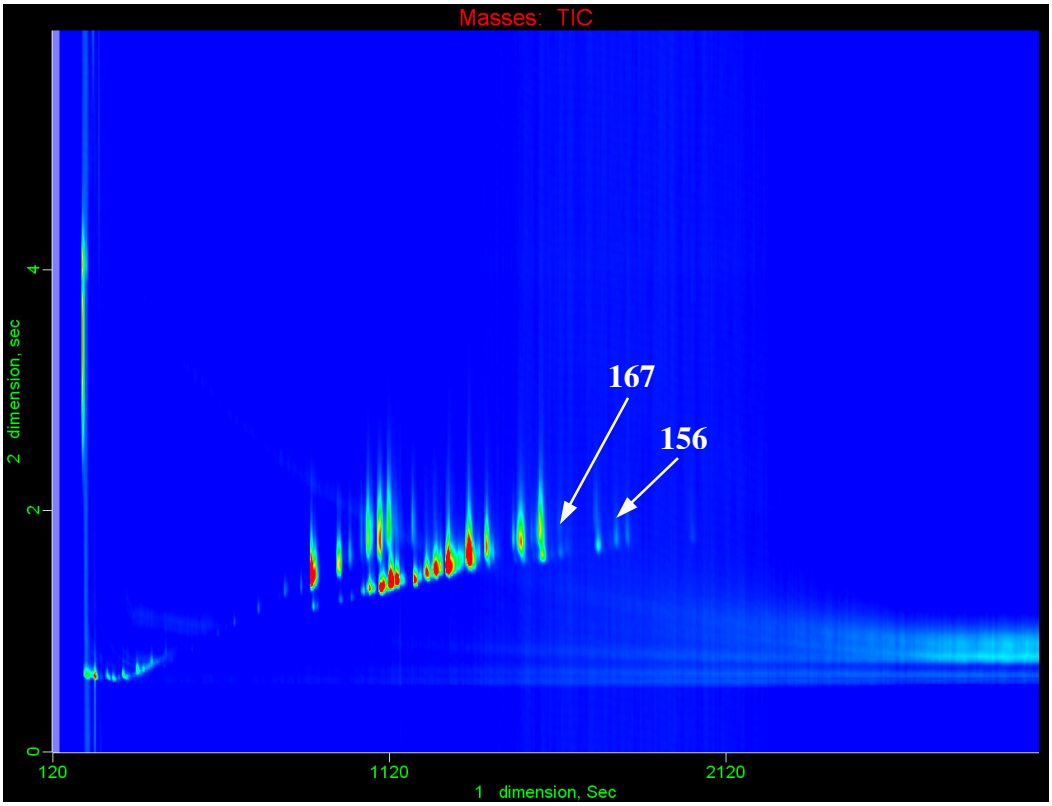
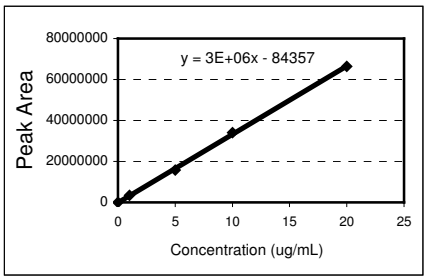


Figure 4-3: Identification of selected PCB congeners in Aroclor 1254

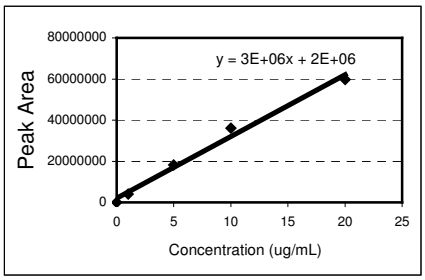
Only PCB 156 and 167 were identified in 1 μL 100 μg/mL Aroclor 1254 with both retention times and mass spectra perfectly matching those of PCB 156 and 167. Although some of the congener peaks had matching retention times, comparison of their mass spectra did not prove identity of the components. These congeners in Aroclor 1254 were thus excluded from the selected 12 PCB congeners.

4.3.1.2 Calibration Curves for the 12 PCB Congeners

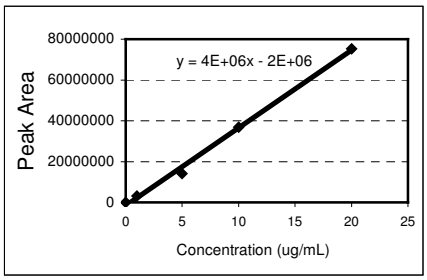
Under the selected conditions, 1 μL of PCB congener mixture was injected and analyzed in triplicate. Peak areas and peak heights of the selected PCB congeners were processed and recorded using Leco ChromaTOF software. It was found that PCB 169 and 189 were not detectable when their concentration in the PCB congener mixture was 1 μg/mL. Therefore, an additional PCB congener mixture with each congener concentration of 2 μg/mL was made as the lowest concentration standard for the detection of PCBs 169 and 189. Calibration curves (peak area vs. concentration and peak height vs. concentration) for each congener were constructed. Figure 4-4 shows the calibration curves of peak area vs. concentration for each congener. Relative standard deviations of peak areas for three repeat measurements were computed and are listed in Table 4-5. The results showed that in the range of 1 ~ 20 μg/mL (2 ~ 20 μg/mL for PCB 169 and 189), linear calibration curves for both peak area and peak height measurement were obtained for each congener. Relative standard deviations of peak area for three repeat measurements were from 2.2 to 31.6%. According to calibration curves of PCB 156 and 167, the concentrations of PCB 156 and 167 in 100 μg/mL Aroclor in hexane (with peak areas of 6.8×10^6 and 3.1×10^6) were about 3.9 and 1.7 μg/mL respectively.



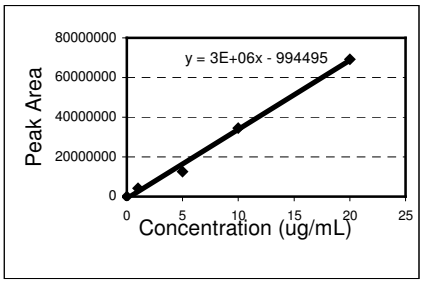
(1) PCB 77



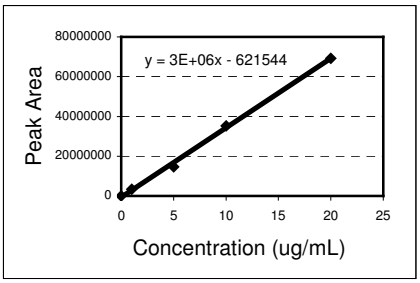
(2) PCB 81



(3) PCB 105



(4) PCB 114



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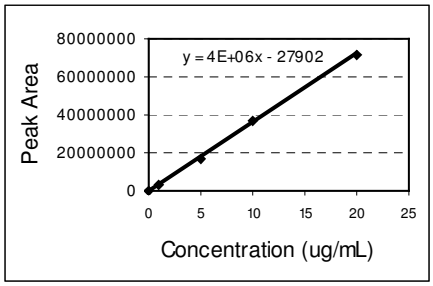
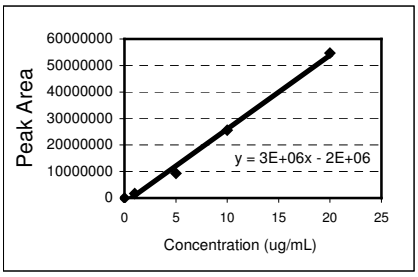


(6) PCB 123



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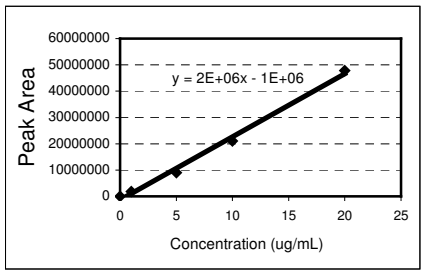

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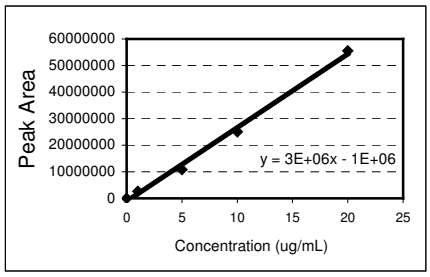
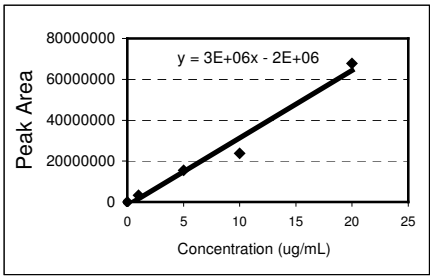
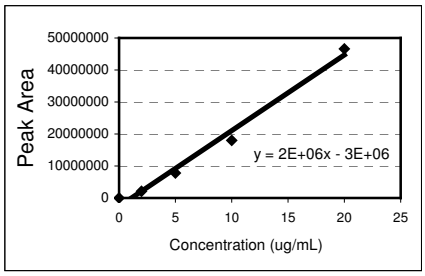


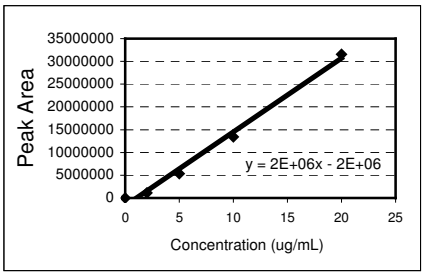
(9) PCB 157



(10) PCB 167



(11) PCB 169



(12) PCB 189

Figure 4-4: Calibration curves for the selected PCB congeners

Table 4-5: Relative Standard Deviations for Repeat Measurements of PCB Congeners

PCB No.	RSDs of peak areas for 3 repeat measurements (%)				
	1 µg/mL	2 µg/mL	5 µg/mL	10 µg/mL	20 µg/mL
77	2.5	/	9.7	10.3	14.7
81	18.2	/	8.7	5.6	10.1
105	13.4	/	7.5	5.9	7.9
114	17.8	/	14.7	10.2	13.1
118	10.5	/	7.7	14.5	6.3
123	12.8	/	7.3	16.5	13.1
126	15.9	/	2.4	9.1	19.7
156	2.2	/	21.9	13.3	31.6
157	26.4	/	21.4	5.3	23.6
167	25.2	/	17.4	8.7	22.8
169	/	27.8	6.2	21.3	20.6
189	/	10.8	7.9	9.4	23.1

4.3.1.3 Limit of Detection for the 12 PCB Congeners

Limits of detection for each congener were determined using the method detection limit (MDL) procedure described in section 2.3.2. Using the selected operating conditions, the estimated detection limit with a chromatographic signal/noise ratio of about 3 to 5 was found to be 0.5 µg/mL for PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, and 167. The estimated detection limit for PCB 169 and 189 was estimated to be 2 µg/mL. Therefore, eight repeat measurements of 1 µL PCB congener mixture with 1 µg/mL concentration of each congener were conducted to test the MDL for PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, and 167. For PCB 169 and 189, eight repeat measurements were performed using the PCB congener mixture with a concentration of 5 µg/mL for each congener. Peak heights of eight repeat measurements were recorded and the MDL for eight peak height measurements were calculated using Equation (1). The concentration corresponding to the MDL of peak height measurement was obtained from the linear peak height vs. concentration calibration curve. The results are listed in Table 4-6.

Table 4-6: Method Detection Limits for the PCB Congeners using GC×GC

PCB No.	STD of peak height for 8 repeat measurements	MDL of peak height	Corresponding concentration (μg/mL)
77	22743	68182	0.61
81	25970	77858	0.46
105	24384	73103	0.86
114	26647	79887	0.76
118	48925	146676	0.95
123	47138	141320	0.97
126	9331	27973	0.42
156	20637	61869	0.87
157	20324	60932	0.85
167	31552	94593	0.91
169	29758	89214	2.12
189	14885	44625	2.36

The results showed that the selected 12 PCB congeners can be divided into 2 categories in terms of the limit of detection: method detection limits for PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, and 167 were in the range of about 0.5 ~ 1 μg/mL, while method detection limits for PCB 169 and 189 were over 2 μg/mL, i.e. over two times the detection limits of the other congeners.

4.3.1.4 Calibration Curve for the Total PCBs Measurement

To establish the calibration curve for the total PCBs measurement using GC × GC – TOF-MS, 1 μL each of 10, 50, 100, and 200 μg/mL Aroclor 1254 in hexane were injected and analyzed in triplicate. Peak areas of individual PCB congeners in Aroclor 1254 were integrated and recorded by the Leco ChromaTOF software. Peak areas of total PCBs were calculated by summing up peak areas of the individual PCB congeners that were detected by the method. RSDs of triplicate measurements were also calculated for each Aroclor 1254 standard. The calibration curve for the total PCB measurement was

constructed with average total peak areas vs. concentration. The results are presented in Table 4-7 and Figure 4-5. A linear calibration curve was obtained. The RSDs for triplicate measurements were from 6.5 to 19.3%.

Table 4-7: Measurements of Total PCBs by GC × GC – TOF-MS

Concentration of total PCBs (Aroclor 1254 in hexane), μg/mL	Average peak area for triplicate measurements	RSDs for triplicate measurements (%)
10	26162626	11.5
50	157328201	6.5
100	303187886	19.3
200	592937979	4.7

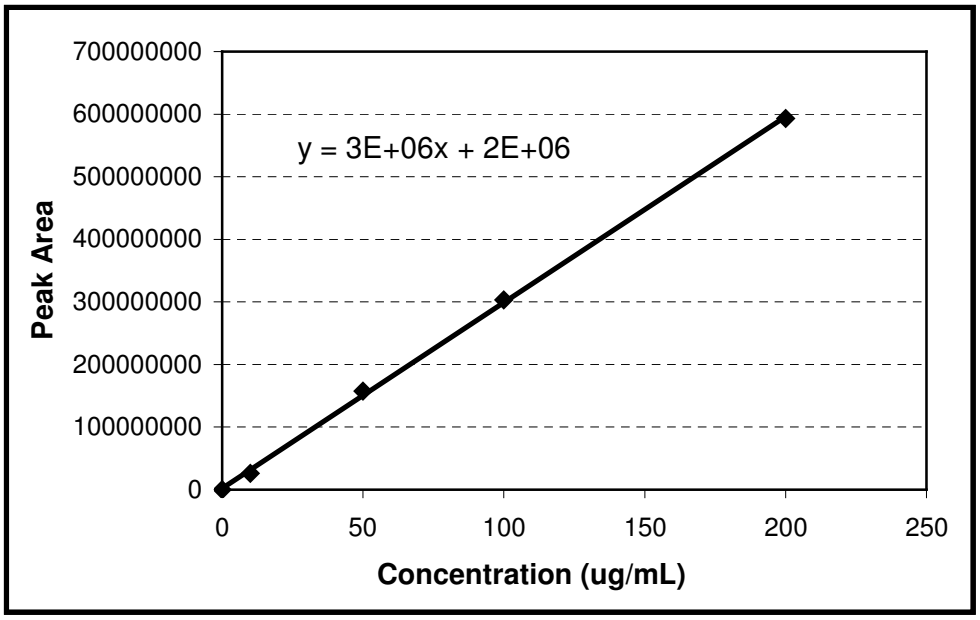
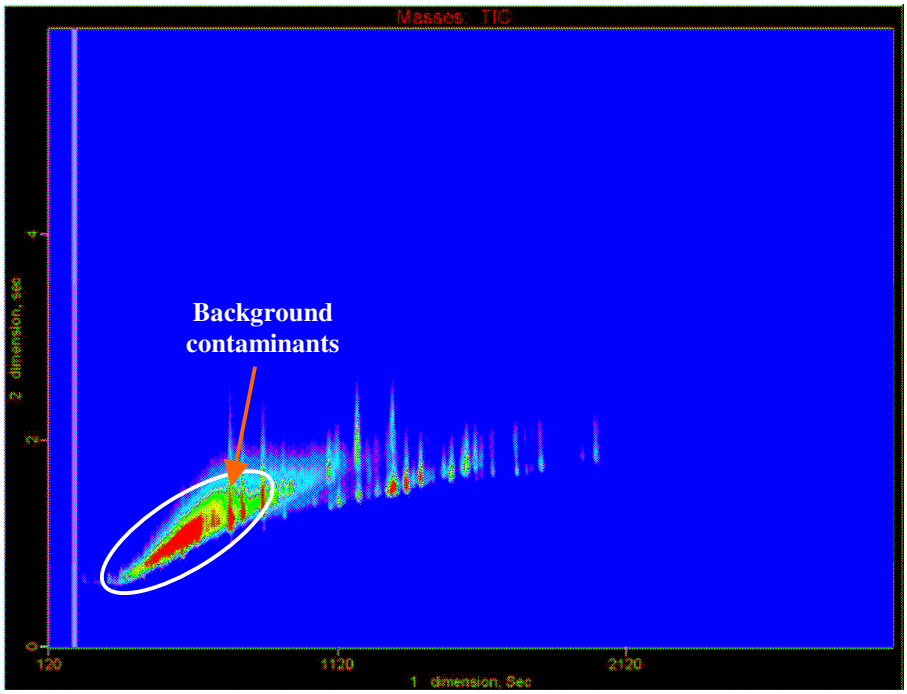


Figure 4-5: Calibration curve for the total PCBs measurement by GC × GC – TOF-MS

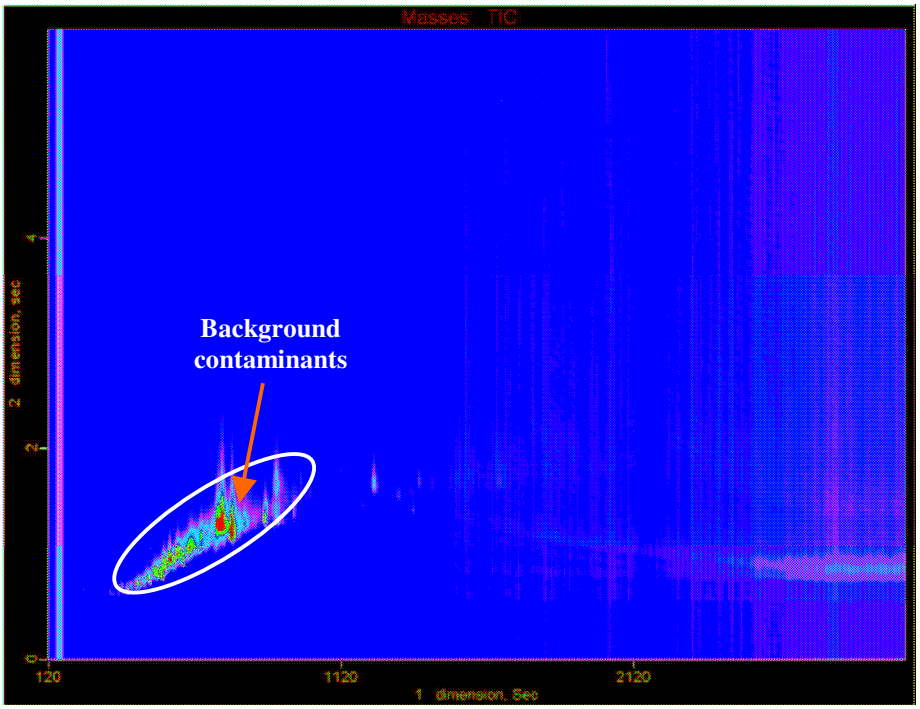
4.3.2 Analysis of PCBs in Environmental Soil Samples

PCBs in the environmental soil samples were analyzed using the GC × GC – TOF-MS method. One microliter aliquots of the extracts of soil samples S677-04, #46, ML

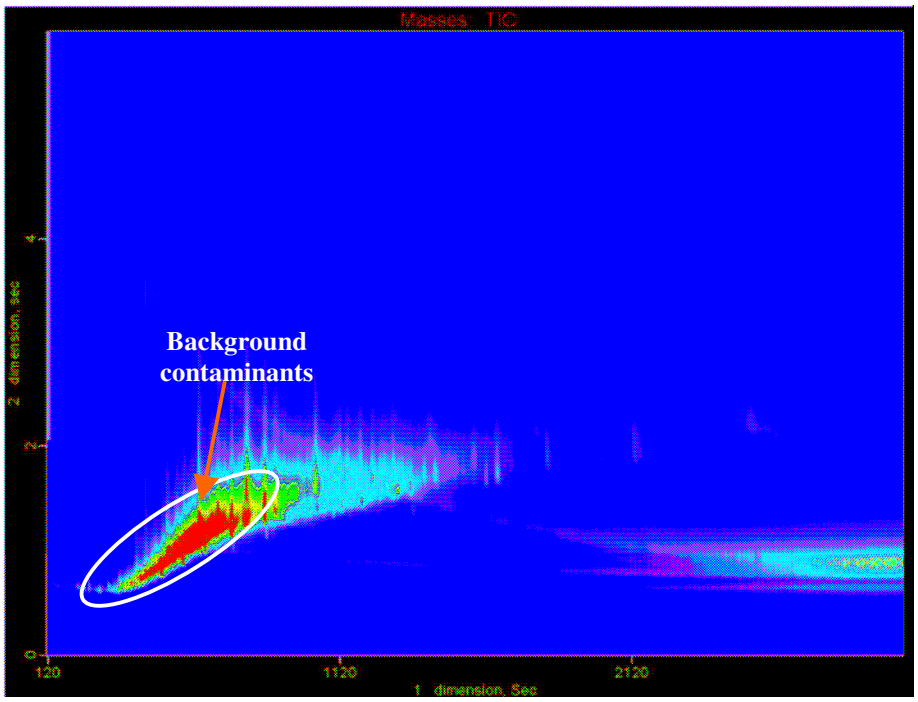
Profile 4 Red Kai and BH 18-1 were injected and analyzed under the selected GC and MS conditions. Analyses of each sample extract were repeated three times. GC × GC chromatograms from each sample extract were analyzed to investigate if any of the 12 target PCB congeners could be identified in the soil samples. During this process, the retention times and mass spectra of the PCB congener peaks were the factors considered. GC × GC chromatograms for the analysis of the 4 environmental soil sample extracts are presented in Figure 4-6.



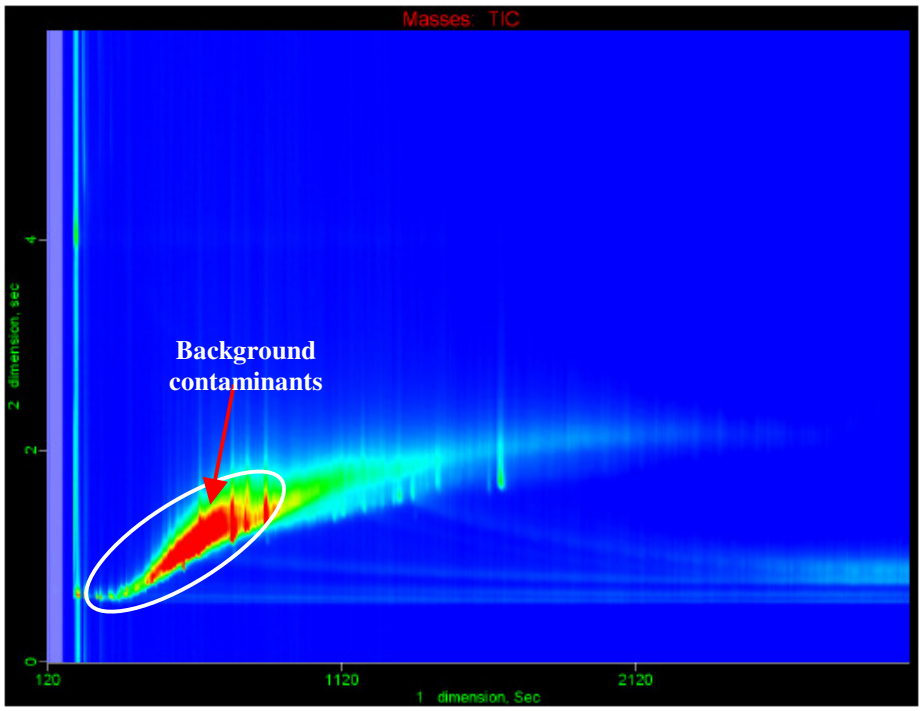
(a) Soil sample BH 18-1



(b) Soil sample S677-04



(c) Soil sample #46



(d) Soil sample ML Profile 4 Red Kai

Figure 4-6: GC × GC chromatograms for the analysis of 4 environmental soil sample extracts

Individual peaks in the GC × GC chromatograms were analyzed one by one by comparison of the retention times and mass spectra to those of the 12 target PCB congeners. The results showed that no peak in all the chromatograms matched those of the 12 PCB congeners, indicating that no target PCB congeners were present in the samples, or that their concentrations were too low in the soil samples to be detected. However, PCBs other than the target congeners were detected in soil sample BH 18-1, #46, ML Profile 4 Red Kai, with their mass spectra closely matching those from Aroclor 1254. PCBs were not detected in soil sample S677-04, most likely due to their low concentration in the sample. The chromatograms also revealed high background contamination in all four soil samples.

Peak areas of the individual PCBs in the chromatograms were then added up to get the peak area of total PCBs. Concentrations of total PCBs in the sample extracts were calculated according to the calibration curve of total PCBs measurement in Aroclor 1254 (Figure 4-5), and the concentration of total PCBs in the soil samples were thus obtained. The results of total PCB measurement for the environmental soil samples are presented in Table 4-8.

Table 4-8: Total PCBs in Environmental Soil Samples determined by GC×GC – TOF-MS

Soil sample	Identification of 12 target PCB congeners	Average total PCBs peak area for 3 measurements	Concentration of total PCBs in sample extract (μg/mL)	Concentration of total PCBs in soil sample (μg/g)	RSDs for triplicate total PCBs measurements (%)
BH 18-1	N/D*	250456566	82.9	2.76	6.4
S677-04	N/D	N/D	/	/	/
#46	N/D	75648568	24.5	0.82	3.2
ML Profile 4 Red Kai	N/D	41280170	13.1	0.44	0.4

* Not detected

Total PCBs in environmental soil sample BH 18-1, #46, and ML Profile 4 Red Kai as measured by GC×GC-TOF MS were 2.76, 0.82, and 0.44 μg/g respectively, with RSDs of triplicate measurements in the range of 0.4 to 6.4%. The comparison of the total PCBs measurement results for the thermal desorption/GC method and Soxhlet extraction/GC × GC – TOF-MS method is presented in Table 4-9. Thermal desorption/GC method gave a 0.01 μg/g total PCBs detection result for soil sample S677-04, while the GC × GC – TOF-MS method was not able to detect total PCBs in the same sample. Therefore, the thermal desorption/GC method provided a more sensitive detection of total PCBs. The reproducibility of repeat measurements was better with the GC × GC – TOF-MS method, likely because the extracts of the soil samples provided

better homogeneity for sample introduction than that of direct thermal desorption of only an aliquot of the soil sample. The percent differences of total PCBs measurements between the two methods were in the range of 18.6 to 90.3%. Considering the completely different character of the two methods, one being geared towards rapid field screening, the other used normally to provide detailed characterization of the samples, the agreement between the two methods can be considered excellent.

Table 4-9: Comparison of Total PCBs Measurement Results between the Thermal Desorption/GC Method and Soxhelet Extraction/ GC × GC – TOF-MS method

Soil sample	Concentration of total PCBs in soil (μg/g)			RSDs for repeat measurement in time	
	Thermal desorption/ GC method*	Soxhelet Extraction/GC × GC – TOF-MS method	% Difference	Thermal desorption/ GC method	Soxhelet Extraction/ GC × GC – TOF-MS method
BH 18-1	1.76	2.76	44.2	9.4	6.4
S677-04	0.01	Not detected	/	9.5	/
#46	0.31	0.82	90.3	11.7	3.2
ML Profile 4 Red Kai	0.53	0.44	18.6	7.9	0.6

* Results from single standard addition procedure

4.4 Conclusions

After total PCBs in environmental soil samples were determined using the thermal desorption/GC method, PCB contents in the environmental soil samples were further characterized in the laboratory using a Soxhlet extraction/ GC × GC – TOF-MS method. Soil samples were extracted in hexane for 24 hours using a Soxhlet extraction apparatus. The GC × GC – TOF-MS was set up with a polar column in the first dimension and a liquid crystal-stationary phase column in the second dimension. A heater-based modulator was applied. Based on the conditions determined in previous studies, optimization of PCB congener separation was obtained using a GC oven temperature

program with a 2 °C/min ramp from 210 to 290 °C. Under the selected operating conditions, the analysis time for the method was 51 minutes.

Using the selected GC × GC – TOF-MS conditions, the 12 target PCB congener standards were analyzed to obtain retention times (both 1^{st} and 2^{nd} dimension) and mass spectra for each target PCB congener. Identification of target PCB congeners in the sample was performed by comparing retention times and mass spectra of the peaks to those of the target PCB congener standards. Linear calibration curves for the measurement of 12 target PCB congeners were established using the congener standards. Method detection limits for the 12 target PCB congeners were found to be in the range of about 0.5 to 2.4 μg/mL. A linear calibration curve for total PCBs measurement was established using Aroclor 1254 in hexane standards. Determination of total PCBs was performed by adding up individual PCB congener peak areas from the GC × GC chromatogram.

The standard of Aroclor 1254 in hexane and extracts of 4 environmental soil samples were tested to identify target PCB congeners. PCB 156 and 167 were found in a 100 μg/mL Aroclor 1254 standard at concentrations of 3.9 and 1.7 μg/mL, respectively. No target PCB congeners were detected in the 4 environmental soil samples. The results of total PCB determination in soil samples with the GC × GC – TOF-MS method were compared to the results from thermal desorption. The thermal desorption/GC with DELCD detection proved to be more sensitive than the GC × GC – TOF-MS for total PCBs measurement. In general, the agreement between the two methods could be considered excellent. The Soxhlet extraction/GC × GC – TOF-MS method provided a

qualitative and quantitative analysis of both PCB congeners and total PCBs that could be used to further characterize and verify the analysis result from the field method.

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