Comparison of Ion Mobility Spectrometry and Gas Chromatography with Dry Electrolytic Conductivity Detection for the Determination of Polychlorinated Biphenyls in Humus-Rich Soil

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

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Abstract

Ion mobility spectroscopy (IMS) has been showen to provide fast on-site analysis of coarse sandy soil for the determination of polychlorinated biphenyls (PCBs). However the presence of humus results in instrument foaling and extensive down time do to instrument clean-up. For this reason a method was investigated for the ultrasonic extraction of PCBs from humus-rich soil that could be used at remote locations. Analysis of the extracted PCBs was conducted using 1) IMS and 2) gas chromatogram equipped with a dry electolytic conductiviy detector (GC/DELCD).

The research conducted for this thesis outlines the method development and analysis of PCBS using these two instruments. The IMS analyiss was found to be complicated by co-extracted matrix compounds. Results and limitations of IMS analysisare present here. The method development and validation of a method for the ultrasonic extraction and analysis of PCBs using the GC/DELCD is provided.

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I would like to dedicate this thesis to my family. To my husband Tom, for his patience and fortitude in dealing with the many ups and downs of research. Your constant support and understanding has helped me throught the many dark days of research when the end was so far way. To my two children Brittany and Matthew, who helped keep my spirits high and a smile on my face. Without the three of you I would have not seen this project to completion and obtained my Masters degree.

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1 Introduction

1.1 History

Despite the fact that polychlorinated biphenyls (PCBs) have not been commercially produced for the past three decades, they still persist in the environment. Industrial production of PCBs commenced in 1929 in the US by treating biphenyl with chlorine. Concerns about human toxicity due to PCB contamination and the persistence of PCBs in the environment resulted in the need to clean up the existing PCB-contaminated sites. In Canada, one area of PCB contamination is in the near north, along the DEW Line (Distant Early Warning Line) sites. The remoteness of these sites results in difficulties with the analysis of PCBs in soil.

Traditionally, two methods of analysis have been used for the on-site determination of PCBs in soil. One method is laboratory analysis based on solvent extraction of the soil followed by GC/ECD or GC/MS analysis [2,3,7,11] . This method is time consuming, as samples must be shipped from the site to a laboratory, extracted, and analyzed. Results are usually available after two to three days from the time of sampling at the earliest; what is more, such "short" turn-around times are only available through payment of an analytical surcharge. With the second method, quicker results can be obtained in the field using enzyme kits. These kits provide results on-site in approximately thirty minutes; however, the results are only semi-quantitative at best, and the cost of the consumables is considerable. Enzyme kits also face interference problems arising from the presence of inorganic chlorides, chlorinated hydrocarbons and solvents in the sample matrix. Consequently, they are not favored for field analysis [3,8].

The need for a reliable on-site method to analyze PCBs remains important as the clean-up of military sites (dating back to the 1940s) is an ongoing concern in many countries. This thesis has investigated 2 techniques for the analysis of PCBs in various types of soils. The first analytical technique involved the use of Ion Mobility Spectroscopy (IMS). The British and U.S. military have used IMS for the analysis of explosives in soils. Previous work [23,24] has been conducted for on-site field analysis of PCBs in coarse sandy soil. The IMS analysis of PCBs in coarse sandy soil addressed the need for a fast, accurate field method for PCBs with sample preparation and analysis times of fifteen minutes or less.

In this previous work, the IMS appeared to be able to differentiate the PCBs from solvents and other hydrocarbons present in the soil. The analysis of PCBs in coarse sandy soil was valid over the range from 0.1 to 10 ppm (w/w) of PCB. Method precision ranged from 34% RSD at the limit of detection (0.1 ppm) to 11% and 15% at 10 and 25 ppm, respectively.[23,24] In a comparison study, concentrations measured with IMS generally exceed reported certified laboratory concentrations, most likely due to the fact that IMS reports concentrations relative to only the fine grain material comprising the desorbed sample. The analysis of PCBs from coarse sand has a total on-site sample preparation time of fifteen minutes, and an analysis time of about ten minutes. Therefore, IMS would be able to provide detailed site assessments for PCBs faster and at lower cost than other available screening technologies.

The advantages of IMS are that it is simple, fast, highly selective, and very sensitive to a wide range of compounds. The durability of IMS during travel and the fact that it ionizes analytes in ambient air at atmospheric pressure makes it seemingly an ideal detector for contaminants in remote locations. However, IMS does have inherent limitations. These

include memory effects, non-linear response, and problems with reproducibility. In addition, ion-molecule mechanisms are not fully understood for complex matrices, and no library exists for compound identification. Some of these limitations have been encountered during the development of the method for the analysis of PCBs in sand described above. The dynamic range of the method spanned only two orders of magnitude in concentration, due to problems with detector overloading at higher concentrations and poor reproducibility at lower concentrations. Furthermore, when soil samples contained humic material or marine material, as found in forested or sediment samples, the combustion products of the organic matrix masked the mobility spectra for PCBs. Currently; the IMS method is only useful for soils that approximate coarse sand with little organic content due to vegetation matter, as found in the far northern areas of Canada.

The second method to be investigated in this thesis involved the use of a field portable gas chromatograph (GC) equipped with a dry electrolytic conductivity detector (DELCD). The field portable GC has a self-contained ambient air compressor with moisture trap to provide constant flow of air as carrier or make-up gas. This eliminates the need to ship compressed air to remote locations. The GC analysis of PCBs has been well documented. By applying the principles of fast GC with information from literature sources, the analytical separation time can be reduced to allow rapid analysis with detection by DELCD. The chromatographic separation was designed to provide analysis for the range of PCB congeners as total PCBs.[31]

The DELCD is a specialized detector for the determination of halides. As compounds elute from the GC column, they are oxidized in the DELCD reaction chamber at high

temperature to form H_2O, CO_2, as well as ionized halides, such as Cl^- or Br^-. The detector measures the gas phase conductivity due to the presence of these ions. The conductivity in the gas phase is proportional to the halide concentrations. Thus, the detector can be used to quantify organohalogens in a sample.[31]

The goal of this thesis was to develop an on-site method for the rapid determination of PCBs by either IMS or GC/DELCD. The research conducted in this thesis will show that even though IMS is capable of ion separation, it is not a viable technique for the analysis of PCBs in extracted soil samples. The alternative method based on GC/ DELCD did allow for the determination of PCBs using a field portable GC. The extraction developed for this method was based on information from literature sources.[2,7] Despite the potential for co-extraction of humic and fulvic acids from the soil, the GC/ DELCD did not require extensive sample clean-up prior to analysis.

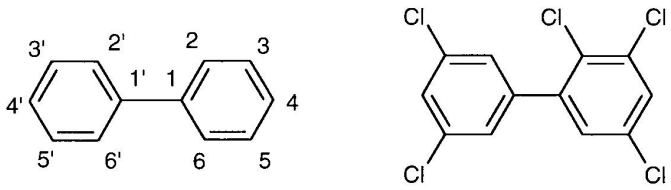
1.2 Polychlorinated Biphenyls

1.2.1 Introduction

Polychlorinated biphenyls (PCBs) do not occur naturally. The industrial production of PCBs began in United States in 1929 by direct chlorination of biphenyl with chlorine gas. This process is not highly selective resulting in a complex mixture of PCB isomers. This synthesis forms a mixture of 209 discrete chemicals, PCB isomers called congeners, whose composition depends on the proportion of chlorine and biphenyl (Figure1.1). PCBs are categorized into ten PCB congener groups (referred to as homologs) based on the number of chlorine atoms attached to the biphenyl (see Table 1.1).

Figure 1.1: Basic polychlorinated biphenyl showing; a) possible chlorine attachment locations and b) an example of a pentachlorinated biphenyl (2,3,5,3',5'-pentachloro-biphenyl) [2]

a) ***b)***



These groups differ in the number and position of chlorine atoms attached to the biphenyl molecule: mono-, di-, tri-, and up to decachlorinated biphenyl. The term PCB refers to the entire class or any subset of 1 or more of these compounds [2].

Table 1.1: Distribution of PCBs by level of chlorination.

Homolog	Molecular Formula	Number of Isomers
Monochlorobiphenyl	$C_{12}H_9Cl$	3
Dichlorobiphenyl	$C_{12}H_8Cl_2$	12
Trichlorobiphenyl	$C_{12}H_7Cl_3$	24
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	42
Pentachlorobiphenyl	$C_{12}H_5Cl_5$	46
Hexachlorobiphenyl	$C_{12}H_4Cl_6$	42
Hetachlorobiphenyl	$C_{12}H_3Cl_7$	24
Octachlorobiphenyl	$C_{12}H_2Cl_8$	12
Nonachlorobiphenyl	$C_{12}H_1Cl_9$	3
Decachlorobiphenyl	$C_{12}Cl_{10}$	1

Monsanto commercially sold PCBs under the trade name "Aroclor", followed by a four number designation in which the first two digits indicated that the PCB is based on biphenyl, and the last two digits referred to the percentage of chlorine in the product. For example, in the case of Aroclor 1260, the first two digits (12) stood for chlorinated biphenyl, and the number "60" indicated 60% weight/weight of chlorine. Aroclors were complicated mixtures containing many different individual PCB congeners. Mixtures with low chlorine content, such as Aroclor 1216, were clear oils with low viscosity, while mixtures with higher chlorine content ranged from viscous, yellow resins to waxy white

solids. PCBs were manufactured under different trade names by various companies. Examples include Chlophen manufactured by Bayer in Germany, Phenochlor and Pyralene manufactured by Caffaro in Italy, Kanechlor manufactured by Kanegafuch in Japan, and Fenchlor manufactured by Prodelec in France [2].

1.2.2 Physical Properties

The physical properties of PCBs are integral to the understanding of their analytical properties and how they interact in the environment. Since PCBs occur as complex mixtures of congeners, their physical properties are dependent on the composition of the mixture. Physical properties vary widely within a homolog group, as the location and arrangement of chlorine atoms contribute to the properties of the PCB. Properties also vary depending on the degree of chlorination of the biphenyl molecule. For example, 3,4-dichlorobiphenyl has a boiling point of 195 to 200°C, while the boiling point of 4,4'-dichlorobiphenyl is over 100 degrees higher (315-319°C) due to the position of the chlorine atoms on the biphenyl [2]. In general, boiling and melting points and octanol-water partition coefficients (log $K_{o/w}$) increase as the degree of chlorination increases, despite the wide variation in values resulting from chlorine substitution positions. As can be seen from the log $K_{o/w}$ values given in Table 1.2, PCBs are extremely lipophillic. The low aqueous solubility and the low vapour pressure of PCBs determine the transport and fate of PCBs in the environment.

Table 1.2: Selected physical properties of PCBs [2]

Homolog	# Chlorine Atoms	Boiling Point (°C) at 750 mm Hg[a]	Vapour Pressure (mm Hg, 25°C)	Melting Point (°C)	Partition Coefficient Log $K_{o/w}$
Biphenyl	0	255	9.5×10^{-3}	71	4.10
Monochlorobiphenyl	1	274 - 291	$1.5 \times 10^{-3} – 8.4 \times 10^{-3}$	16.5 –77.7	4.56 – 4.72
Dichlorobiphenyl	2	315-324	$1.9 \times 10^{-5} – 1.8 \times 10^{-3}$	22 –149[b]	5.02 – 5.34
Trichlorobiphenyl	3	nd	$9 \times 10^{-5} – 3.0 \times 10^{-4}$	28.1 –102	5.64 – 6.1
Tetrachlorobiphenyl	4	nd	$2.3 \times 10^{-6} – 8.8 \times 10^{-4}$	41 – 198	5.94 – 6.67
Pentachlorobiphenyl	5	nd	$5.8 \times 10^{-7} – 2.1 \times 10^{-5}$	81 – 123	6.38 – 7.51
Hexachlorobiphenyl	6	nd	$1.6 \times 10^{-6} – 1.3 \times 10^{-5}$	69.5 –202[b]	7.12 – 8.26
Hetachlorobiphenyl	7	nd	$6.3 \times 10^{-7} – 2.3 \times 10^{-6}$	109 –163	7.93
Octachlorobiphenyl	8	nd	nd	132 –161	8.42 –8.68
Nonachlorobiphenyl	9	nd	nd	204.5 –206.5[c]	9.14
Decachlorobiphenyl	10	nd	nd	nd	9.60

a: data could be found for only a limited number of congeners at ambient pressure.
b: some congeners in this homolog exist as oil at ambient temperature and pressure not a soil.
c: data found for only 1 congener
nd: no data found

1.2.3 Industrial Synthesis and Uses

Industrial production of PCBs was controlled by controlling the reaction conditions during the chlorination of biphenyl with chlorine gas [2]. By varying reaction conditions products could be made with varying amounts of chlorination and therefore different physical properties. Table 1.3 illustrates the various mixtures (degree of chlorination and weight percent of chlorine in the mixture) of homologs in some Aroclor products commonly used in North America. Table 1.4 provides physical properties of these Aroclors.

Table 1.3: Average molecular composition (wt %) of some common Aroclors [2]

Homolog Series # Chlorine atoms	1242	1248	1254	1260
1	1			
2	12	1		
3	45	2	1	
4	31	49	15	
5	10	27	53	12
6		2	26	42
7			4	38
8				7
9				1

Table 1.4: Physical properties of some common Aroclors [2]

Arolcor	Wt % Chlorine	Viscosity (Saybolt) at 98.9 °C	Flash Point (°C)	Distillation Range (°C)	Dielectric Constant		Water Solubility (µg/L) at 25 °C
					At 20°C	At 100 °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	nf	365 - 390	5.0	4.3	12
1260	60	72 - 78	nf	385 - 420	4.3	3.7	3

nf: no flash point

Total worldwide production of PCBs at the end of 1976 was estimated to be 6.1 x 10^8 Kg. Monsanto, US, accounted for approximately 93% of total world production of PCBs [2]. Although the Aroclor trade name is associated with polychlorinated biphenyls, it was also used for other polychlorinated polyphenyls such as Aroclor 5460, a complex mixture of polychlorinated terphenyls containing 60% chlorine by weight. In this text, the term Aroclor is used to refer only to mixtures containing biphenyl.

Table 1.4 provides the physical properties of some common Aroclors. The unusual chemical stability and electrical resistance of PCBs, together with their low volatility and resistance to degradation at high temperatures, made them ideal for use in a wide range of industrial applications, especially during the 1940s and 1950s [2]. These included uses as dielectric fluids in capacitors and transformers, hydraulic fluids in mining equipment, heat transfer and vacuum pump fluids (these were the so-called closed uses), plasticizers, flame retardants, and additives in cement, paints, casting agents, lubricating and cutting oils, and in copying paper, carbonless copy paper and printing inks. [2,5,6,7]

The use of PCBs fell into 3 categories: controllable closed systems, uncontrollable closed systems and dissipative uses [2]. Controllable closed systems included machinery that had

the same expected lifetime as the PCBs. These included electrical transformers and large capacitors that have been properly designed not to leak. When this type of equipment is removed from service, the large quantities of PCBs are drained and safely disposed of. Uncontrollable closed systems use PCBs as heat transfer and hydraulic fluids that permit leakage. In these systems small quantities of fluids are constantly being replaced making recovery impractical. PCBs have also been used in small capacitors. These capacitors are difficult to collect for disposal resulting in the widely dispersed sources of PCBs. When PCBs are used in lubricating or cutting oils, as plasticizers in paints, adhesives, sealants or plastics, etc. they come in direct contact with the environment through a number of different routes. There is no way of recovering the PCBs from these dissipative sources when the product is scrapped. The major source of concern for PCBs in the environment is 1) large quantities of contamination due to leakage from large transformers, capacitors or from metal drums that have been stored or disposed of in either registered or illegal landfills and 2) from accidental industrial spills.[2]

1.2.4 Environmental Concerns

Due to their inherent stability, PCBs have proven to be extremely persistent in the environment, despite restrictions on their use over the past three decades. Concerns over the persistence of PCBs resulted in protests against their release into the environment during the 1970s. The production of PCBs ceased in most countries by the end of the 1970s [2].

Since production began, large quantities of PCBs have made their way into landfills. Unfortunately, PCBs are very slow to degrade, and do not necessarily stay where they have been put. The significant vapour pressure of low molecular weight PCBs (less than

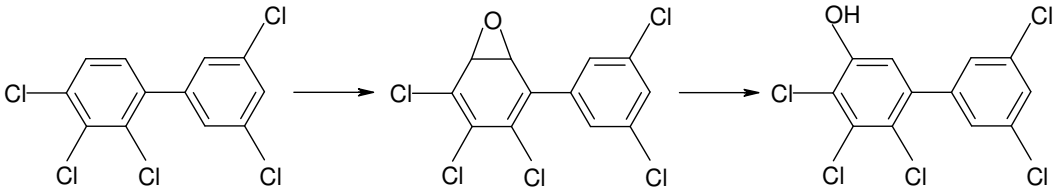
penta-CB) at ambient temperatures provides a mechanism for the remobilization of low molecular weight PCBs into the air from soil and water [4,5,9]. Rain or snow then redeposit these compounds elsewhere. This is one pathway that accounts for the detection of PCBs in Arctic and Antarctic samples from remote sites. The redistribution of the individual congeners with varying volatilization and degradation rates explains the differences in composition of PCBs extracted from environmental samples compared to the commercial products [2,7].

Polychlorinated biphenyls are lipophilic and persistent in the environment, and therefore bioaccumulate. They are found in nearly all marine plant and animal specimens, including fish, birds (especially fish eating), bird eggs and mammals [2], with body accumulation occurring in fatty tissue with long term exposure. Distribution of PCBs throughout body tissue occurs as follows: adipose tissue contains higher concentrations of PCBs than skin, which is higher than liver, then muscle, and finally blood. Such distribution is determined by the fact that concentrations are dependent on the lipid content of the tissue [2,7]. Polychlorinated biphenyls magnify through the food chain. A concentration factor of nearly 10^8 was observed between Lake Ontario water concentration and Herring gulls feeding on fish from the lake [4]. The 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 of the world where their production never occurred. Deposition in these areas occurs from air by rain or snow, by dry fallout, and vapour phase deposition [2].

In higher organisms, the initial metabolites of PCBs result from hydrolysis of the PCB to mono- and dihydroxychlorobiphenyls. These metabolites are more water-soluble than the

initial PCBs and are excreted in the urine. A secondary reaction may occur to form the glucuronide conjugate, which is even more water-soluble. This hydrolysis reaction, and therefore also the subsequent conjugation, can only take place for PCBs that have 2 adjacent unsubstituted carbons on the biphenyl ring, as indicated in Figure 1.2.

Figure 1.2: Biotransformation mechanism of PCBs in higher organisms via hydrolysis to allow excretion as mono-hydroxychlorobiphenyl [6]



The acute toxicity of PCBs is low; however, since they bioaccumulate, chronic toxicity is a concern. Chronic toxicity of PCBs is dependent on the degree of chlorination and the isomer. PCBs that have only meta- and para- substitutions can assume a planar configuration, which can interact with biological receptors [2,6]. The congeners of specific concern are 3,3',4,4'-tetrachlorobiphenyl, 3,3',4,4',5-pentachlorobiphenyl and 3,3',4,4'5,5'-hexachlorobiphenyl. These are highly toxic dioxin-like molecular configurations that can form covalent bonds with DNA resulting in alteration of the DNA function [2].

A low rate of reproduction due to PCB-induced damage to the female reproductive system was observed in many marine birds and mammals. Most human studies were concerned with cancer resulting from occupational exposure in men. Concerns about exposure to PCBs in the general human population occur mostly due to eating of contaminated foods, such as fish, dairy and meat. The effect of subchronic PCB exposure

from these sources on human reproductive and learning impairments has not been fully addressed [2].

1.2.5 Removal and Regulatory Guidelines for PCBs

As PCBs are very stable, they are difficult to degrade. Under certain conditions, PCBs may be decomposed chemically, thermally, or by biochemical processes. Intentional destruction of PCBs requires high heat or the use of catalysts. The most cost-effective means of intentional destruction of PCBs is incineration utilizing high heat (~1200°C), long residence times (>2 sec), mixing using rotary kilns to mix and move solids through the heated zone, and systems to control emission of pollutants [2]. Environmental degradation occurs primarily by photolysis. The half-life for photodegradation of PCBs is dependent on the degree of chlorination of the compound, with mono-PCB having a half-life between 0.62 and 1.4 days, while that of penta-PCB is 67 days. Photodegradation occurs more rapidly for PCBs in the vapour phase [2].

Microbial degradation of PCBs is dependent on both the degree of chlorination of the compound and the position of the chlorine substitution. Lower molecular weight PCBs (i.e. less than penta-CBs) are more readily biotransformed than higher chlorinated PCBs, while PCBs with an ortho-substituted chlorine degrade more slowly than PCBs with meta- and para-positioned chlorine atoms [2].

Cleanup of contaminated sites has begun over the past five years and various methods have been used to remove PCBs from the soil. Limited degradation of PCBs in soil has been carried out using fungi and microorganisms to deal with low-level concentrations [5]. However, high concentrations in soil (>50ppm) must be thermally destroyed in specially

designed furnaces to prevent by-products of combustion from being released into the atmosphere. The Canadian Environmental Quality Guidelines (CEQG)[1] for total PCBs in soil provide limits of 0.5 ppm (mg/kg) for agricultural use, 1.3 ppm for residential and parkland use, and 33 ppm for commercial and industrial use.

1.3 Ion Mobility Spectrometry

1.3.1 History of IMS

Modern IMS was developed by Dr. Frank W. Karasek at the University of Waterloo in the late 1960s and trademarked as Plasma Chromatography [10,16]. The Smiths Detection Inc. (formerly Barringer Instrument Corp.) purchased the rights to IMS in the 1970s. The benefits of a simple, fast, highly selective and very sensitive detection method applicable to a wide range of compounds allowed Smiths Detection to market this instrument for the detection of organic compounds in air. Despite these benefits, the growth of IMS in the 1970s and 1980s slowed down due to unmet expectations and misunderstanding of the response characteristics. Since the 1980s, interest in IMS was re-established as a result of military interest in the US and UK [10,11]. The military found IMS useful for the identification of explosives in soil. This aided in the location and disposal of undetonated landmines in military zones. Further uses of the IMS technology have been developed for airport surveillance of passengers for narcotics and explosives.

Advances in IMS instrumentation and better understanding of the ion-molecule chemistry in air at atmospheric pressure rekindled IMS in the 1980s and gave it a unique niche in analytical chemistry [10]. However, the use of IMS as a quantitative analytical tool has yet to be fully developed.

1.3.2 IMS Instrumentation

The instrument to be used for this project is the Smiths Detection IonScan model 350. Figure 1.3 shows a cutaway of the IonScan (the terms IMS and IonScan are used interchangably in this thesis). It consists of a sample carriage or platform, thermal desorption anvil, sample inlet, ionization source and chamber, sample grid, drift tube and detector plate. Samples are sealed in the IMS sample inlet and thermally desorbed at a predetermined temperature to volatilize analytes. The vapour is carried to the ionization chamber, where the analyte is ionized using a ^{63}Ni source. This creates negative ions with a –1 charge. Electronic gates (ion shutter and guard grid) control the flow of ions to the collector. When open, the ions drift toward the positively charged collector against a countercurrent drift flow of uncharged ambient air. The drift time for analytes against this current has been empirically determined, and is characteristic for particular ions. The analyte ions are collected at the positive plate. The electronic signal from the collector is proportional to the concentration of the analyte ions in the sample. By comparing the sample signal to the signal from standard soil preparations of known concentration, the concentration of analytes in the soil may be calculated. A schematic of this process is illustrated in Figure 1.4.

Figure 1.3: Cutaway of IonScan drift tube with sample, desorption anvil and detector [13]

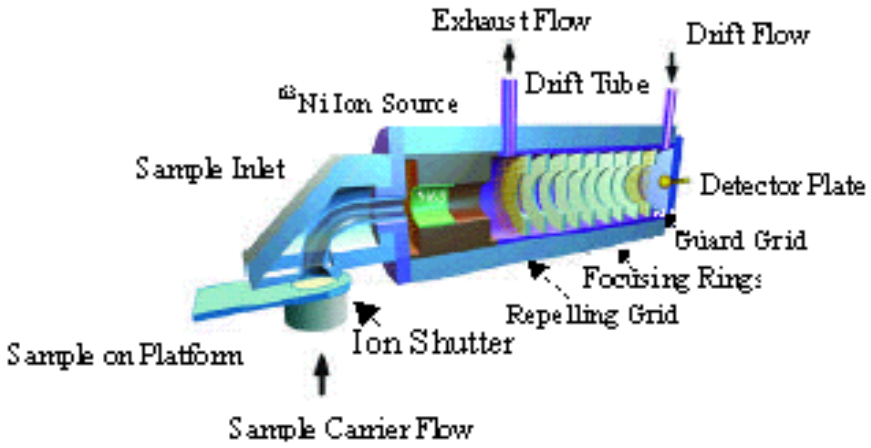
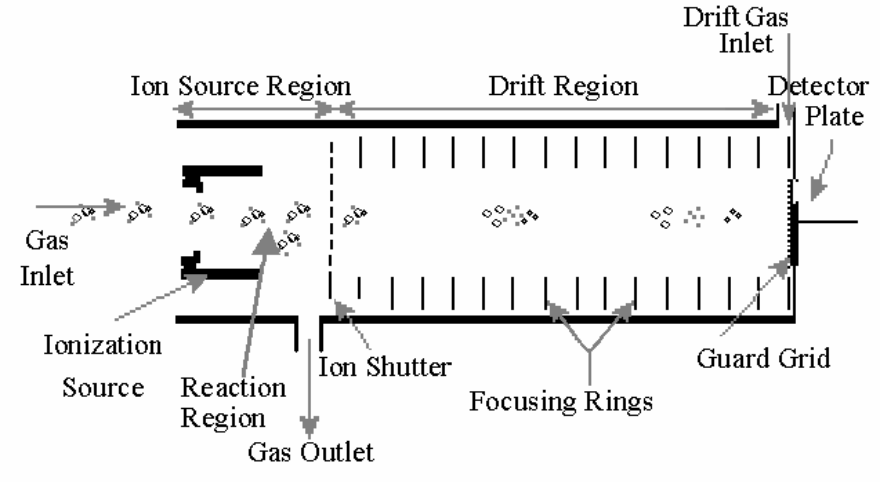


Figure 1.4: Passage of ions through the IonScan drift tube [12]



1.3.3 IMS Theory

Once formed, the ions pass into the drift tube through an ion shutter. Ions move forward through the drift tube in a gas under the influence of an electric field. Different forces act upon the ions, including resistance encountered by the drift gas molecules, collisions with other molecules and drift tube walls, and electrostatic forces [3,16,21,22,25-27].

The electric field propels the ions toward the detector with an average velocity proportional to its magnitude. Ions striking a flat plate detector provide a mobility spectrum, which is plotted as detector current (A) vs. drift time, t_d, (s). Analyte selectivity is based on the differences in drift times for different compound ions.

The drift time, t_d (s), is characteristic for the analyte ion in a given electric field E (V/cm) with a drift tube of length L (cm). It is related to the velocity, v_d (cm/s) of the analyte ion by:

Equation 1.1: $v_d = L / t_d$

The velocity (from equation 1) is related to the mobility of the ion through the proportionality constant K ($cm^2/V*s$), where:

Equation 1.2: $K = v_d / E$

Movement of ions in the IMS is complicated by the presence of a counter-current gas flow (drift flow). The ion is accelerated by the electric field until it collide with a gas molecule. This collision causes the ion to lose part or all of its forward momentum. The electric field then accelerates the ion once again until the next collision occurs. Therefore, increasing the electric field will increase the ion velocity, but increasing the drift flow will reduce the ion velocity by increasing the number of collisions and thereby reducing the kinetic energy of the ion as a result of these collisions.

Drift times are also dependent on the temperature and pressure in the IMS system. Ion mobility can only be compared between analytes by normalizing it to a reduced mobility, K_0. The reduced mobility converts the measured mobility to a common base temperature, pressure and electric field. This provides the best parameter for plotting mobility spectra

and comparing data. Values of K_0 are specific for individual analytes and have been well established in the last 20 years; however, for most organic molecules, accurate prediction of K_0 is not possible.

There are many factors affecting the mobility of an ion. These include the ionic charge, size of the ion, molecular mass, and polarizability of the drift gases [17]. Ion separation in IMS is based on the size-to-charge ratio, whereas in MS, separation occurs based on the mass-to-charge ratio [10]. Consequently, ion size is an important parameter for determining theoretical mobility values. This value is difficult to establish, particularly if clustering occurs. As the focus of this research was applied, no attempts were made to determine theoretical mobilities for the analytes measured.

1.3.4 Principles of Atmospheric Pressure Chemical Ionization

The process of ionization and subsequent reactions that occur in IMS is termed atmospheric pressure chemical ionization (APCI) [10]. The ionization process starts with the emission of β-particles from ^{63}Ni. These particles are high-energy electrons that react with nitrogen to form positively charged nitrogen ions called reactant ions [19]. By collision with reactant ions, other molecules are ionized, producing positively or negatively charged ions. In purified air containing 1-10 ppm water, positively and negatively charged reactant ions occur simultaneously; they include NO^+, $H^+(H_2O)_n$, O_2^-, CO_3^-, CO_4^-, plus clusters with water to form species such as $(H_2O)_nO^-_2$ [3,19,20]. The reactant ions formed reflect the chemical composition of the gas supplied to the ionization region; therefore, it must be kept clean and consistent to allow for comparison of results.

The formation of product ions occurs in the ionization region by collisions of sample molecules with reactant ions to form positively and negatively charged molecular ions. These collisions cause little fragmentation and produce mainly M^+ and MH^+ in positive mode, and M^- and MO^-_2 during negative ionization. If a compound does not form an ion in the ion source, it will not be recognized as a peak in the mobility spectrum [10,16,17].

The large number density of ions and molecules and the low, near-thermal energies of these ions encourage the formation of ion-molecular clusters when reactant ions or multiple component samples are ionized. Ion-molecular clusters occur for both reactant and product ions, and their formation is dependent on temperature and vapour concentrations of the neutral species. In general, ion-molecular cluster formation is reduced when the ionization chamber temperature is set higher. Karasek [18] observed this ion-molecular cluster formation in his work using water as a reagent in the ion source.

Preston and Radjadhyax [19] suggested that ions and molecules associate and dissociate in a localized equilibrium on a fast scale in the drift region during transit between the ion shutter and the detector plate. This equilibrium can be described in the following way [10]:

Equation 1.3: $MH^+ + S \Leftrightarrow SMH^+$ or $MH^+ + M \Leftrightarrow M_2H^+$

where MH^+ is the product ion, S is a small polar molecule, SMH^+ is a cluster ion and M_2H^+ is a dimer ion.

The behaviour of polar or thermally unstable compounds, such as butylacetates, in the drift region was investigated in detail by Eiceman *et al.* [20]. In this work, ions were injected into the drift region intact. These ions were found to undergo fragmentation reactions while traveling through the drift region over a time period comparable to the

molecular ion drift times. These reactions were found to be irreversible as one fragment is accelerated forward by the drift current and the other is swept away with the drift gas. These frgamented ions manifested themselves as broad, unresolved, skewed peaks. Eiceman *et al.* [20] suggested that such fragmentation occurs by intermolecular rearrangements and is highly sensitive to temperature.

Investigations by Vandiver *et al.* [21] indicated that ^{63}Ni-induced ionization is governed by thermodynamic rather than kinetic mechanisms. Vandiver also concluded that determination of absolute rate constants was limited by uncertainties regarding recombination coefficients and total reactant ion densities; thus, only relative rate constants could be used to determine the rate of ionization and its mechanisms.

A major advantage of using ^{63}Ni source for IMS is the flexibility in adjusting the ion-molecule chemistry [22]. As ion species formation depends on the proton affinities of the neutral vapour species, the formation of the ions can be adjusted through the use of appropriate reactant ions. Molecules with a proton affinity below that of the reactant ions would not be detected, and therefore would be chemically transparent in the ion mobility spectra.

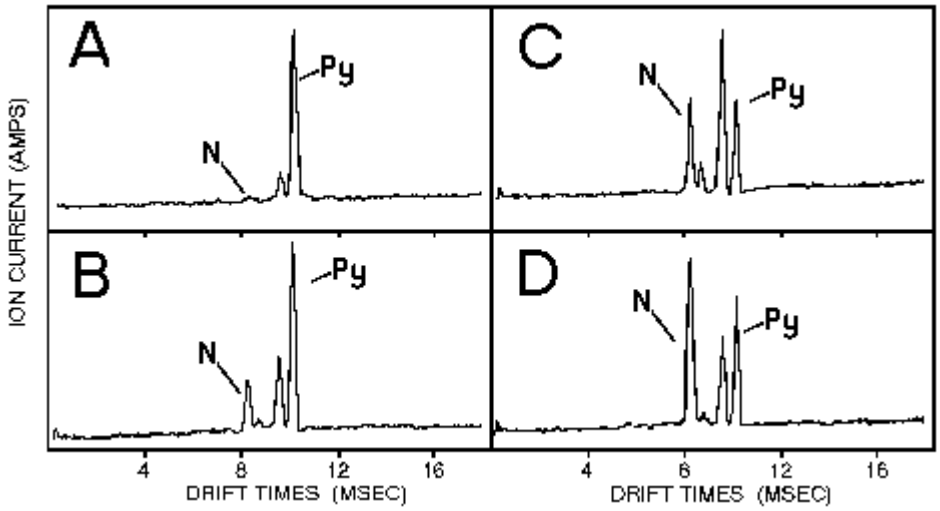
The effectiveness of IMS as a chemical analyzer is directly related to the ionization parameters of the target analyte. When the ionization parameters for target analytes are vastly different, the components can be selectively analyzed in the sample matrix. In mixtures where components have comparable ionization parameters, IMS has neither predictive nor interpretive properties. Vandiver *et al.* [21] showed the dramatic effect of proton affinities on the mobility spectra of binary and ternary mixtures. This is illustrated in Figure 1.5, where the proton affinities of naphthalene (196.3 kcal/mole) and pyrene

(208.5 kcal/mole) are compared to the proton affinity of the reactant ion ammonium (207 kcal/mole). It can be seen in Figure 1.5 that the increase in naphthalene concentration affects the peak height of pyrene owing to the closeness of the proton affinities. Despite the fact that the pyrene concentration was kept constant, the pyrene peak height decreased as the naphthalene concentration ratio was increased from 14,000:1 naphthalene to pyrene to 720,000:1 (Figure 1.5). In such cases, it is advisable to use pre-separation prior to the IMS analysis [14,15,28].

A serious limitation of the existing IMS database is the dependence of mobility spectra on temperature and concentration [10]. Temperature effects were initially considered to be irrelevant, as reduced mobility values were normalized for temperature. Mobility spectra at different IMS drift temperatures can also be complicated by the presence of different mixtures of ions in the ion source. As mobility analysis reflects these differences, failure to realize that clustering and fragmentation occurs in the IMS drift region can lead to flawed conclusions regarding the reproducibility of IMS.

When product ions are formed, the total ion charge in the chamber is conserved, thereby gradually reducing the total number of reactant ions [21]. Typically, 10^8 to 10^9 reactant ions are produced during ionization with a ^{63}Ni source. The neutral vapour density (i.e. gas phase concentration of molecules) has an effect on the mobility spectra. At low analyte concentrations, the reactant ion charge is consumed proportionally to the number density of the analyte in the sample vapour. As vapour level concentrations increase, the accumulation and decay of the vapour in the ion source result in severe overload and memory effects in the mobility spectra.

Figure 1.5: The effect of concentration on peak height with a binary mixture of polycyclic aromatic hydrocarbons. The proton affinities for naphthalene and pyrene are 196.3 and 208.5 kcal/mol, respectively, and are relative to proton affinity for ammonia (207 kcal/mol). Ratios of concentrations for naphthalene (N) to pyrene (Py): A) 14,000:1, B) 42,000:1, C) 91,000:1, and D) 720,000:1. [21]



1.4 Gas Chromatography

1.4.1 Introduction

Gas chromatography (GC) is an analytical technique for the separation of components of a mixture in the gas phase. The mixture can be introduced into the GC as either a liquid or a gas of known volume. Its components are separated based on partitioning of the gas phase molecules between the stationary phase of the column coating and the gas phase of the carrier gas.

A liquid sample is vapourized in the heated injector inlet of the GC. The vapourized components are then swept onto the head of the GC column by the carrier gas flow. As the molecules encounter the stationary phase of the column coating, molecules partition into the stationary phase to the extent dependent on their affinity to it. Molecules in the

gas phase are carried along the column length by the carrier gas. The selection of the GC stationary phase and physical dimensions of the column affect the degree to which the components in a mixture can be separated from each other. These parameters are chosen to optimize the separation of components. When the molecules reach the end of the GC column, they enter the detector where their presence is converted to an electrical signal. This signal is converted from analog to digital and displayed at a computer workstation or another recording device. The area under each component peak is computed and reported for purposes of quantitation of the components in the mixture.

1.4.2 Injectors

The purpose of the GC injector is to introduce a sample into the GC column. There are two basic types of split/splitless and direct on-column injectors. In the split/splitless injectors, the injector body contains a glass liner through which the carrier gas travels. A sample is introduced into the glass linear using a syringe. The high heat of the injector rapidly volatilizes components of the sample. The carrier gas mixes with the vapourized compounds and carries onto the column. In the split mode a controlled portion of the sample enters the column. The remaining portion is diverted through a split vent. The split ratio is set at the GC. To increase the amount of sample entering the GC, a split/splitless injector can be operated in the splitless mode where most of the vapourized sample enters the GC column. [29,30] The split/splitless injectors operate at high temperatures. However injection at high temperatures using a syringe with a metal neelde may lead to degredation of thermally labile compounds or needle discrimination.

This disadvantage is over come by using an on-column injector. Here the liquid is injected directly into the column. The initial oven temperature is lowered to slightly below the boiling point of the solvent being used during injection. In this manner the solvent does not evaporate in the syringe needle eliminating discrimination. As the oven temperature is increased the solvent gradually evaportates from the tail edge of the injected liquid focusing the analytes into a narrower band until all solvent is evaporated. The analyte evaporates and migrates through the column after the solvent [29].

1.4.3 GC Columns

Modern GC columns are open tubular coulmns.They are for the most part made up of fused silica, a high purity silica, externally coated with polyamide to provide flexible mechanically stable tubing that is easy to handle. Metal capillary columns are also available. These are made of stainless steel or nickel with an inner surface that has been deactivated with a thin layer of fused silica [29].

The liquid stationary phase is coated onto the wall of the tubing. The stationary phase is bonded to the tubing wall and futher stabilized by crosslinking of the polymer. Common stationary phases include dimethyl polysiloxane with varying degrees of substitution with functional groups such as cyano groups to provide stationary phases with varying degrees of polarity. Analyte separation occurs by partitioning of the analyte between the gas and liquid phase. The more time the analyte spends in the liquid phase the longer it takes for the analyte to elute from the column. Differences in the partitoning of compounds between the gas and liquid phases provides separation of the analytes for quantitation [29].

1.4.4 Use of a Retention Gap

A retention gap is a section of uncoated deactivated tubing or pre-column and is usually used when injecting directly onto the column. The rentention gap is used to focus vapourized compounds on the head of the GC column. The retention gap is connected to the analytical column with low dead volume connectors. The sample is injected into retention gap where it vaporizes. As there is no stationary phase in the retention gap section, the vaporized compounds travel with the carrier gas until they reach the beginning of the coated section of the column. On reaching the start of the column coating, the analyte migration rate is significantly slowed as analytes begin to partion into the stationary phase. This focuses the analyte at one point in the column. In this way analyte molecules that vapourize more slowly from the front of the analyte band catch up with the molecules that first vapourized from the tail of the band.

Using a pre-column, non-volatile components from an injection that would accumulate in the analytical column will be deposited instead in the pre-column. This extends the life of the analytical column by protecting it from deterioration. The pre-column may be easily replaced without affecting the performance of the analytical column [29].

The retention gap technique is normally used in conjunction with temperature programming, the program being initiated at a fairly low temperature. The lower initial temperature aids in the accumulation of all the solutes where the stationary phase coating begins.

1.4.5 GC Detectors

As the compounds elute from the GC column, they interact with the detector. The detector creates an electrical signal in the presence of the eluting compound that is proportional to the amount of the compound. Graphic representation of the detector signal with respect to time generates a chromatogram. Various general and selective detector types are available. Universal detectors such as a flame ionization detector (FID) respond to the presence of any hydrocarbon. Other detectors are selective to the presence of a specific type of atom or functional group; examples include electron capture (ECD) and dry electrolytic conductivity (DELCD) detectors [29].

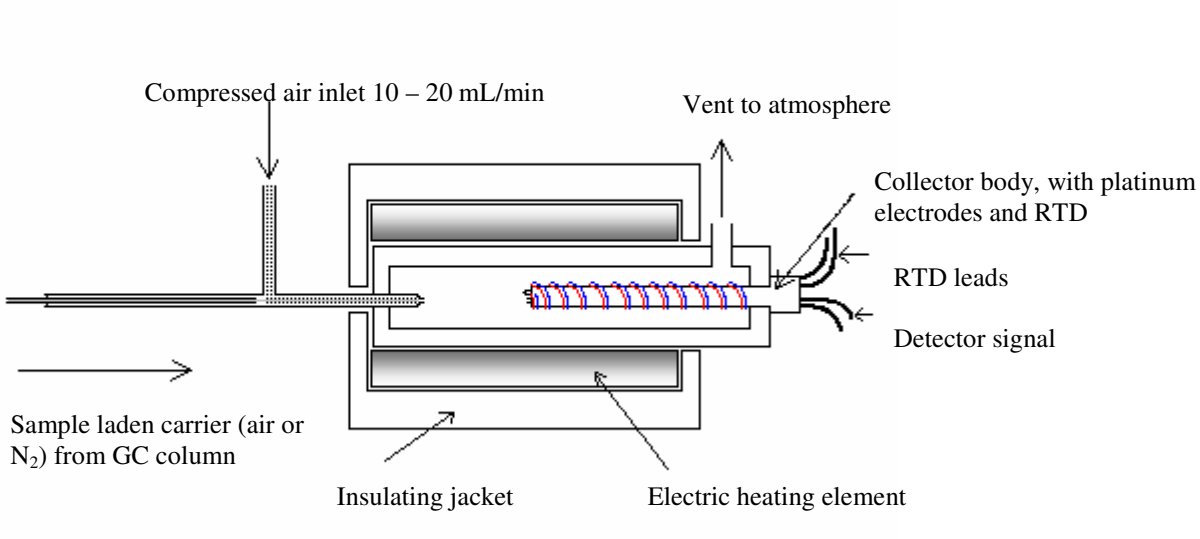
In the FID a collector electrode is located above a hydrogen-air flame tip (jet). An electrical potential of several hundred volts is applied between the electrode and the jet. Effluent from the column enters the hydrogen-air flame where combustion of the organic molecues creates ions. These ions give rise to a small electric current between the electrode and the jet. This current is proportional to the number of carbon atoms present in the detector at any given time. As a result many different compounds will have similar response in an FID. Because the FID responds to the presence of carbon atoms it is of limited usefullness in environmental analysis where trace components are being quantitated in a complex matrix.

The ECD is another type of ionization detector. In the ECD a radioactive source (usually ^{63}Ni) emits β-radiation. When molecules of the make-up gas (high purity nitrogen or argon with 5% methane) collide with the high energy β-electron, thermal electrons are created producing a standing current. The presence of electron-capture compounds eluting from the GC reduces the concentration of free electrons in the detector. This

decrease in the standing current is recorded as a detector signal. The ECD is a selective detector that responds to molecules with high electron affinity. Halogenated compounds and compounds containing nitro-groups have the strongest response in an ECD. The ECD response depends on the number and type of electron capturing groups in a molecule. Therefore it must be calibrated for each analyte being quantitated. This detector is used in environmental analysis because of sensitivity and selectivity the ECD has toward compounds of environmental concern, such as organochlorine pesticide and PCBs.

The dry electolytic conductivity detector (DELCD) is used for the determination of halogenated compounds. The DELCD is similar in sensitivity to an ECD, but is more selective to halogens and is insensitive to oxygenated compounds. The DELCD uses a ceramic reaction chamber in which compounds are oxidized at a high temperature (1000°C) in an oxygen-rich environment. The detector is equipped with a set of platinum electrodes. Figure 1.6 presents a schematic diagram of the DELCD reaction cell.

Figure 1.6: Schematic diagram of the dry electrolytic conductivity detector reaction cell [31]



The DELCD reactor chamber is composed of a heavily insulated ceramic cylinder with an inner diameter of 5 mm. The temperature within the reactor is thermostatically maintained at 1000°C by an electric heating element wrapped around the exterior of the ceramic cylinder. A ceramic probe holds a resistive temperature detector (RTD) in place along with platinum detector anode. Oxidation of the gas phase compounds occurs in an oxygen-rich environment, provided by compressed air from the GC, as they pass through the cell.

Sample-laden carrier gas eluting from the GC column is directed over a parallel helically wound platinum electrode in a reactor cell. Under the extreme temperature of the reactor chamber, chlorinated and brominated compounds form gas phase ions. These compounds conduct current between the DELCD electrodes. The higher the concentration of gas phase ions, the higher the conductivity between the electrodes, which allows more current to pass through the detector circuit. The current passing through the DELCD circuit is measured to provide a signal for quantitation [29].

The RTD and a platinum electrode are built into the collector body. The RTD measures the temperature at the reaction site. The electrodes are mounted in the carrier gas flow path exiting the GC column. The DELCD operates in oxidative mode and requires a continuous flow of compressed air (provided as make-up gas) into the reactor cell in order for the oxidation reaction of analytes to occur. The optimum air flow occurs between 10 and 20 mL/min, depending on the type and flow of carrier gas [29].

This detector is less subject to interferences from non-halogenated compounds than ECD. The DELCD response is proportional to the number of halogen atoms in a molecule.

1.4.6 Field Portable GC

As the goal of this research was to develop an on-site method for environmental analysis, a field portable GC was used. The GC used for this research was an SRI Instruments Model 310 Gas Chromatograph (Figure 1.7) equipped with an on-column injector and a dry electrolytic conductivity detector (DELCD). The small size of this GC, 12.5" wide x 13.5" high x 14.5" deep, makes it portable and easy to use in the field [31].

The Model 310 GC column oven is temperature programmable from ambient to 400°C. The GC can accommodate up to four detectors mounted simultaneously and is equipped with an on-column injector. The Peak Simple data system is run on a personal computer connected to the GC.

Figure 1.7: SRI Instruments model 310 gas chromatograph [31]

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2 Analysis Using Ion Mobility Spectroscopy

2.1 Model 350 IonScan Operation

2.1.1 Instrument Conditions

The model 350 Ionscan was used for all analyses using IMS. This instrument is commercially available from Smiths Detection (Mississauga, Ont). Instrument operating conditions are given in Appendix 1.

Instrument conditions were set by opening the IMS software package provided by Smiths Detection, using a personal computer. This opens a DOS based program where parameters may be set as outlined in Section 2.14. Once all parameters were correctly entered, the IMS may be updated and this program saved and closed.

2.1.2 Preparation of Sample Cards

Teflon sample cards were used for sample desorption and introduction into the IMS. The cards were composed of two Teflon pieces, a top ring and a sample base, between which a Teflon filter was held. The top ring and sample base were washed with acetone and allowed to air dry. Once dry, a Teflon filter was placed over the opening in the sample base and the top ring was pressed down to the opening of the sample base. In this manner, the filter was secured in place. It was advantageous to prepare a large quantity of sample cards for analysis simultaneously. Completed sample cards were stored in metal containers fitted with push-on lids. When enough sample cards were prepared to fill a container, the container with the cards and the lid were baked overnight at 200°C in a convection oven to remove any trace contaminants before storage. After baking, the

container and lid were allowed to cool on the counter until the container was just warm to touch. The lid was replaced on the container and left in place until cards were required for use.

To prevent contamination of the sample inlet with soil, two Whatman GF/C glass fiber filters (available from VWR International Inc.) were used as sample cover. These filters were also stored in metal containers fitted with push-on lids. The containers with glass fiber filters and the lids were baked prior to use overnight at 200°C in a convection oven to remove any trace contaminants before storage. After baking, the container and lid were allowed to cool on the counter until the container was just warm to touch. The lid was replaced on the container and left in place until the filters were required for use.

2.1.3 Verification of Instrument Operation

The IMS was examined to check if it was in good operating condition prior to the start of each set of analyses. This ensured the accuracy and reliability of sample results for the analysis of PCBs in soil. Below is a description of the quality control procedures that were implemented prior to the start of each workday.

At the start of each workday, instrument parameters and function were monitored by analyzing the instrument background and instrument blank (Figure 2.1 and Figure 2.2, respectively). The instrument background showed the presence of any residual contaminants that could interfere with the soil analysis. During instrument background check the IMS bypassed the sample inlet. The resulting scan showed the instrument operation and detection between the ion source and the collector only. Each background scan (Figure 2.1) was electronically collected and printed for visual inspection in the

region of interest (between 12 and 20 ms). This step verified that the internal areas of the instrument were free from contamination.

Cumulative amplitude (Cum Amp) values for O_2, Cl^- and calibrant determined from the instrument background were used to prepare the IMS background control chart. Under optimum conditions, the Cum Amp for O_2 should be less than 75 Cl^- should be greater than 400, and the calibrant should be greater than 300.

The instrument blank was examined using an empty sample card on the sample platform. This blank run would show the presence of contamination between the sample desorption area and the ion collector. An example of an instrument blank is given in Figure 2.2. Instrument blank scans were electronically collected and printed for visual inspection in the region of interest (between 12 and 20 ms). This step provided verification that the instrument, sample platform, and desorption anvil were free from contamination.

To ensure optimal sensitivity of the instrument, the values for O_2, Cl^- and calibrant from the instrument blank scans were recorded in the IMS blank control chart. Instrument sensitivity was determined to be optimal when the values for O_2 were less than 200 du, Cl^- was $\geq$ 370du, and the calibrant was $\geq$ 240du. Values for the calibrator were automatically plotted on the control chart in Figure 2.3 using an Excel spreadsheet.

Values for O_2, Cl^- and the calibrant were maintained above -2 sigma as indicated on the control chart. To maintain this level of sensitivity, the instrument was routinely baked out, the inlet tube replaced and the sample platform and desorption anvil cleaned with acetone as required. If values for O_2, $Cl^-$and the calibrant were found to be above +1 or +2 sigma, no corrective action was required as this indicated improved instrument sensitivity. If the control chart indicated a drop in the values for the calibrant (at or

below -1 sigma level), the instrument bake out procedure was run until the calibrant values could be established within the control chart parameters.

Figure 2.1: IMS scan of instrument background

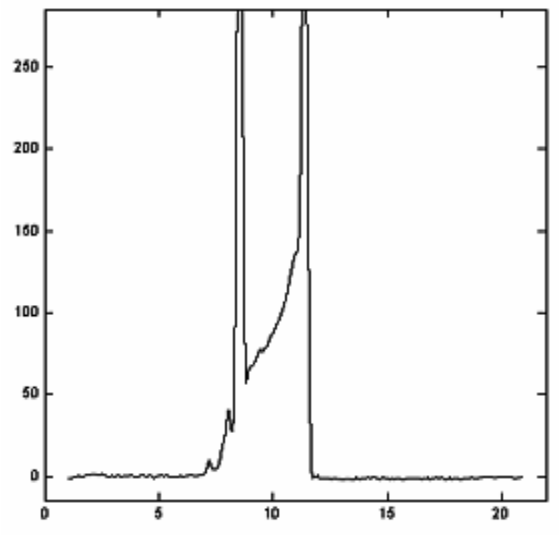


Figure 2.2: IMS scan of instrument blank

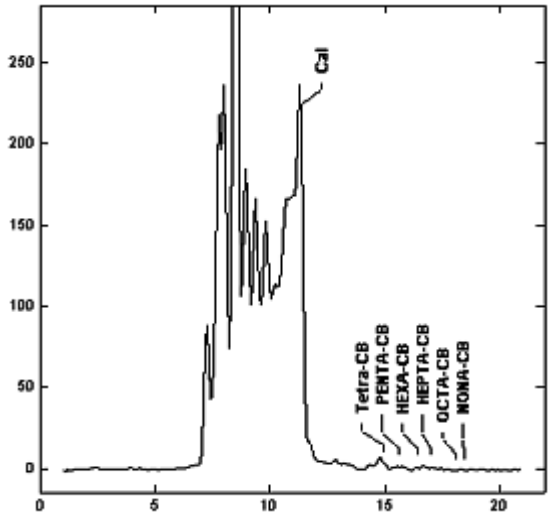
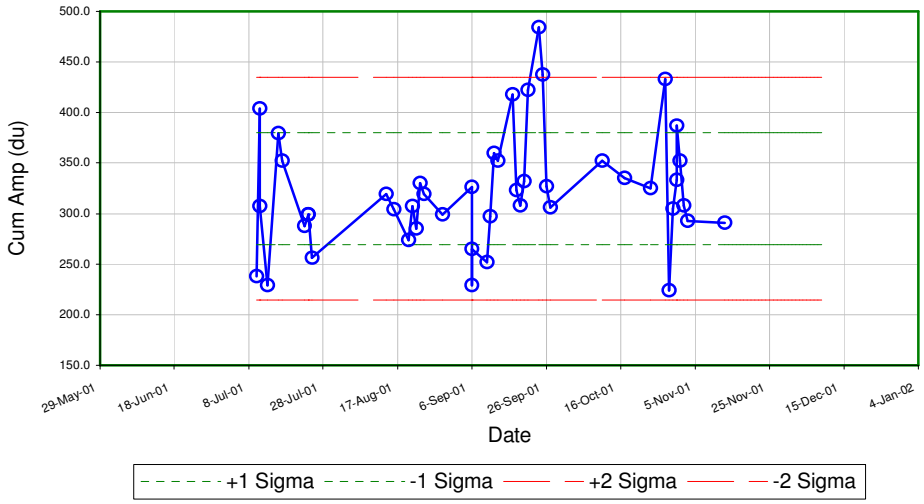


Figure 2.3: Calibrant control chart for instrument blank



2.1.4 Analysis Using the Model 350 IonScan IMS

The following procedure was used in the operation of the Model 350 IonScan:

2.1.4.1 Instrument Blank:

The IonScan IM software was opened using a personal desktop computer interfaced with the model 350 Ionscan. The “Ionscan” tab on the display screen was opened using the left mouse button and from the drop down box, “background” was selected. The background analysis was automatically started and the results were provided by the IonScan IM software on the computer monitor. This scan was visually inspected for contamination prior to analysis (refer to Section 2.1.3)

2.1.4.2 Sample Blank or Conditioning of New Sample Card Prior to Analysis

A new empty sample card was placed in the sample carriage and two glass fiber filters were placed over the top of the sample. The sample carriage was moved into place over the desorber anvil. The sample analysis started automatically once the sample carriage

was over the desorber anvil. The IonScan IM software provided the visual record of the sample desorption and analysis on the computer monitor (Figure 2.4). When this scan was used as a blank scan for instrument verification, the cumulative amplitude (Cum Amp) data for the calibrant were entered into an Excel spreadsheet. When this procedure was used for the conditioning of a new standard or sample analysis, the scan was inspected for signs of contamination in the range of the PCB peaks. The blanked card was used for a standard or sample desorption when the card showed no contamination.

2.1.4.3 Sample Analysis:

A 1g sample of sand or soil was weighed onto a new blanked Teflon sample card. The card was placed in the sample carriage and two glass fiber filters were placed over the top of the sample. The sample carriage was moved into place over the desorber anvil. The sample analysis started immediately once the sample carriage was over the desorber anvil. The IonScan IM software provided the visual record of the sample desorption and analysis on the computer monitor (Figure 2.5). Total Cum Amp for each component was recorded from the monitor into an Excel spreadsheet. Each sample was consecutively desorbed a minimum of five times or until no response was seen for PCBs. A new sample card was conditioned prior to the next standard or sample desorption.

For liquid samples, a 1g portion of clean sand was weighed onto the sample card. Up to 100 µL of liquid was added to the sand. Any solvents present in the liquid was allowed to evaporate prior to desorption. The sand was then desorbed as for soils.

Figure 2.4: IonScan IM software report for a blank sample card

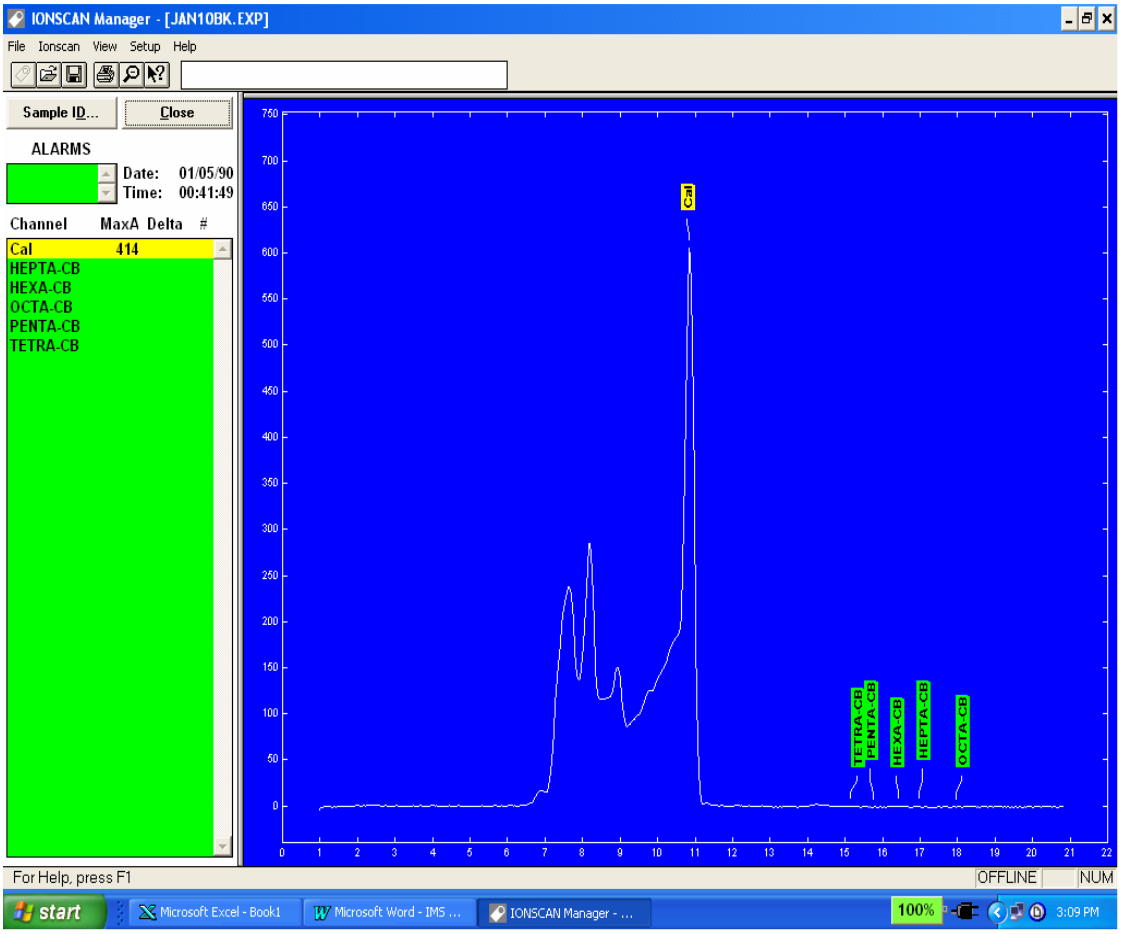
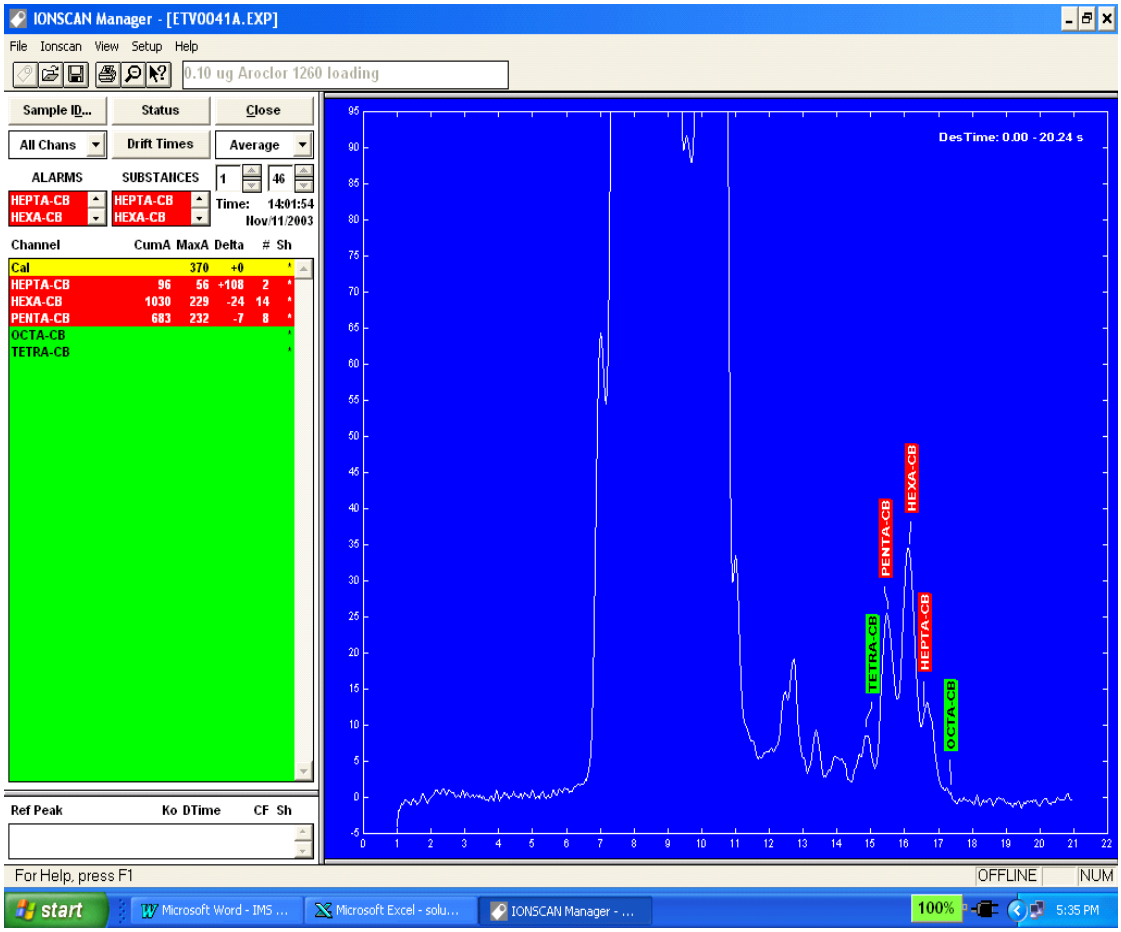


Figure 2.5: IonScan IM software report for the desorption of a PCB standard



2.2 Experimental Procedures

2.2.1 Preparation and Analysis of Liquid Standards

2.2.1.1 Preparation of Liquid Standards

For the purpose of this thesis, the term PCB(s) will be used interchangeably with Aroclor 1260. A series of liquid standards were prepared from a 1000 µg/mL Aroclor 1260 stock solution (from Sigma-Aldrich) The liquid standard series was prepared by volumetric dilution to 5 mL with acetone (HPLC grade) according to the chart given in Table 2.1.

Table 2.1: Liquid standards of PCB in acetone

Stock Solution Concentration of Aroclor 1260 in Acetone:			**1000 µg/mL**
Aroclor 1260 Concentration Stock Solution (µg/g)	**Total Volume of Acetone (mL)**	**Aroclor 1260 Stock Solution Used (µL)**	**PCB Spiking Solution Concentration (µg/mL)**
1000	0	0	1000
1000	5	500	100
1000	5	250	50
1000	5	125	25
1000	5	50	10

2.2.1.2 Analysis of Liquid Standards

A new sample card was conditioned in the IMS inlet (refer to section 2.1.4.2). After conditioning, a known volume of PCBs in acetone was spiked into the center of the sample card directly onto the Teflon filter using a glass syringe (see Table 2.2 for volumes and concentrations of PCB spiking solutions used). The acetone from the PCB spike was allowed to evaporate from the Teflon filter. Once the sample card appeared visibly dry, the sample carriage was moved onto the thermal desorber to begin analysis. The acetone drying time was keep to a minimum to prevent analyte loss. The maximum time required to remove the acetone was found to be less than 2 min. This procedure was repeated at each concentration.

Table 2.2: Loading of total PCBs using liquid standards into IMS

Aroclor 1260 Concentration Stock Solution (µg/g)	Volume of Stock Solution Used (µL)	PCB Spiking Solution Concentration (µg/mL)
1000	50	50.0
1000	25	25.0
1000	10	10.0
1000	5	5.0
1000	1	1.0
100	5	0.50
100	1	0.10
50	1	0.05
10	1	0.01

Each sample card containing the dried liquid PCB standard was desorbed for 20 s using a desorption anvil temperature of 330°C. IMS integration provided Cum Amp values for tetra-CB, penta-CB, hexa-CB, and hepta-CB on the IMS scan. These values were recorded on an Excel spreadsheet. Consecutive desorptions of the same liquid standard were conducted until all analyte was removed from the sample card. Cum Amp values for tetra-CB, penta-CB, hexa-CB and hepta-CB in each of the consecutive desorptions were recorded and summed to determine the total Cum Amp for the PCB found as a result of all consecutive desorptions (see Table 2.3 for an example of sample spreadsheet). At least 5 consecutive desorptions were carried out at any given concentration.

Table 2.3: Example Spreadsheet for the Analysis of Liquid PCB Standards

Total PCB Loading µg	Desorption Number	Cum Amp for Tetra -CB	Cum Amp for Penta -CB	Cum Amp for Hexa -CB	Cum Amp for Hepta -CB	Sum of Cum Amp
0.5µg	1	0	3444	6709	1355	11508
0.5µg	2	0	62	1201	39	1302
0.5µg	3	0	0	277	0	277
0.5ug	4	0	0	51	0	51
0.5ug	5	0	0	15	0	15
Total Cum Amp		0	3506	8253	1394	13153

Consecutive desorption of a single dried liquid standard was used to determine the number of desorptions required to remove all PCB from the sample card. The response

for liquid PCB standards was determined by graphing the total Cum Amp against the total concentration of PCB loading into the IMS (total µg). Cum Amp values for the desorption of PCB from liquid standards were compared to values found for the desorption of PCB from the sand standards spiked directly with PCB and the PCB sand standards prepared in 50 g batches.

2.2.2 Preparation and Analysis of Sand Standards

Sample standards were prepared individually and in bulk to provide a large quantity of sand containing a consistent concentration of PCB. Clean sand was conditioned by baking it for 8 hours (overnight) at 200°C, then cooling to room temperature. The baked sand was analyzed by IMS prior to use in the preparation of sand standards to ensure no interferences in the area in which PCBs elute (between 12 and 20 ms). The IMS scan of the sand was electronically collected and printed for visual inspection in the region of interest. This step provided verification that the sand was free from contamination.

2.2.2.1 Direct Spiking of Liquid Standard Solution onto Clean Sand

Individual directly spiked standards were prepared by weighing 1g of clean sand directly onto sample analysis cards. Known quantities of Aroclor 1260 stock or spiking solutions were spiked onto the sand immediately prior to analysis using a glass syringe. The sand for each standard was weighed and spiked within 2 minutes of analysis to minimize analyte loss. The results of the analysis for the spiked sand standards were compared to sand standards prepared in 50 g batches to provide comparison for the 2 methods of standard preparation.

Clean baked sand was prepared as above. A new sample card was conditioned in the IMS inlet. After conditioning, 1 ±0.01 g of clean sand was weighed onto the sample card. A known quantity of PCB in acetone was spiked into the center of the 1g pile of sand on the sample card (see Table 2.4 for quantities and concentration of PCB spiking solutions used). The acetone from the PCB spike was allowed to evaporate from the sand. Once the sand appeared visibly dry, the sample carriage was moved onto the thermal desorber to begin analysis. The acetone drying time was kept to a minimum to prevent analyte loss. The maximum time required to dry the sand was found to be less than 2 min This procedure was repeated at each concentration.

Table 2.4: Preparation of PCB sand standards by direct spiking onto 1g clean sand

Desired Concentration of Total PCBs in Sand (µg/mL)	Concentration Aroclor 1260 in Acetone (µg/mL)	Volume of Stock Aroclor 1260 in Acetone (µL)
100.0	1000	100
25.0	1000	25
10.0	1000	10
5.0	1000	5
1.0	25	40
0.5	25	20
0.1	25	4

Each sample card containing 1g of PCB-spiked sand standard was desorbed for 20 s at a desorption anvil temperature of 330°C. IMS integration provided values for tetra-CB, penta-CB, hexa-CB, and hepta-CB in the IMS scan. These values were recorded in an Excel spreadsheet. Consecutive desorptions of the same liquid-spiked sand standard were conducted until all analyte was removed from the sample card. Cum Amp values for tetra-CB, penta-CB, hexa-CB, and hepta-CB in each of the consecutive desorptions were recorded and summed to determine the total Cum Amp for PCB found as a result of all consecutive desorptions (see Table 2.5 for a sample spreadsheet). At least 5 consecutive desorptions were carried out at any given concentration.

Table 2.5: Example spreadsheet for the IMS analysis of sand standards directly spiked with PCB solution.

Total PCBs µg/g sand	Desorption Number	Cum Amp for Tetra -CB	Cum Amp for Penta -CB	Cum Amp for Hexa -CB	Cum Amp for Hepta -CB	Sum of Cum Amp
0.5µg/g	1	0	3370	10884	4230	18484
0.5µg/g	2	0	693	3545	359	4597
0.5µg/g	3	0	0	1165	20	1185
0.5µg/g	4	0	0	1019	0	1019
0.5µg/g	5	0	0	489	0	489
Total Cum Amp		0	4063	17183	4609	25855

The instrument response for liquid PCB-spiked sand standards was determined by graphing the total Cum Amp against the total amount of PCB loaded into the IMS (total µg). Cum Amp values for the desorption of PCB from liquid-spiked sand standards were compared to values found for the desorption of PCB from the liquid standards and the PCB sand standards prepared in 50 g batches.

2.2.2.2 Batch Preparation of PCB Sand Standards

Sand standards were prepared in 50 g batches to provide a consistent source for each standard concentration. Clean sand (50g) was weighed into tared, labeled 40 mL wide mouth vials fitted with Teflon lined screw caps (Refer to Table 2.6). Approximately 20 mL of HPLC grade (99.9+% pure) acetone was added to each vial using a 50 mL glass syringe. Acetone was added to improve analyte mixing and contact with the sand, therefore accurate addition of the acetone was not required.

Aliquots of 1000 µg/mL solution of Aroclor 1260 in acetone were added into each vial as outlined in Table 2.6, using an appropriately sized glass syringe. The vials were then capped with Teflon-lined screw caps and shaken vigorously using vortex type mixer. Any sand that clung to the top portion of the vial was shaken down from the cap. Each cap was labeled and removed from the vial. The open vials were place in a fumehood to

allow the solvent to evaporate overnight. Caps were replaced on the vials. The vials were then shaken thoroughly for 1 minute by hand.

These sand standards were used for the determination of analyte response, effect of desorption temperature, and the effect of storage temperature.

Table 2.6: PCB Concentration in Sand for Analytical and Quality Control Standards

Stock Standard Solution Concentration (Available from Sigma-Aldrich)	**Aroclor 1260 in Acetone**	**1000 µg/mL**
Final weight of Sand used (g)	**Stock Solution Used (mL)**	**Actual Final Concentration (µg/mL)**
50.00	2.50	50.00
50.04	1.25	25.00
50.00	0.50	10.00
50.00	0.25	5.00
50.00	0.05	1.00
50.00	0.03	0.50
50.00	0.005	0.10
50.00	0.003	0.05

Each sample card containing the PCB sand standard was desorbed for 20 sec at a desorption anvil temperature of 330°C. IMS integration provided Cum Amp values for tetra-CB, penta-CB, hexa-CB, and hepta-CB in the IMS scan. These values were recorded in an Excel spreadsheet. Consecutive desorptions of the same sand standard were conducted until all analyte was removed from the sample card. Cum Amp values for tetra-CB, penta-CB, hexa-CB, and hepta-CB in each of the consecutive desorptions were recorded and summed to determine the total Cum Amp for all PCBs found as a result of all consecutive desorption (see Table 2.7 for a sample spreadsheet). At least 5 consecutive desorptions were carried out at any given concentration.

Table 2.7: Example Spreadsheet for the Analysis of PCB Sand Standards (prepared in 50 g batches) by IMS

PCB µg/g sand	Desorption Number	Cum Amp for Tetra -CB	Cum Amp for Penta -CB	Cum Amp for Hexa -CB	Cum Amp for Hepta -CB	Sum of Cum Amp
0.5µg/g	1	0	7699	4946	0	12645
0.5µg/g	2	0	2877	9041	2944	14862
0.5µg/g	3	0	217	2057	54	2328
0.5µg/g	4	0	0	286	0	286
0.5µg/g	5	0	0	427	0	427
Total Cum Amp		0	10793	16803	2998	30594

The analyte response for batch-prepared PCB sand standards was determined by graphing the total Cum Amp against the total amount of PCB loaded into the IMS (total µg). Cum Amp values for the desorption of PCB from batch prepared sand standards were compared to values found for the desorption of PCB from the liquid standards and the PCB sand standards prepared by direct spiking into 1g of clean sand.

2.2.3 The Effect of Extract Clean-Up on PCB Analysis in Spiked Potting Soil Extracts

Blended potting soil (10 g) was weighed into clean, labeled 20 mL vials and spiked with stock PCB solutions to provide a concentration range of 0.04 to 5.0 µg/g. Each spiked soil was prepared in duplicate. One of the duplicate extraction solvents was concentrated and reconstituted as outlined below. The duplicate extraction solvent was passed through a sample cleanup step using a commercially available Supelclean LC- Florisil SPE tube, a solid phase extraction (SPE) cartridge (available from Supelco) over a Supelclean LC- Si SPE tube (available from Supelco. Extraction solvent (15 mL HPLC grade acetone) was added to each vial of spiked soil. The vials were sealed with aluminum foil-lined screw caps and placed in an ultrasonic bath. Water was added to the ultrasonic bath until the water level reached approximately one half of the way up the 20 mL vials. The spiked

soils were sonicated at room temperature for 20 min After extraction, the vials were allowed to cool to room temperature before opening. An aliquot of acetone (5 mL) was removed from each vial and transferred to a clean, labeled 20 mL vial. The acetone was evaporated under a gentle stream of compressed air until less than 1 mL of the solvent remained.

For soil extracts that were not to be treated with solid phase extraction clean-up, the acetone was transferred to a clean labeled 2 mL vial using a disposable pipette along with three acetone rinses (0.5 mL) of the 20 mL vial. The solvent in the 2 mL vials was evaporated to dryness under a gentle air stream. The dried soil extract in the 2 mL vial was then reconstituted with 500 µL of acetone and mixed using a vortex mixer. The reconstituted soil extracts were analyzed by IMS and quantified using an external standard method. These extracts will be referred to as "untreated extracts".

For soil extracts that were treated with solid phase extraction clean-up, the acetone was transferred to a pair of SPE cartridges arranged with the silica gel cartridge draining directly into the Florisil cartridge. The SPE cartridges were preconditioned with 5 mL of iso-octane [3]. The extraction solvent was washed through the SPE cartridges using five 2 mL portions of hexane [1,2,3] to elute the PCBs from the SPE cartridges. All solvent eluting through the SPE cartridges was collected and evaporated to less than 1 mL, then transferred to a clean, labeled 2 mL vial using a disposable pipette along with the 3 hexane rinses (0.5 mL each) of the collection vial. The solvent in the 2 mL vials was evaporated to dryness under a gentle air stream. The dried soil extract was then reconstituted with 500 µL of acetone and mixed using a vortex mixer. The reconstituted soil extracts were analyzed by IMS and quantified using external standard method.

2.2.4 Thermal Desorption of PCBs from Solid Phase Extraction Media

Direct thermal desorption of PCBs from the SPE sorbent into the IMS was investigated as an alternative to the cleanup of soil extracts. The PCB standards and untreated extracts of spiked soils prepared in section 2.2.3 were used for this investigation.

An aliquot of the PCB standard and the untreated soil extract were spiked onto 0.25g of Florisil (16-30 mesh, granular, from Sigma-Aldrich) to provide 1 µg PCB loading to the IMS. The sample card was covered with two 2 µm glass fiber filers to prevent contamination of the IMS with the Florisil. Each sample was desorbed consecutively (up to 36 times or until no PCBs were detected) into the IMS using a desorption anvil temperature of 330°C . The cumulative amplitude for each homolog was recorded. The cumulative amplitudes for all homologs were summed to calculate the total cumulative amplitude.

2.3 Results and Discussion

2.3.1 IMS Response for Liquid PCB Standards

The liquid Aroclor 1260 stock solution (1000 µg/mL in acetone) and liquid spiking solutions, as required, were used to load PCB at varying concentrations onto the Teflon filter in the sample card. Acetone was used due to its rapid evaporation rate. The length of time required to evaporate the acetone was found to be less than 1 minute for volumes up to 50 µL of stock or spiking solution. Appendix 1 gives IMS parameters for the analysis of all instrument response data.

The instrument response for each homolog desorbed from the dried liquid PCB (Table 2.8) was plotted against PCB loading (µg PCB) into the IMS. Figure 2.6 illustrates the IMS response for Total Cum Amp plotted against total PCB loading (µg). It can be seen in Figure 2.6 that the Cum Amp for the individual homologs provided plots that had lower slopes than those for the Total Cum Amp (which represents the sum of all Cum Amp for the individual homologs). This result was expected, as the variations in desorbed analyte concentrations were averaged out.

By summing the individual homolog Cum Amp, a Total Amp was obtained. When this value was plotted against total PCB loading (Figure 2.8) a non-linear relation was seen.

Table 2.8: Liquid PCB Standards in acetone analyzed by IMS; averaged data for cumulative amplitudes for homologs.

PCB Loading	Instrument Response (Cum Amp, du)							
	Penta-CB		Hexa-CB		Hepta-CB		Total PCBs	
(µg)	Average	STD	Average	STD	Average	STD	Average	STD
0.01	83	41.5	2394	103.4	5	11.2	327	144.0
0.1	242	29.6	508	59.7	27	19.2	776	97.8
0.5	217	53.2	633	158.6	199	212.8	1049	356.2
1	639	170.2	2278	330.9	244	61.8	3162	473.6
5	989	132.9	4257	227.1	1146	501.9	6392.2	775.9
10	3221	1081.4	7875	1352.4	1430	161.9	12526	2343.1
25	2235	573.7	8473	992.2	8642	616.3	19350	1459.5
50	5594	766.9	20098	2020.1	4308	489.5	29999	2365.4

Figure 2.6: IMS response for all PCB homologs in liquid standards desorbed from 1g sand.

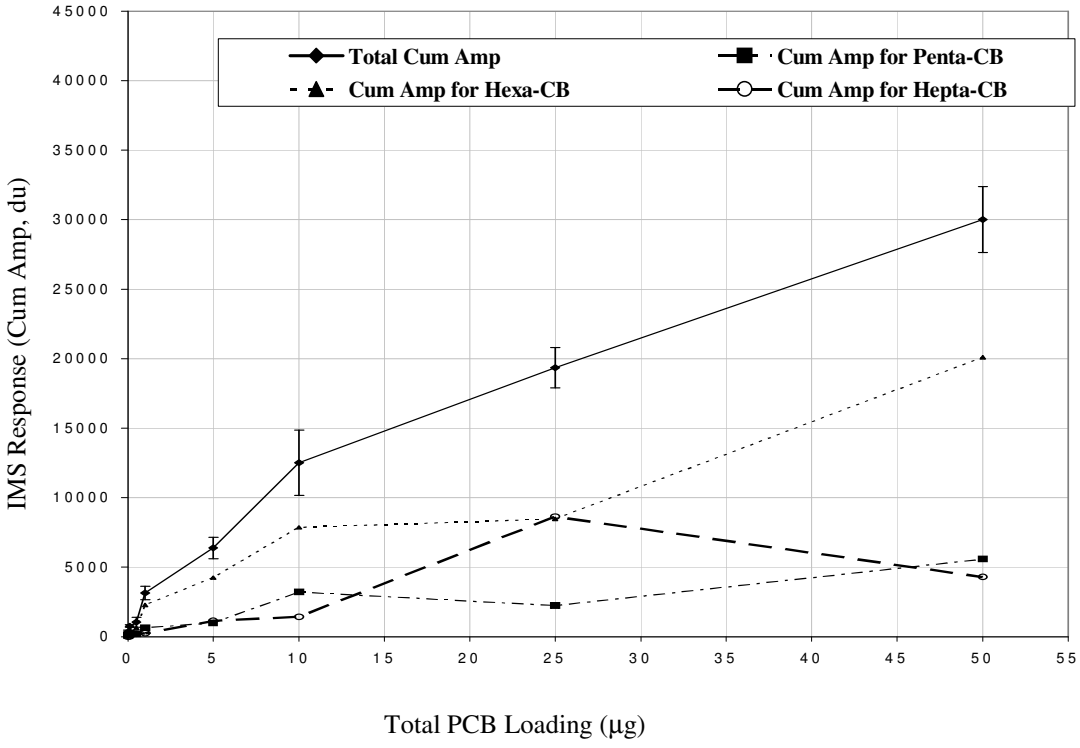
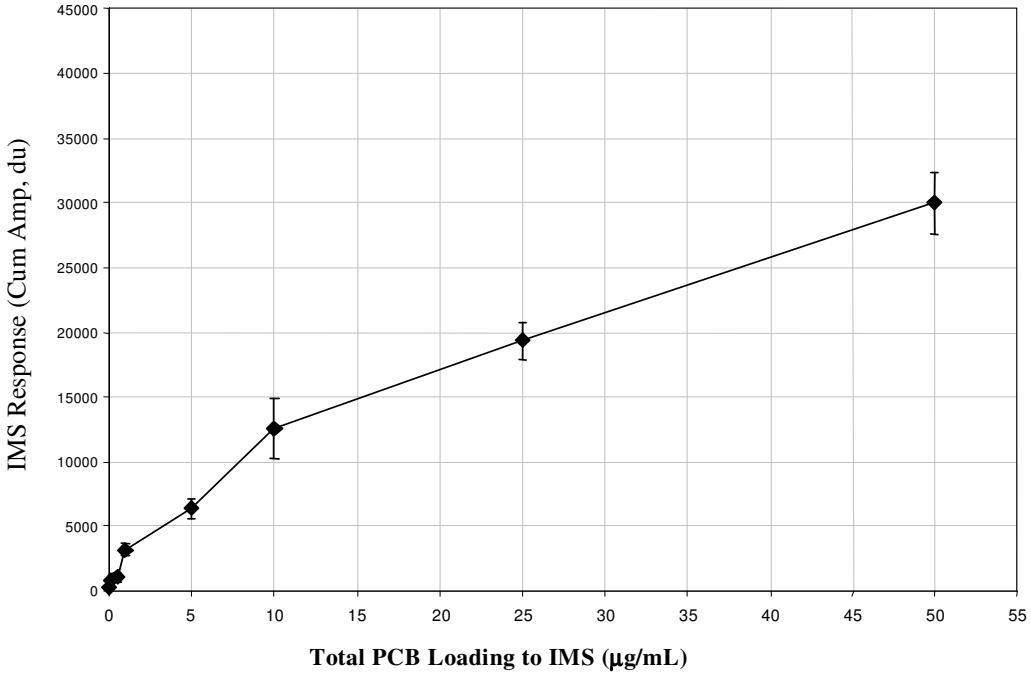


Figure 2.7: IMS response for total PCBs in liquid standards desorbed from 1g sand.



2.3.2 Instrument Response for Sand Standards

Sand standards were prepared by directly spiking standard PCB solutions onto 1.00 ±0.01 g of sand to provide concentrations of 0.05, 0.1, 0.5, 1.0, 5.0, 10.0, 25.0 and 50.0 µg/g. Each standard (1g) was analyzed using the IMS parameters found in Appendix 1. The Cum Amp values for the individual homologs and for the total Cum Amp (sum of Cum Amp for the individual homologs in a given desorption) were plotted against PCB concentration (Table 2.9 and Figure 2.6). As seen in Figure 2.8, the Cum Amp for hexa-CB makes up the largest portion of the total Cum Amp. Penta-CB and hepta-CB confirm the peaks seen in the IMS scan are due to the presence of PCBs.

Bulk sand standards were prepared at similar PCB concentrations as the directly spiked sand standards. Each standard was analyzed using the IMS parameters found in Appendix 1 for all instrument response data. The Cum Amp values for the individual homologs and for the Total Cum Amp (sum of Cum Amp values for the individual homologs in a given desorption) were plotted against PCB concentration (Figure 2.10). Bulk prepared PCB spiked sand show a similar response as for liquid standards spiked onto 1 g of sand. This is evident in Figure 2.10, where the response of liquid standards on sand and bulk prepared spiked sand follow a similar curve.

2.3.3 Comparison of Liquid and Sand PCB Standards

Table 2.10 and Figure 2.10 illustrate the comparison of average Total Cum Amp values for PCBs in liquid, directly spiked sand and bulk sand standards. The plots for both sand standards had a similar shape to that for the liquid standards. However, both sand standards produced higher levels for Total Cum Amp. This was likely due to more even

and consistent heat transfer from the desorption anvil to the 1 g mass of sand. The sample card with dried liquid standard had a very small mass, hence the heat from the desorption anvil could have caused evaporation of the PCBs before the sample card was fully sealed in the desorber inlet. This might have resulted in analyte loss to the atmosphere. This loss appeared to be reproducible.

As can be seen in Figure 2.10, both sets of sand standards provided higher levels for the total Cum Amp compared to liquid standards. By utilizing the total Cum Amp for sand standards, a better comparison should be achieved with field soil samples. However, since the relationship was non-linear, it would be advisable when using sand standards to estimate the total PCB concentration in field soil samples and use a standard with a similar concentration to that of the sample.

Table 2.9: Cumulative Amplitude for sand standards directly spiked with liquid PCB solutions and analyzed by IMS

PCB Loading (µg)	Instrument Response (Cum Amp, du)									
	Tetra-CB		Penta-CB		Hexa-CB		Hepta-CB		Total	
	Average	STD	Average	STD	Average	STD	Average	STD	Average	STD
0.01	0	0.0	196	320.3	355	421.3	0	0.0	551	730.1
0.1	0	0.0	570	398.4	850	686.9	0	0.0	1420	1081.3
0.5	5	15.2	2526	2206.3	4173	2751.3	409	447.9	7113	5259.6
1	0	0.0	5158	1003.2	8949	1558.3	348	168.5	14455	1543.7
5	0	0.0	4385	2540.7	13199	1939.3	2379	891.3	19963	3666.1
10	0	0.0	6462	2609.1	18442	1974.5	4186	1501.9	29090	3923.1
25	0	0.0	8358	3269.6	22518	4093.4	4228	570.5	35104	7656.1
50	0	0.0	10837	1490.1	26351	5006.9	5074	2042.2	42262	6290.5

Figure 2.8: IMS response for all PCB homologs for 1g of sand standards directly spiked with liquid PCB solutions.

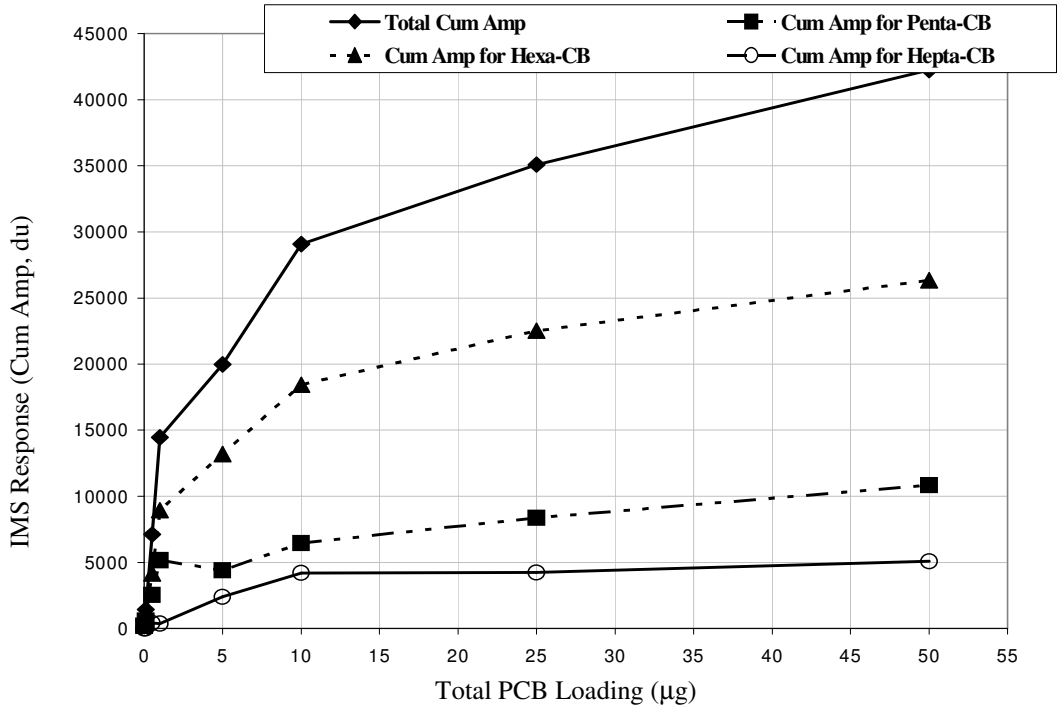


Figure 2.9: IMS response for all PCB homologs for batch-prepared 1g sand standards.

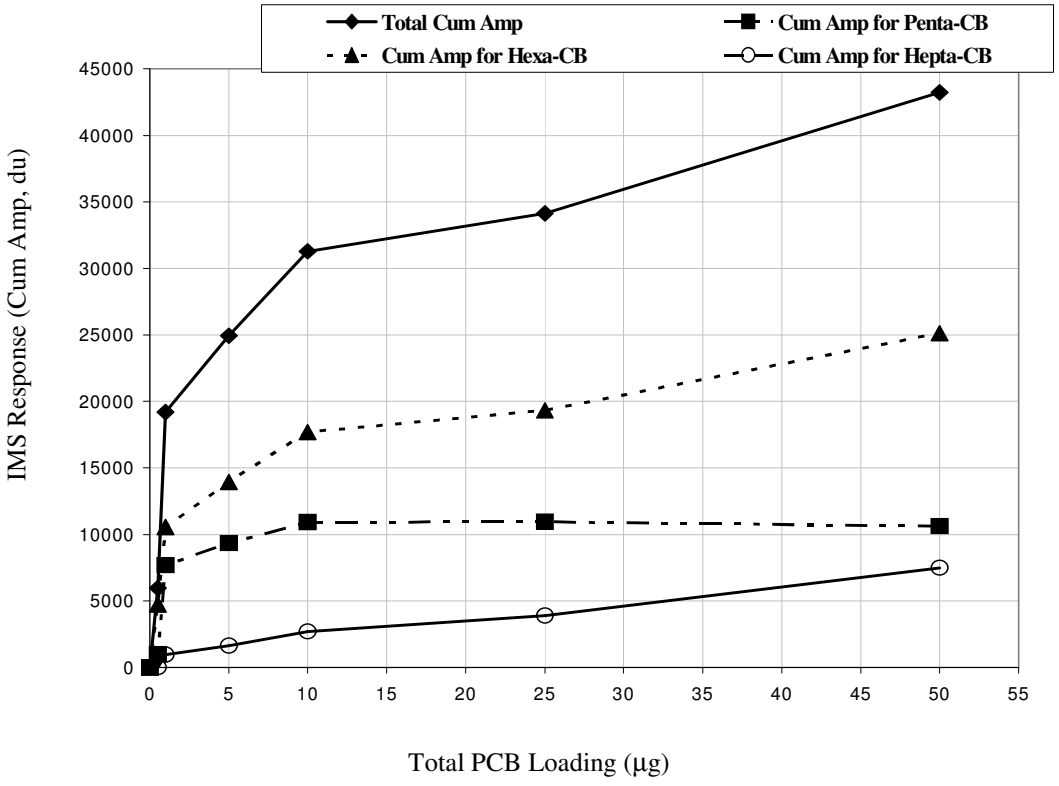
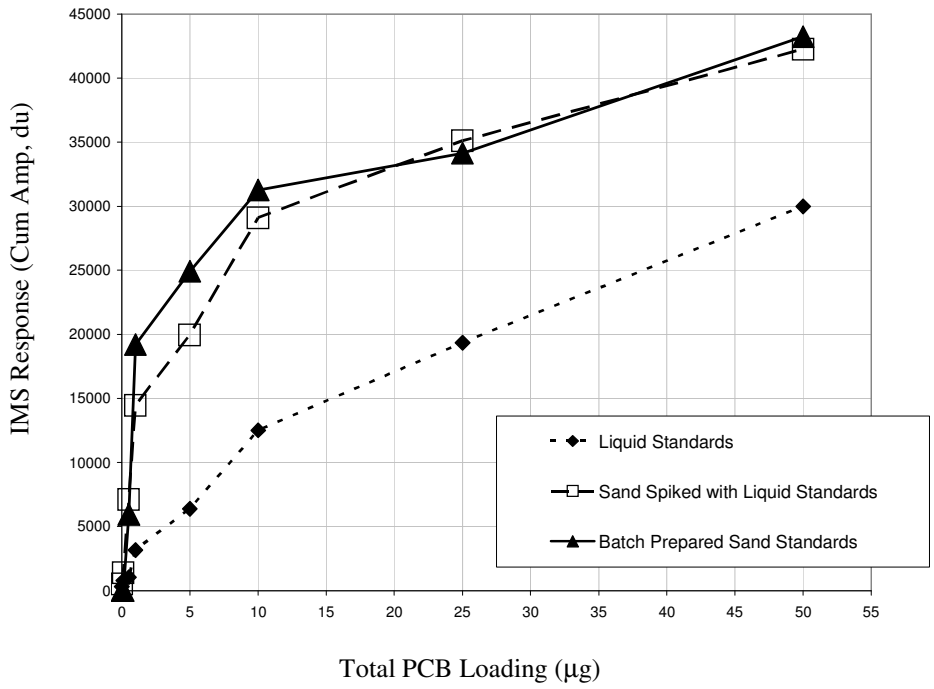


Table 2.10: Comparison of IMS response (total Cum Amp) for various PCB standard preparation techniques

PCB Loading to IMS (µg)	Liquid Standards		Sand Spiked with Liquid Standards		Batch Prepared Sand Standards	
	Average	STD	Average	STD	Average	STD
0.01	327	144.0	551	730.1	0	0.0
0.1	776	97. 8	1420	1081.3	-----	-----
0.5	1049	356.2	7113	5259.6	5952	8207.8
1	3162	474.0	14455	1543.7	13462	4763.7
5	6392	775.9	19963	3666.1	24930	3093.5
10	12526	2343.1	29090	3923.1	31276	2729.3
25	19360	1454.5	35104	7656.1	34149	7136.6
50	29999	2365.4	42262	6290.5	43234	6777.2

Figure 2.10: Comparison of Total Cum Amp response for liquid, directly spiked sand and batch-prepared sand PCB standards



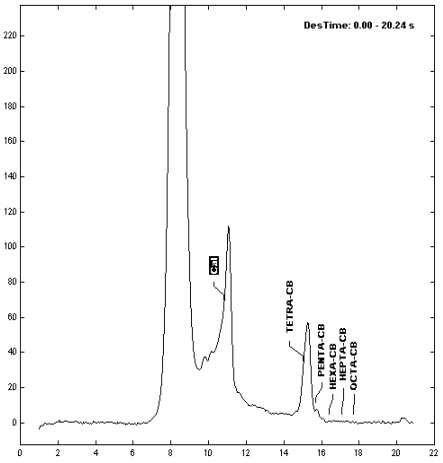
2.3.4 The Effect of Extract Clean-Up on PCB Analysis of PCB Spiked Potting Soil Extracts

The two SPE cartridges used in this portion of the investigation have affinity towards polar compounds. During sonication of the potting soil, the acetone extracts humic and fulvic acids along with sulfurous compounds. Extract cleanup with either Florisil or silica gel cartridges have been suggested in the literature for the removal of humic and fulvic acids [1,2,3]. A combination of the two cartridges is suggested for soil extract cleanup in the cartridge manufacturer's application notes.[3] To maximize the cleanup, the two cartridges were used in series with the Florisil on top of the silica gel cartridge. Column conditioning of the two cartridges was conducted using iso-octane as a conditioning solvent [2,3]. After application of the soil extract, the SPE cartridges were eluted using hexane [1,2]. During elution, the PCBs partition into the hexane from the SPE sorbent

surface. The hexane washes were collected into 20 mL vials. Once the hexane had evaporated the extract was reconstituted with hexane. The clean extract was analyzed by desorption from coarse sand into the IMS. An example of the resulting scans for extracts with and without sample cleanup are provided in Figure 2.11 and Figure 2.12.

Figure 2.11: IMS analysis of 0.762 µg PCB loading with no sample cleanup compared with a 0.5 µg loading of liquid standard, both desorbed from coarse sand

a) 0.762 µg PCB loading no SPE clean-up



b) liquid standard, 0.5 µg PCB loading

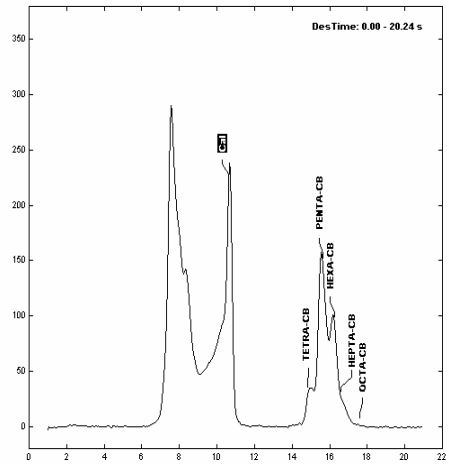
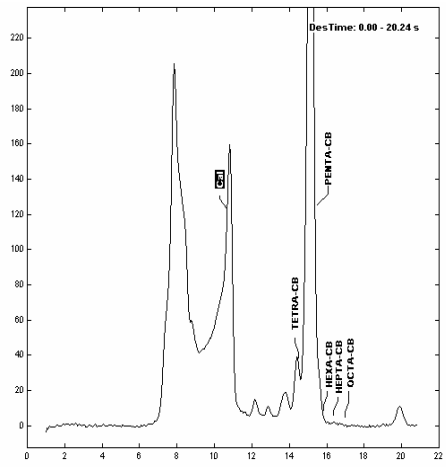
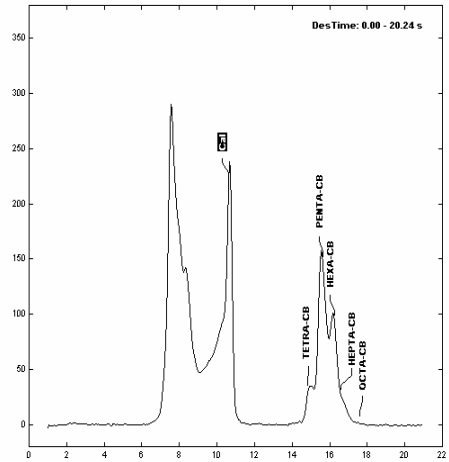


Figure 2.12: IMS analysis of 0.0062 µg PCB loading with sample clean-up up compared with a 0.5 µg loading of liquid standard both desorbed from coarse sand

a) 0.0062 µg PCB loading with SPE clean-up



b) liquid standard, 0.5 µg PCB loading



In the soil extract not cleaned using SPE (Figure 2.11), the only peak seen that may be attributed to PCB is the tetra-CB homolog with a small shoulder at penta-CB. However the typical PCB fingerprint is not present, as seen in the liquid PCB standard (Figure 2.11b), indicating that the peak at tetra-CB may not be due to the PCBs. In fact, the Aroclor 1260 used for the preparation of the PCB stock standard contains no tetra-CB homologs, therefore the presence of this peak cannot be attributed to the PCBs. The loss of the PCB peaks may be due to reduced ionization of the PCBs caused by the presence of co-extracted compounds that may have higher ionization affinity or might be present in much higher abundance. This will reduce the amount of PCBs that are ionized and detected by the IMS.

When a soil extract had been passed through the SPE cartridges, penta-CB was detected. Figure 2.12a illustrates an SPE-cleaned extract of 0.006 µg PCB loading to the IMS. In this scan, the extract concentration is 100 fold lower than the non-cleaned extract given in Figure 2.11a. The penta-CB peak seen in this scan (Figure 2.12a) is much higher than seen in the liquid standard indicating the peak is not due only to the penta-homologs. Also, the typical PCB fingerprint used to identify PCBs by IMS is not detected in the SPE-cleaned extract. This may be due to the presence of interfering compounds that were not removed by the SPE cartridges. As the extract was applied in acetone, the small amount of acetone present during extract application to the SPE cartridges may have carried over compounds from the extract or contaminants from the SPE cartridge.

The comparison of IMS response for PCBs in an acetone standard and PCBs in the Florisil cleaned extract of spiked soils can be seen in Table 2.11 and Figure 2.13. In Figure 2.13, the Cum Amp value for total PCBs in the Florisil-cleaned extracts appears to

provide increased detection based on the higher Cum Amps. However, upon inspection of Table 2.11, the homologs that are detected in the Florisil cleaned extracts do not compare to the homologs from the standard PCB solutions in acetone. As seen in Figure 2.11 and Figure 2.12 the Florisil cleaned extracts were comprised mainly of tetra-CB and penta-CB, including high levels of these two homologs in the blank extracts. On the other hand, the acetone standards showed the two main homologs (hexa-CB and hepta-CB) that comprise the Aroclor 1260 used to prepare the PCB standards and spikes. Figure 2.14 illustrates acetone extracts of clean blank potting soil treated with Florisil and a combination of Florisil with silica gel. In both cases small peaks are seen in the IMS scans for tetra-CB and penta-CB. These peaks would indicate that the blank soil extract is not a major source of the increased response of penta-CB in the SPE cleaned extracts.

Table 2.11: IMS response comparison between PCBs in acetone standards and PCBs from Florisil cleaned extracts of spiked soil.

	PCBs in Acetone Standards IMS Response as Cum Amp (du)				
µg PCB /10g soil	**Tetra**	**Penta**	**Hexa**	**Hepta**	**Total PCBs for Acetone Standards**
0.107	314	0	572	519	1405
0.250	0	0	3595	3451	7152
0.533	65	0	6736	4574	11375
1.066	0	0	9749	11230	20979
2.665	0	0	13936	11920	25913
5.012	0	77	8197	14485	22985

	PCBs in Florisil cleaned extracts of spiked soil IMS Response as Cum Amp (du)				
µg PCB /10g soil	**Tetra**	**Penta**	**Hexa**	**Hepta**	**Total PCBs for Florisil Cleaned Soil Extracts**
0	426	5116	0	0	5542
0	23411	3207	0	0	26618
0	24605	13484	0	0	76178
Average	16147	7269	0	0	36113
STD	13628	5466	0	0	36263
0.107	29611	695	0	0	30306
0.107	47001	20127	83	0	134422
0.107	1992	8717	78	0	21574
Average	26201	9846	54	0	62101
STD	22697	9765	47	0	62784
0.533	76871	18383	0	0	95254
0.533	13108	2483	0	0	15591
Average	44990	10433	0	0	55423
STD	45087	11243	0	0	56330
5.33	43722	6463	0	0	100370

Figure 2.13: Comparison of total PCBs in acetone standards and PCBs in Florisil -cleaned extracts of spiked soil by IMS.

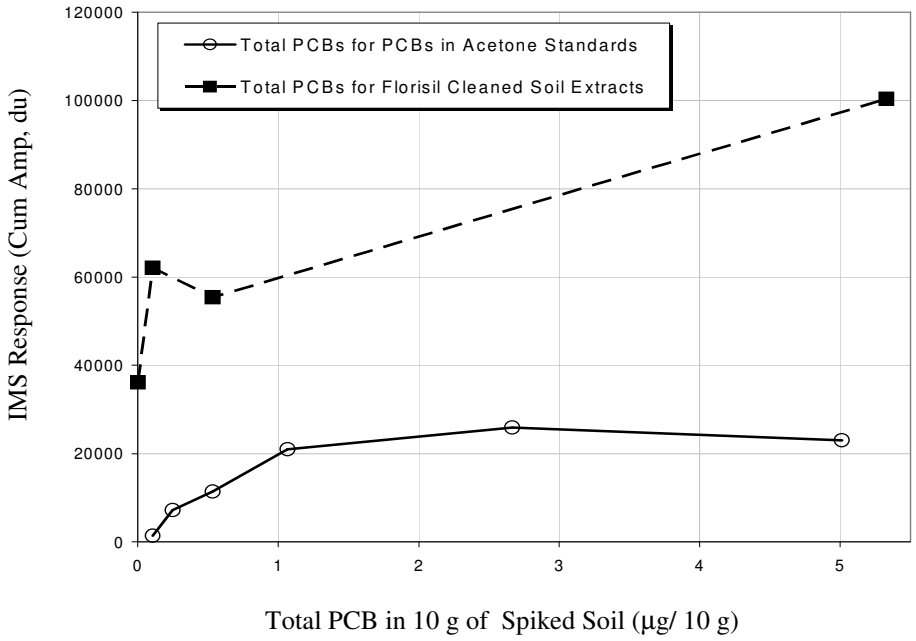
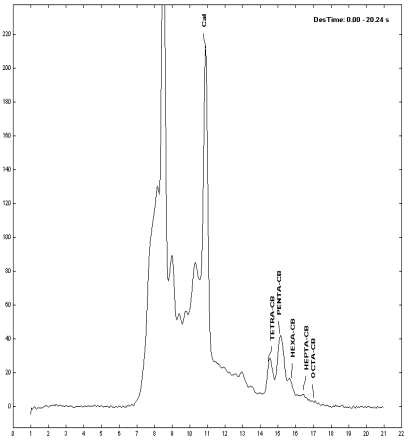
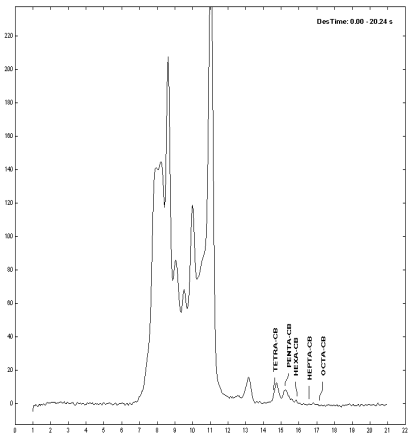


Figure 2.14: Comparison of Florisil and Florisil with silica gel for clean-up of extract of blank soil

a) using Florisil



b) using Florisil and silica gel



2.3.5 Thermal Desorption of PCBs from Solid Phase Extraction Media

Until this point in the investigation, all desorptions into the IMS were conducted using 1 g of clean coarse sand in the sample card holder. The sample to be desorbed was added to the coarse sand as a liquid, either from a standard solution or from a soil extract. In this portion of the investigation, the sand was replaced with 0.25g of Florisil.

The results for the repeated desorptions of 1 µg PCB from the acetone standard and the extracted spiked soil are provided in Table 2.12 and Figure 2.15. Examples of the IMS scans for the desorption and detection of 1 µg PCB in an acetone standard and in extracted soil are illustrated in Figure 2.16 and Figure 2.17, respectively.

It can be seen in Table 2.12 that the desorption patterns from Florisil for the PCB homologs in the soil extract differed from those from the acetone standard. The predominant peaks in the PCB standard were penta-CB and hexa-CB, with the typical PCB fingerprint (Figure 2.16). The soil extract desorbed from Florisil showed the predominant peaks at tetra-CB, with smaller peaks at penta-CB and hexa-CB and no PCB fingerprint present (Figure 2.17). The intensity of the tetra-CB peak in the soil extract was similar to those found in the cleaned soil extracts (Table 2.11), where the greatest portion of the total Cum Amp was due to species eluting at the position of tetra-CB. When the total Cum Amp were plotted against desorption number (Figure 2.15), the PCB standard provided increasing levels of PCBs slowly desorbed until the 36^{th} desorption, when the process was stopped. This curve indicates that Florisil was able to retain the PCBs. Release of the PCBs in a liquid standard from Florisil at 330°C was found to be very slow. Not all of the 1 µg PCBs in the acetone standard were released after the 36^{th}

desorption, as indicated by the increasing slope of this line. The graph for PCBs desorbed from Florisil (Figure 2.15) would indicate that desorption of the PCBs from the soil extract was complete, as the desorption curve began to level off after the 22nd desorption. However, when the Cum Amp values for the peaks due to the PCBs only (penta-CB and hexa-CB) were summed and plotted for both of these desorptions (Figure 2.15), the result for PCBs present in the soil sample was much lower than for the standard solution. The total Cum Amp for the sum of penta-CB and hexa-CB in the soil extract represented only 11.5% of the sum for the penta-CB and hexa-CB Cum Amps in the standard. This indicates that there was still a remaining interference that was not resolved when analyzing the soil extracts by IMS.

Table 2.12: Comparison of 1 µg of PCB loading to the IMS from a standard solution in acetone and soil extract desorbed with anvil temperature of 330℃. (data used for Figure 2.15)

Desorption Number	1 µg PCB STD in acetone on 0.25 g Florisil						1 µg PCB in extract on 0.25 g Florisil					
	Tetra-CB	Penta-CB	Hexa-CB	Hepta-CB	Total PCBs	Total Cumulative Amplitude	Tetra-CB	Penta-CB	Hexa-CB	Hepta-CB	Total PCBs	Total Cumulative Amplitude
1	0	0	905	0	905	905	0	785	547	0	1332	1332
2	0	2677	2912	0	5589	6494	11723	0	0	0	11723	13055
3	0	4777	3199	0	7976	14470	21277	0	0	0	21277	34332
4	0	4332	3172	0	7504	21974	9293	0	366	0	9659	43991
5	0	2912	1566	0	4478	26452	6362	0	510	0	6872	50863
6	0	3476	1918	0	5394	31846	3481	0	570	0	4051	54914
7	0	811	744	0	1555	33401	2560	0	511	0	3071	57985
8	0	2452	1319	0	3771	37172	1688	0	470	0	2158	60143
9	0	2727	1522	0	4249	41421	1303	0	489	0	1792	61935
10	0	2969	1799	0	4768	46189	1033	0	426	0	1459	63394
11	0	2505	1441	0	3946	50135	718	0	346	0	1064	64458
12	0	2452	1529	0	3981	54116	902	0	400	0	1302	65760
13	0	2248	1268	0	3516	57632	580	0	292	0	872	66632
14	0	2265	1500	0	3765	61397	848	0	516	0	1364	67996
15	0	1947	807	0	2754	64151	205	268	391	0	864	68860
16	0	1652	938	0	2590	66741	132	133	242	0	507	69367
17	0	1821	1020	0	2841	69582	178	0	285	0	463	69830
18	0	1711	1109	0	2820	72402	0	128	0	0	128	69958
19	0	1794	1128	0	2922	75324	0	245	227	0	472	70430
20	0	1696	1160	0	2856	78180	0	299	239	0	538	70968
21	0	1683	1167	0	2850	81030	0	227	311	0	538	71506
22	0	1165	978	0	2143	83173	0	258	214	0	472	71978
23	0	1141	541	0	1682	84855	0	196	207	0	403	72381
24	0	1381	695	0	2076	86931	0	0	0	0	0	72381
25	0	908	883	0	1791	88722	0	204	222	0	426	72807
26	0	995	833	0	1828	90550	0	187	0	0	187	72994
27	0	985	731	0	1716	92266	0	0	0	0	0	72994
28	0	864	708	0	1572	93838	0	178	145	0	323	73317
29	0	1041	684	0	1725	95563	0	136	0	0	136	73453
30	0	706	624	0	1330	96893	0	0	0	0	0	73453

Figure 2.15: Comparison of 1 µg of PCB loading to the IMS from a standard solution in acetone and soil extract desorbed from 0.25g Florisil at an anvil temperature of 330 ℃.

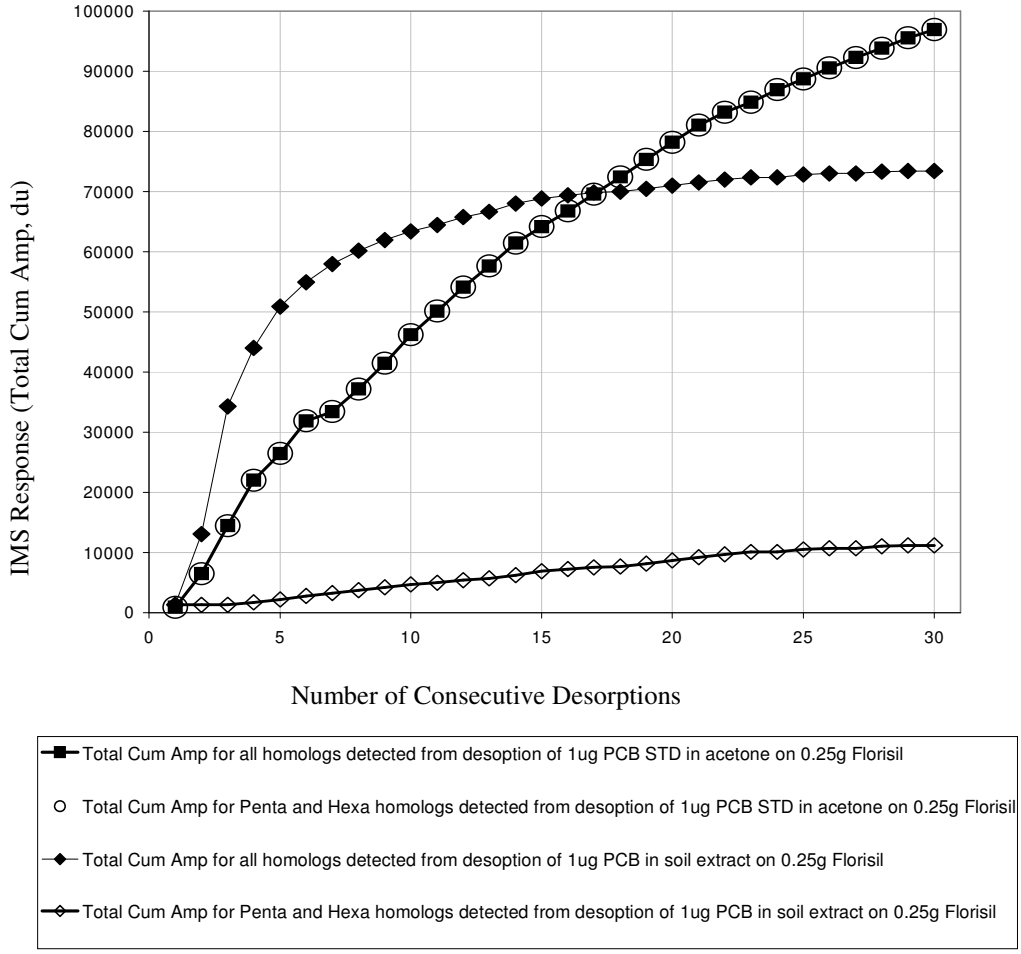


Figure 2.16: Desorption of 1 µg PCB in acetone standard.

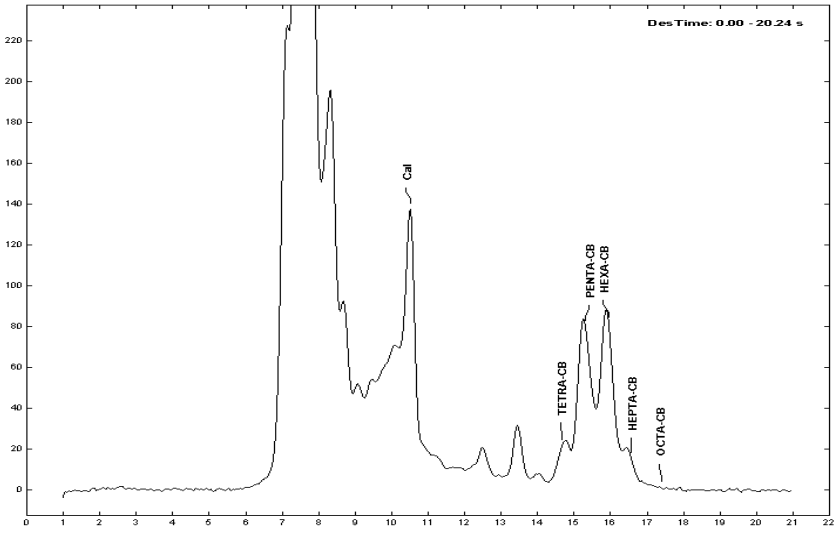
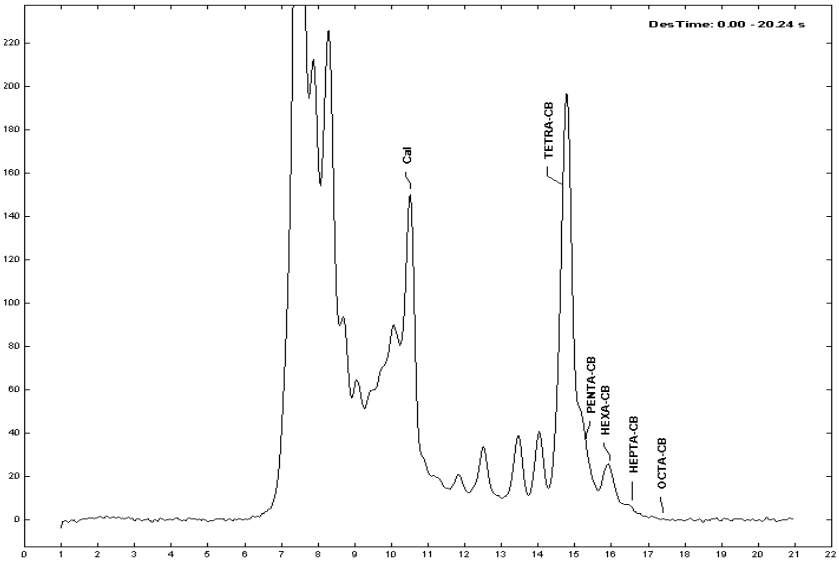


Figure 2.17: Desorption of 1 µg PCB in extracted spiked soil.



2.4 Conclusions

Spiking of a clean soil extract with PCBs provided proof that the soil matrix interfered with the IMS analysis of PCBs. These interferences result from co-extracted matrix compounds such as humic and fulvic acids. Soil extracts spiked with a liquid standard showed lower response for PCB homologs. The use of solid phase extraction media was not found to be effective for the removal of humic and fulvic acids from the soil extract. Extracts treated with one or both of the sorbents tested (Florisil and silica gel) resulted in loss of the PCB fingerprint pattern used for verification of the of the PCB homologs. Without the presence of this fingerprint pattern there was no confirmation that the compounds identified were indeed resulting from PCBs. Loss of this pattern due to sample preparations is significant as PCBs do not significantly degrade in the environment and lost of heavier PCB homologs to environmental transport is limited therefore the fingerprint pattern should be identifiable.

A comparison of thermally desorbed PCB (1 μg loading) from Florisil was also conducted as a method of reducing the effect of matrix compounds. The 1 μg loading of PCBs was applied as a liquid standard to the Florisil. This sample was desorbed 36 consecutive times without completely removing all the PCBs from the Florisil. Conducting the same procedure using spiked soil extract indicated complete desorption of PCBs within 20 consecutive desorptions. However the desorption pattern seen in the IMS scan still lack the PCB fingerprint pattern used for identification of the PCB homolgs as seen in the liquid extracts.

Previous work [4,5] has shown that IMS provides a rapid on-site analysis for PCBs in coarse sandy soil. However in the presence of humus-rich soil IMS has been found to be unsuitable for the direct thermal desorption of PCBs due to combustion of humus in the soil. Extraction of the PCBs from humus-rich soil was used to separate the PCBs from combustible material in the soil. However IMS analysis proved unable to adequately detect and identify the presence of PCBs in extraction solvent.

2.5 References

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2. Simpson N. J. K. 2000. Solid Phase Extraction, Principles, Techniques, and Applications, Marcel Dekker Inc.

3. Supelco Co., 2005, Sample Preparation Applications, Supelco 2005/2006 Catolog.

4. Orton, M.L., Gregor, D.J., and Weir, D., EnviroAnalysis 2002, Proceeding of the Fourth Biennial International Conference on Monitoring and Measurement of the Environment, Toronto, Canada, May, 517, 2002

5. Orton, M.L., and Gregor, D.J., Attachment 8 of Environmental Technology Verification: ToxSense™ Analysis of PCB Contaminated Soil for SNC Lavalin at Ramore, Ontario – Description and Verification of Selected Sample., CanDetec Inc. Confidential Report, June, 2004.

3. Gas Chromatographic Analysis

3.1 Equipment

An SRI Instruments model 310 ultracompact field portable gas chromatograph (GC) equipped with a dry electrolytic conductivity detector (DELCD) was used for the separation and detection of total PCBs. The GC system was fitted with a direct injection port that permitted on-column injections. A 1 µL volume of the liquid extraction solvent was injected into the GC using a 10 µL syringe. Total PCBs separation was compared using uncoated 0.53 mm I.D. Silcosteel tubing with a 0.5 m 0.53mm I.D. and a Silcosteel column coated with 0.5 µm MXT-1.

Both ambient air and dry compressed nitrogen (N_2) were used as carrier gas for this GC Ambient air was supplied from a built-in compressor through a make-up gas line to the detector at a flowrate of 10-20 mL/min to provide oxygen for combustion of organic compounds in the DELCD. Throughout this work the detector heater and reactor temperatures remained unchanged at 300°C and 1000°C respectively.

Integration of the eluted peaks was conducted using Peak Simple Chromatographic Data System (SRI Instruments) installed on a 486 personal desktop computer. This integration software required manual initiation at the time of injection. The raw data and integration results were automatically stored by Peak Simple software on this computer.

A vortex type mixer equipped with a one-touch variable speed mixer capable of 100 to 3200 rpm was used to mix the standards.

Ultrasonic water bath; equipped with digital timer, capable of ultrasonic frequency sweep from 50 to 60 Hz was used for the extraction of spiked soils.

3.2 Determination of GC Conditions for the Separation of Total PCBs

Total PCBs were directly transferred to the detector using the deactivated Silcosteel tubing, where only the halogenated compounds provided a signal for quantitation. Next a 0.5 m MXT-1 column was used to separate the PCBs as a group from other matrix compounds. The detector selectivity for halogenated compounds allowed for a faster analysis time, as separation of the PCBs from other non-halogenated compounds was not necessary. Results obtained with a transfer line were compared to results obtained with the use of an analytical column with a 0.5 μm MXT-1 stationary phase. The length and column coating in conjunction with the column flowrates and temperature program were optimized to provide a fast separation for total PCBs that would allow 10 min. or less between injections. This time criteria was chosen to maximize the sample turn-around time in the field.

3.2.1 Liquid PCB Standards

3.2.1.1 Total PCB Stock Solution

A stock solution of Aroclor 1260 was prepared from neat Aroclor 1260 stock standard (Supelco). Acetone (2-4 mL) was added to two vials, each containing neat Aroclor 1260. The Aroclor 1260 in each vial was dissolved by mixing using a vortex-type mixer. The content of each vial was transferred to a pre-weighed 10 mL volumetric flask using a disposable glass pipette. The acetone was removed from the Aroclor 1260 with a stream of dry compressed N_2, arranged so that the N_2 flow entered the bulb of the volumetric flask through a 20 gauge needle. The needle supplying the N_2 was not allowed to come into contact with the acetone solution. Once all acetone had evaporated, only neat

Aroclor 1260 remained in the volumetric flask. The flask was reweighed to determine the weight of neat Aroclor 1260 by difference. Acetone (approx. 5 mL) was then added to the volumetric flask. The flask contents were mixed to dissolve the Aroclor 1260. Once all Aroclor 1260 had dissolved, the flask contents were diluted to the mark with acetone. Table 3.1 provides the final concentration for the Aroclor 1260 stock solution. The flask was stoppered and shaken well to mix the contents. The stock standard was then partitioned between six 1.5 mL vials, sealed with Teflon-faced silicon septa and hole top screw caps. All vials with stock standard were stored at 4°C until required.

Table 3.1: Stock Aroclor 1260 Standard Concentration

Empty Volumetric Flask Weight (g)	31.6892
Volumetric Flask plus Neat Aroclor 1260 (g)	31.7712
Neat Aroclor 1260 Weight (g)	0.0820
Final Dilution Volume (mL)	10.00
Final Concentration of Stock Aroclor 1260 Standard Solution (µg/mL)	8200

3.2.1.2 Serial Dilutions

A solution of Aroclor 1260 prepared to a nominal concentration of 500 µg/mL was used in section 3.2.2 for the determination of GC column and GC conditions for the separation of total PCBs in acetone. This solution was prepared by diluting 65 µL of the stock standard (8200 µg/mL total PCBs as Aroclor 1260) with 1 mL of acetone in 1.5 mL vial fitted with a Teflon-faced silicon septa in a hole top screw cap. A 100 µL syringe was used to measure the stock solution and a 500 µL syringe was used to measure the acetone.

A dilution series of Aroclor 1260 was prepared in two steps to provide a range of total PCB concentrations (as Aroclor 1260). Intermediate level standards (1230 – 4100 µg/mL) were prepared from the stock standard solution (Table 3.2). Low range standards (1.23 – 820.0 µg/mL) were prepared using standards from the intermediate standard

series (Tabel 3.3). Each series was prepared by dilution of an aliquot of the selected standard with an aliquot of acetone in a 1.5 mL vial. Size appropriate syringes were used for each measurement. Vials were sealed using Teflon-faced silicon septa and hole top screw caps. Each standard was thoroughly mixed using a vortex-type mixer.

Table 3.2: Dilutions for intermediate PCB standard solutions in acetone for GC analysis

Intermediate Concentration (µg Total PCB /mL)	Volume 8200 µg/mL Stock Aroclor 1260 Standard Solution (µL)	Volume Acetone (µL)	Total Dilution Volume (µL)
4100	500	500	1000
2050	250	750	1000
1230	150	850	1000

Table 3.3: Dilution data for low range PCB standard solutions in acetone for GC analysis

Serial Dilution Concentration (µg Total PCB /mL)	Stock Aroclor 1260 Standard Solution (µL)	Concentration of Standard Used for Dilution (µg/mL)	Volume Acetone (µL)	Total Dilution Volume (µL)
820	100	8200	900	1000
615	300	2050	700	1000
410	50	8200	950	1000
205	100	2050	900	1000
123	100	1230	900	1000
103	90	1230	990	1080
80.4	20	4100	1000	1020
61.5	50	1230	950	1000
24.1	20	1230	1000	1020
12.2	10	1230	1000	1010
6.12	5	1230	1000	1005
2.46	2	1230	1000	1002
1.23	1	1230	1000	1001

3.2.2 Determination of GC Conditions and Column Selection for the Separation of Total PCBs

The effect the oven temperature ramp had on the injector temperature and therefore on the rate at which the solvent and PCBs would evaporate was investigated by placing a K-type thermocouple inside the injector. The tip of the thermocouple was placed at the point where injected liquid would exit the syringe. Actual oven and injector temperatures were recorded and plotted against run time. For this investigation, the initial oven temperature

was set to 50°C and held for 1 min. The oven temperature was then increased to 300°C at a rate of 100°C/min. and held at 300°C for 3 min. The oven temperature readings were recorded from the digital oven temperature readout on the GC. Injector temperature readings were recorded from the thermocouple readout.

An initial determination for total PCBs was conducted using a 5.8 m long 0.53 mm I.D. deactivated Silcosteel tubing to transfer the PCBs directly to the detector. To determine the optimal GC conditions, an acetone solution of Aroclor 1260 was prepared to a nominal concentration of 500 µg/mL (see section 3.2.1.2). Using the transfer line, PCB migration was based on the boiling points of Aroclor 1260 components. The initial oven temperature was held at 50°C for 1 min. The temperature was then increased by 75°C/min to a final temperature of 250°C. The carrier gas and detector make-up gas was ambient air at a flow rate of 10 and 10 mL/min, respectively. The detector heater temperature was 300°C, and the reactor temperature was maintained at 1000°C. The upper oven temperature (300°C) was chosen to ensure the removal of all trace contaminants.

A second investigation was conducted using a 0.5 m x 0.53 mm I.D. Silcosteel column coated with 5 µm MXT-1 (a 100% polydimethylsiloxane coating). This column was tested with and without a section of 0.5 m uncoated 0.53 mm I.D. deactivated Silcosteel tubing installed before the MXT-1 analytical column. The installation of this tubing before the analytical column provides a retention gap to focus the PCBs onto the MXT-1 column. The 2 sections were connected using a metal connector fitted with metal ferrules. The 500 µg/mL (nominal concentration) total PCB solution was used for these experiments. Initial oven temperatures were varied between 75, 125, and 150°C and held

for 1 min. The upper temperature rating for the stationary phase was 300° C, so the final oven temperature was reduced to 275°C. The oven temperature ramp rate was set to 75°C/min. As the column coating needed to be protected from oxidation at higher temperatures, the carrier gas was changed to purified dry N_2 at a flow rate of 10 mL/min. Ambient air was used for detector make-up gas at a flowrate of 10 mL/min.

3.2.3 Dry Electrolytic Conductivity Detector Response to Total PCBs

After the determination of the optimal choice of GC column and conditions were completed, the detector response curve for total PCBs in acetone was evaluated using the low range PCB standards. A 1µL volume of each standard solution was injected into the GC and integration was started by depressing the space bar on the system computer. Each standard concentration was injected in triplicate. The average raw peak area counts were then plotted against the standard concentration.

3.2.4 Limit of Detection

The limit of detection (LOD) was determined for total PCBs using a 0.5 m long 0.53 mm I.D. 5µm MXT-1 Silcosteel column between two 0.5 m long 0.53 mm I.D. segments of uncoated deactivated Silcosteel tubing with an oven temperature program of 150° C held for 0.5 min, increased 75°C /min to 250°C and held for 3 min, with N_2 column flowrate of 20 mL/min and ambient air detector make-up gas flow of 10 mL/min. Using these conditions, seven repeat injections of 1 µL of the 1.23 µg/mL total PCB standard solution were made. Peak heights were determined using the Peak Simple software for each injection.

The LOD was calculated for this method by determining the instrument response for seven repeat analyses by GC for the lowest standard concentration (1.23 µg/mL). The average peak height for total PCBs and the standard deviation were calculated based on these seven repeat analyses. For a population of seven data points, the Student's t-value was obtained from reference tables [1] where the number of degrees of freedom (n) was determined as the number of repeat analyses minus one (n = 7 – 1 = 6). The LOD was then calculated by multiplying the Student's t-value [1] (t = 2.447) at the 95% confidence level for the seven repeat analyses, see Equations 3.1.

Equation 3.1 $$LOD = t_{value} \times H_{1.23}$$

Where: t_{value} = value from Student's t-value[1] at the 95% confidence level for 6 degree of freedom

= 2.447

$H_{1.23}$ = average peak height for 7 repeat analysis of 1.23 µg/mL total PCB standard solution

3.2.5 Extraction of Spiked Soils

To determine extraction conditions, recovery and precision, humus-rich soil was spiked with Aroclor 1260. Commercial potting soil, available at most grocery stores or garden nurseries, was used for this investigation. To this mixture commercial peat moss was added at approximately 10 % w/w. The soil was mixed in a 10 L pail and stored in plastic bags at room temperature. This mixture was used for all soil spikes and extractions.

To determine the effect the matrix had on the response to total PCBs, a series of standards were prepared using the acetone extract of blank soil as the solvent. The soil extract was prepared by sonication of 100 g clean potting soil with 160 mL of acetone for

60 min in a clean 500 mL glass jar fitted with a polyethylene lined screw top. The solution was allowed to settle overnight. An aliquot of 100 mL of the extraction solvent was pipetted into a 250 mL vial, then taken to dryness under a gentle stream of N_2. The dried extract was reconstituted in 10 mL of fresh acetone and mixed well using a vortex mixer. The reconstituted extract was used to prepare a series of diluted standards for the analysis. The results obtained for samples prepared in this way were compared with the results obtained for PCB standards in pure acetone.

To prepare spiked soils, 10 g of potting soil mixture was weighed into a labeled 20 mL vial. An aliquot of PCB standard solution was added to the soil using an appropriately sized syringe. Table 3.4 illustrates the volumes and concentrations of total PCB standard solutions used for spiking potting soil. Solvent was allowed to evaporate from the spiked soils in the fumehood prior to the addition of the extraction solvent. Spiking of potting soil was repeated a minimum of three times at each concentration level or extraction time to be tested.

To each vial 15 mL of solvent was added using a 25 mL solvent dispenser. The vials were capped with aluminum foil-lined screw caps and extracted for varying lengths of time using an ultrasonic bath.

Table 3.4: Total PCB concentration spiked into humus-rich soils

Concentration of Total PCBs in Spiked Potting Soil (µg/g)	Potting Soil Weight (g)	Liquid Standard Used for Spiking Potting Soil (µg total PCB/mL)	Volume Liquid Standard Spiked into Potting Soil (µL)
0.492	10	6	820
0.820	10	10	820
1.640	10	20	820

After completion of the extraction, 6 to 8 mL of the solvent was removed to a second labeled 20 mL vial using a 2 mL disposable glass pipette to allow any suspended soils to

settle. A syringe was used to measure and transfer a 5 mL aliquot of the extraction solvent to a labeled 7 mL vial. The 7 mL vial was placed under a gentle air stream in such a manner as to ensure that no extract was lost. When the extract was concentrated almost to dryness, the remaining solution was transferred to a labeled 1.5 mL vial. The 7 mL vial was then rinsed with three aliquots (each not more than 0.5 mL in volume) of solvent. Each solvent rinse was transferred to the 1.5 mL vial containing the concentrated extract. The 1.5 mL vial was then placed under a gentle stream of air to evaporate the extract to dryness.

After all solvent had been evaporated, the dried extract was reconstituted with 0.5 mL acetone delivered by a syringe. Each vial was sealed using Teflon-faced silicon septum and a hole top screw cap. Each vial was then mixed thoroughly using a vortex-type mixer. Reconstituted extracts were compared to solutions of total PCB prepared at the same concentration as would be obtained for 100% extraction of PCBs from the soil (Table 3.5). Reconstituted extracts that were not used immediately were stored at 4^{o}C.

Table 3.5: Concentration of reconstituted solvent extracts from spiked potting soils

Concentration of Total PCBs in Spiked Potting Soil (µg/g)	Weight of Spiked Potting Soil (g)	Volume of Solvent Used for Extraction (mL)	Volume of Extract Used for Concentration (mL)	Reconstitution Volume (mL)	Concentration of Total PCBs in Reconstituted Extract (µg/mL)
0.492	10	15	5	0.25	6.15
0.820	10	15	5	0.25	10.25
1.640	10	15	5	0.25	20.50

3.2.6 Extraction Time Profile

The optimum solvent for the extraction of PCBs from soil and the time required for maximum extraction efficiency were determined for three solvents: acetone, hexane and a mixture of 50 % acetone in hexane. Triplicate potting soil samples (10 g) were spiked to a concentration of 0.492 µg/g and extracted as described in Section 3.2.5 using 15 mL of

either solvent. Extraction times tested included 5, 10, 20, 25, 30, 35, 45, 60, and 90 min for each solvent.

Spiked potting soil extracts were analyzed using GC/DELCD (see Table 3.8 for detailed GC parameters). The PCB peak area was determined using Peak Simple software. The total PCB concentration was calculated based on a 6.15 µg/mL total PCB in acetone standard. The calculated total PCB concentration was plotted against extraction time to determine extraction time profiles for each solvent. Optimum extraction solvent and extraction time were chosen based on these time profiles.

3.2.7 Extraction Efficiency and Precision

Seven repeat extractions of potting soils spiked at the 0.00, 0.492, 0.820 and 1.64 µg/g total PCBs in soil levels were conducted for 60 min. using ultrasonication [3,4,5,6]. Each extraction and reconstitution of the extract was conducted as outlined in Section 3.2.5. The reconstituted extracts were analyzed using the SRI model 310 GC with a DELCD detector. Total PCB peak area was determined by integration using the Peak Simple software and compared to an external standard of the same concentration to calculate the concentration of extracted total PCBs. The GC conditions are given in Table 3.8. The concentration of total PCBs in soil was calculated (see Equation 3.2) by comparison of the extracted total PCB peak area to that for external liquid standard as prepared in Table 3.6. An external quality control standard at 6.15 µg/mL total PCB in acetone was used to account for variability in the in detector response over the duration of the analysis. All values for calculated concentrations for total PCBs extracted from soil were corrected for any variability using the quality control standard.

Equation 3.2: $$C_{extract} = \frac{A_{extract} \times C_{std} \times R \times E}{A_{std} \times S \times W}$$

Where: $C_{extract}$ = Calculated total PCB concentration in soil (µg/g)

$A_{extract}$ = Peak area for total PCBs in the extract as determined by GC analysis

C_{std} = Concentration of external liquid standard (µg/mL)

R = Volume of reconstitution solvent (mL)

E = Volume of solvent used for the extraction (mL)

S = Aliquot volume of extraction solvent used for concentration of extract (mL)

W = Weight of soil extracted (g)

A_{std} = Peak area for total PCBs in the external liquid standard as determined by GC analysis

Calculated concentrations were compared to the actual spike values and the extraction efficiency was determined based on the percent total PCB recovered from the extracted spiked potting soil (Equation 3.3).

Equation 3.3: $$\%\text{recovery} = \frac{C_{extract}}{C_{spike}} \times 100$$

Where: $C_{extract}$ = Calculated total PCB concentration in soil (µg/g)

C_{spik} = Concentration of total PCBs spiked into potting soil (µg/mL)

Precision was determined based on the percent relative standard deviation (%RSD) for each set of seven repeat extractions as calculated with Equation 3.4.

Equation 3.4: $$\%RSD = \frac{STD}{Avg} \times 100$$

Where: STD = Calculated standard deviation for repeat extraction of total PCBs from spiked soil

Avg = Average calculated concentration of total PCBs extracted from spiked soil (µg/g)

3.3 Results and Discussion

The goal of this research project was to validate an on-site method for the analysis of total PCBs in soil. Factors considered in the development of this method included the need for a fast analysis time that would allow for the separation of PCBs from other potential components in the soil extract using a combination of GC separation and detector selectivity.

Sample analysis time was minimized by the use of a short length column (as provided in Section 3.2). The rapid analysis time for this method was primarily due to the use of a DELCD for the specific detection of halogens[7]. The use of this detector reduced the need for separation of all compounds extracted from the soil as the DELCD responds only to halogen ions in the gas phase. This reduced the number of compounds visible to the detector, thereby reducing the analysis time. Since total PCB determination was the goal, baseline separation of individual congeners was not required. The final analytical method was based on the detector response for a combined peak containing all the PCB congeners to determine a value for total PCBs. The use of these two factors resulted in a rapid sample turnaround time for this method.

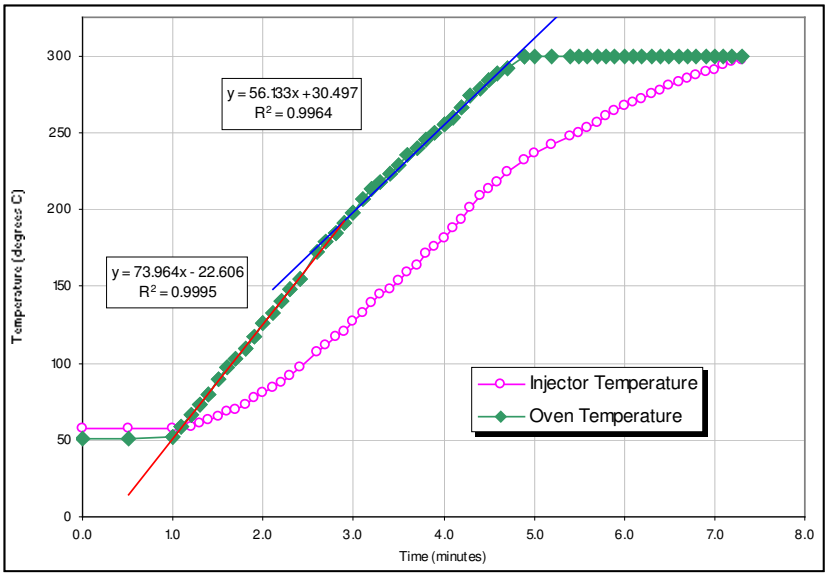
3.3.1 Determination of GC Conditions and Column Selection for the Separation of Total PCBs

In the SRI model 310 GC, the direct on-column injector is housed in a Swagelok fitting inside of the GC oven. The effect this metal fitting had on the actual injector temperature was investigated. The temperature of the injector was monitored by placing a K-type

thermocouple inside at the location where the syringe tip would deposit the liquid. The raw temperature data for this investigation are provided in Appendix 2. Figure 3.1 compares the actual oven temperature recorded while the oven temperature ramp was set to increase by 100°C/min with the injector temperature recorded with the thermocouple. Figure 3.2 illustrates the effect of the actual oven temperature ramp rate on the injector temperature ramp rate.

This experiment confirmed that the actual injector temperature was slower to respond to the oven temperature ramp as the metal body of the Swagelok fitting was slower to reach equilibrium with the oven temperature. It was also discovered that the actual oven temperature did not rise as rapidly as the programmed setting indicated.

Figure 3.1: Comparison of oven and injector temperatures during increase of oven temperature by 100 °C/min (nominal).

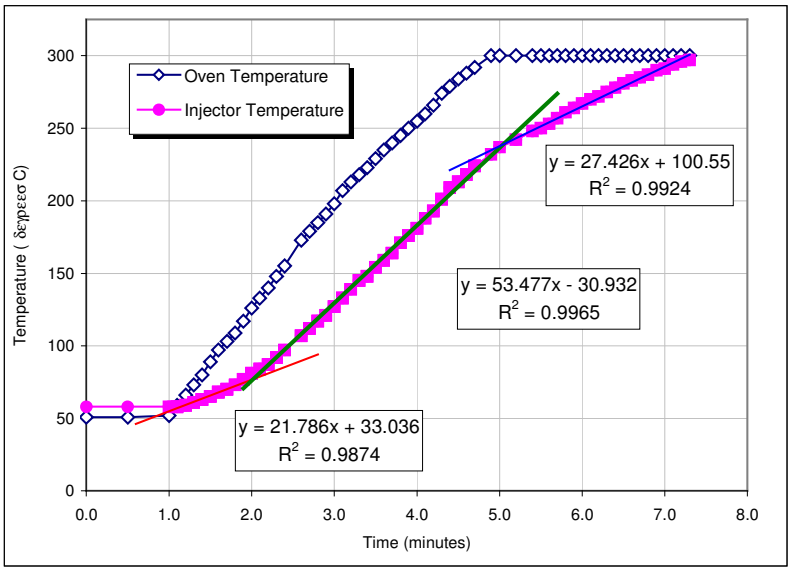


With the oven temperature ramp set at 100°C/min, the oven temperature should have reached the desired final temperature in 2.5 min. However, the oven took approximately 5 min to reach the final temperature setting of 300°C. As illustrated in Figure 3.1, the

actual oven temperature increase could be approximated by two steps. During the first 2.5 min of temperature increase, the GC actually increased the oven temperature at a rate of 74°C/min, with oven temperature at the end of this period equal to 155°C. After reaching an oven temperature of 155°C, the oven temperature continued to increase; however, the rate of temperature increase was found to be lower than in the first step (56°C/min) and continued for an additional 2.4 min until the final oven temperature (300°C) was reached. Overall, the SRI model 310 GC was found to be capable of increasing the oven temperature at an average maximum rate of 64°C/min. As the maximum oven temperature ramp rate was found to be 74°C/min, the maximum temperature ramp rate setting should be no higher than 75°C/min.

The injector temperature was found to increase in three steps (see Figure 3.2). For the first 1.8 min, while the oven temperature was increasing at a rate of 74°C/min, the injector body began to heat up at a slower rate of 22°C/min. After 1 min the injector body began to heat up at a slightly faster rate of 53°C/min until the oven equilibrated at the final oven temperature (300°C). The average rate for the injector temperature was determined to be 45°C/min during the 3.9 min that the oven temperature took to increase to and stabilize at the final temperature setting. Once the oven temperature had stabilized, the injector continued to heat at a slower rate (27°C/min) until the end of the GC run (7.9 min total run time).

Figure 3.2: Effect of 100 ℃/min nominal oven temperature increase on the temperature of SRI on-column injector.

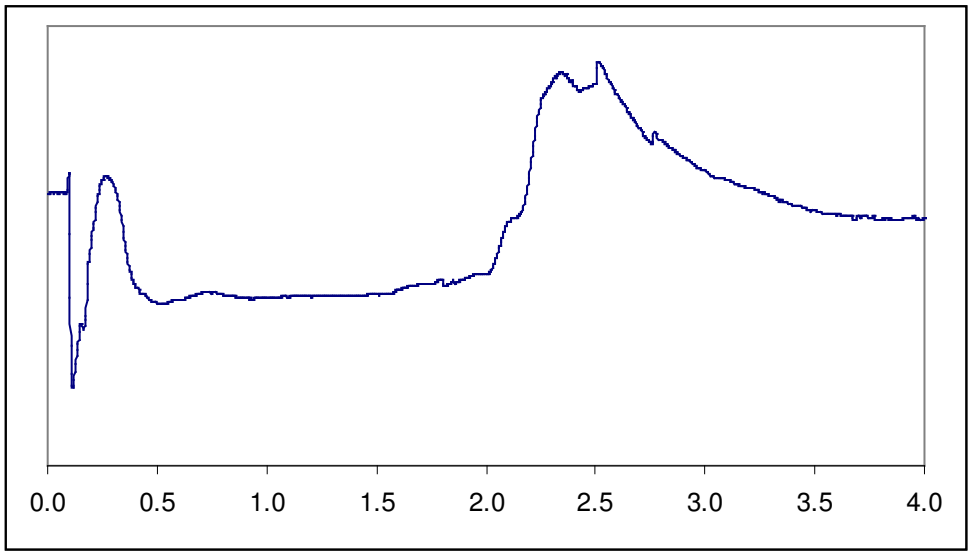


Initially a 5.8 m long, 0.53 mm I.D. segment of deactivated Silcosteel tubing was used to introduce the PCBs into the detector (see Figure 3.3 for sample chromatogram). This tubing acted as a transfer line, which allowed for the fastest separation of the compounds based solely on their volatility. In this case, the PCBs volatilized as the oven temperature increased and traveled the length of the column as rapidly as the oven temperature and carrier gas propelled them. Separation of the compounds could only be achieved due to differences in their boiling points.

In Figure 3.3, the total PCB peak was seen as broad, poorly separated series of 4 peaks. The largest of this series of peaks eluted at 2.33 min. The width of this large combined peak was 2.30 min. This broad peak represented the 166 congeners that made up the 5 homologs of Aroclor 1260. For the purposes of this method separation of the congeners is not required, as only total PCBs will be reported. The separation developed through this

research was intended to be used only as a pre-separation technique, and not to provide complete separation of each component in the mixture. Other halogenated contaminants that could be present in soil (such as pesticides) would be sufficiently separated from the PCBs based on the boiling point. The use of the DELCD provided identification of only the halogenated compounds eluting from the GC[7], thus eliminating the need for separation of PCBs from other non-halogenated compounds.

Figure 3.3: Chromatogram of 536 µg/mL total PCBs (peak at 2.33 min) separated using a 5.8 m long, 0.53 mm I.D. deactivated Silcosteel column. Oven temperature programming was 50 ℃ initial temperature held for 1.0 min, then ramped to 300 ℃ at a rate of 75 ℃ /min. Carrier gas was ambient air at a flow rate of 10 mL/min with 10 mL/min makeup to detector.

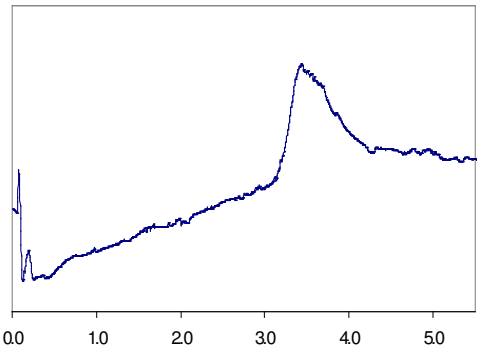


To reduce the total PCB peak width, Aroclor 1260 (500 µg/mL nominal concentration) was injected at varying initial oven temperatures. The oven temperatures tested included 50, 100, 125, and 150°C. Each initial oven temperature was held for 1 min before the oven was ramped by 75°C/min to a final temperature of 300°C. Chromatograms of the eluting PCB peak are provided in Figure 3.4. As the initial oven temperature increased from 50, to 100, to 125 and 150°C, the retention time for the total PCB peak decreased

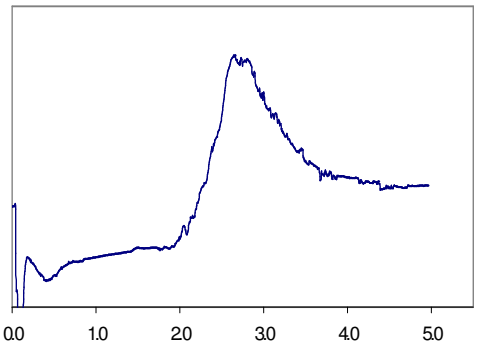
from 3.44, to 2.71, to 2.39 and 1.65 min. Table 3.6 provides the total PCB peak width as measured along the peak base. Using a flowrate of 10 mL/min peak width decreased with increasing initial oven temperature from an average of 2.21 min for 50 to 100°C to 0.73 min at initial oven temperature of 150°C. This decrease in peak width was expected, as at the higher initial temperatures the evaporation of the PCBs was faster.

Figure 3.4: Chromatogram of 536 µg/mL total PCBs separated using a 5.8 m long 0.53 mm I.D. deactivated Silcosteel column. The initial oven temperature was varied (a) 50 °C (b) 100 °C (c) 125 °C (d) 150 °C. held for 1 min then ramped to 300 °C at a rate of 75 °C /min and held for 3 min. Carrier gas is ambient air at a flow rate of 10 mL/min with 10 mL/min makeup to detector.

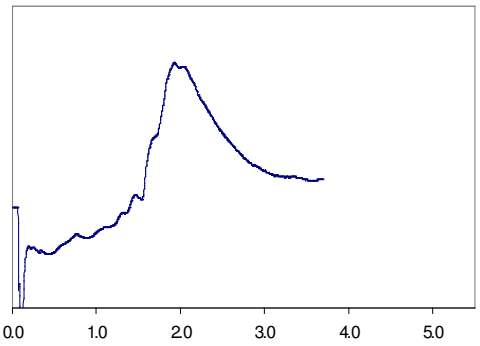
(a) Initial oven temperature set to 50 °C



(b) Initial oven temperature set to 100 °C



(c) Initial oven temperature set to 125 °C



(d) Initial oven temperature set to 150 °C

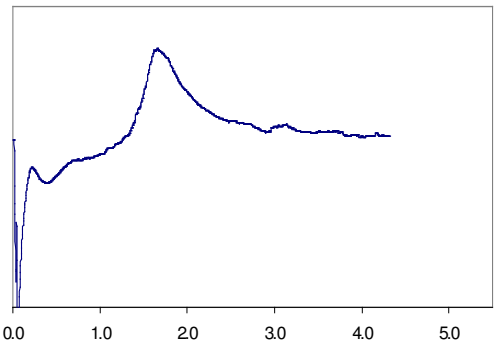
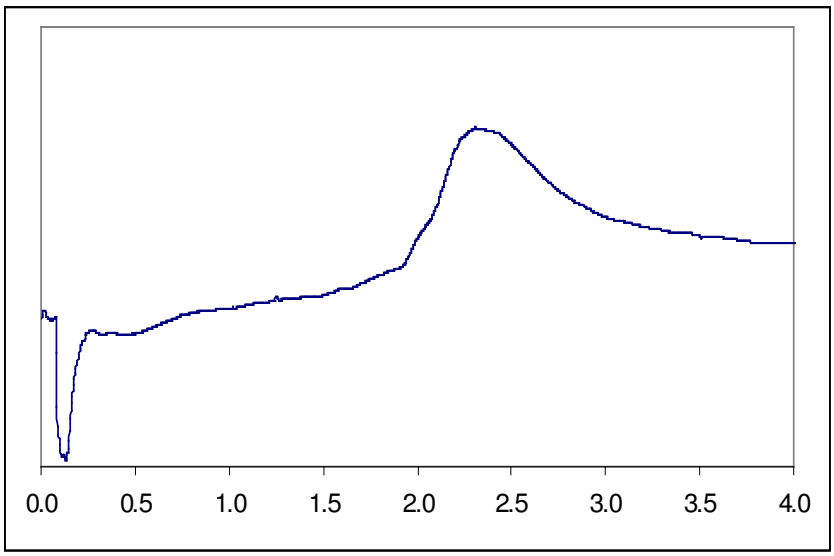


Table 3.6: Total PCB peak width at varying initial oven temperatures

Initial Oven Temperature (°C)	50	100	125	150	50
Ambient Air Flow rate (mL/min)	10				20
Peak Start Time (min)	2.97	1.91	1.34	0.92	1.39
Peak End Time (min)	5.18	4.22	3.15	1.65	2.36
Peak Width (min)	2.21	2.31	1.81	0.73	0.97

Figure 3.5: Chromatogram of 536 µg/mL total PCBs (peak at 2.31 min) separated using a 5.8 m long 0.53 mm I.D. deactivated Silcosteel column. Oven temperature programming was 50 ℃ initial temperature held for 1.0 min then ramped to 300 ℃ at a rate of 75 ℃ /min. Carrier gas was ambient air at a flow rate of 20 mL/min with 10 mL/min makeup to detector.



To sharpen the PCB peak using the 5.8 m long 0.53 mm I.D. deactivated Silcosteel column and bring all homolog peaks together, the air flow rate was increased to 20 mL/min. All other chromatographic parameters were kept constant. The resulting chromatogram is illustrated in Figure 3.5. In this chromatogram, the PCBs eluted at 2.31 min as a single, generally symmetrical peak with a small shoulder on the rising side. The increase in flowrate improved the peak shape but not the peak width, which was 0.97 min. The temperature range that the PCBs elute at could be determined using the oven temperature ramp of 75 °C/min. The PCBs started to elute at approximately 79°C and

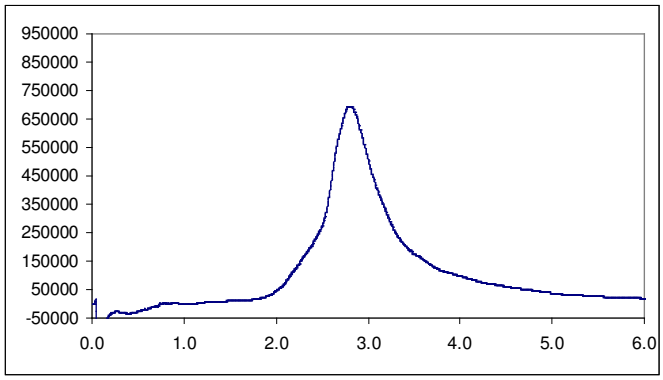
finished at a temperature of 185°C. The PCB peak apex occured at an oven temperature of approximately 148°C.

To improve peak shape and selectivity, the column was changed from the 5.8 m, 0.53 mm I.D. uncoated segment of deactivated Silcosteel tubing to a 0.5 m, 0.53 mm I.D. Silcosteel column coated with 5 µm MXT-1, a 100% polydimethylsiloxane coating. A section of deactitavted tubing (transfer line) was left in place at the outlet of the analytical column. As can be seen in Figure 3.6, the retention time for total PCBs decreased as the initial oven temperature increased. The retention times decreased from 2.82, to 2.03, to 1.63 min for the initial oven temperatures of 75, 125, and 150°C, respectively. However, these peaks appeared very broad, with peak widths at the base of 3.30, 2.10 and 3.58 min (Table 3.7) for the initial oven temperatures of 75, 125, and 150°C, respectively. The transfer line was moved to the front of the MXT-1 analytical column, to act as a retention gap. The total PCB peak appeared sharper on the leading edge (see Figure 3.7).

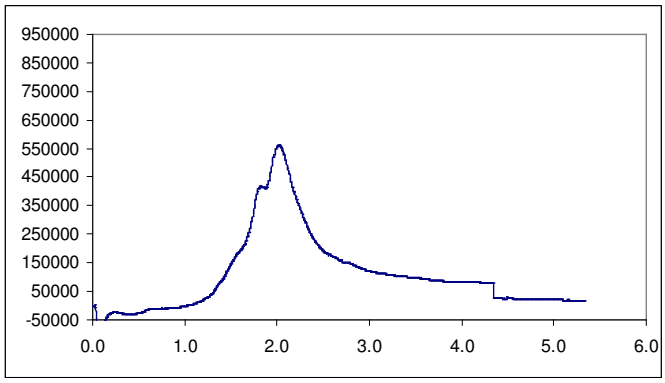
Even though the final oven temperature was reduced to 250°C to protect the analytical column, the high temperature from the detector inlet (300°C) caused deterioration of the stationary phase. The degradation products can be seen in Figure 3.7 as a series of peaks on the tailing edge of the total PCB peak that continue to elute for the full 7 min run time. This configuration of retention gap followed by the MXT-1 analytical column was only tested using an initial oven temperature of 75°C due to the decomposition of the stationary phase. Therefore the use a transfer line at the end of the analytical column was important to protect the column phase from breaking down due to the elevated temperature at the detector inlet.

Figure 3.6: Chromatogram of 536 µg/mL total PCBs separated using a 0.5 m long 0.53 mm I.D. MXT-1 Silcosteel column followed by 0.5 m long 0.53 mm I.D. segment of deactivated Silcosteel tubing. The initial oven temperature was varied (a) 75 °C, (b) 125 °C, (c) 150 °C then ramped to 275 °C at a rate of 75 °C /min and held for 3 min. Carrier gas was N_2 at a flow rate of 10 mL/min, with ambient air as detector make-up gas at 10 mL/min.

(a)Total PCB retention time 2.82 min, using an initial oven temperature of 75 °C



(b)Total PCB retention time 2.03 min, using an initial oven temperature of 125 °C



(c) Total PCB retention time 1.63 min, using an initial oven temperature of 150 °C

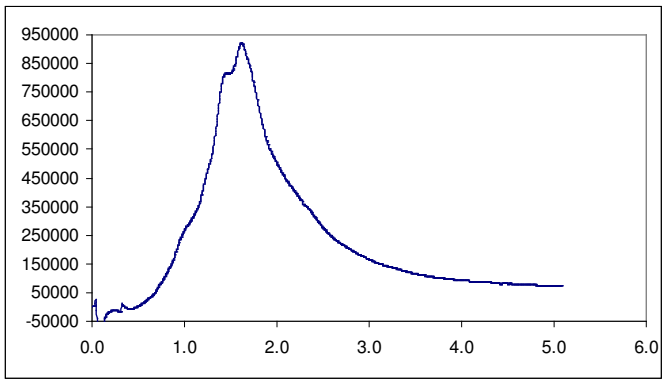
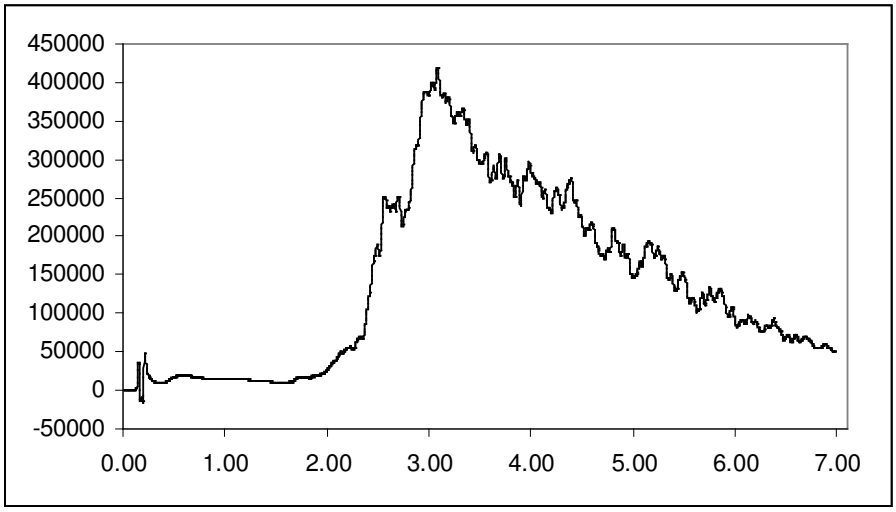


Figure 3.7: Chromatogram of 536 µg/mL total PCBs separated using 0.5 m long 0.53 mm I.D. deactivated Silcosteel tubing (retention gap) followed by a 0.5 m long, 0.53 mm I.D. MXT-1 Silcosteel column. The initial oven temperature was 75 ℃ then ramped to 275 ℃ at a rate of 75 ℃ /min and held for 3 min. Carrier gas was N_2 at a flow rate of 10 mL/min, with ambient air as detector make-up gas at 10 mL/min.



To prevent deterioration of the stationary phase the carrier gas was changed to N_2 at a flowrate of 20 mL/min. The make-up gas flowrate was 10 mL/min ambient air. Using N_2 as the carrier gas the effect of the retention gap on the peak shape can be seen in Figure 3.8. In this figure the oven was set to three different initial temperatures: 75, 125 and 150°C. The oven was then ramped to 250°C at a rate of 75 °C/min. The effect of varying the initial oven temperature on the retention time of total PCBs using the MXT-1 column located between two 0.5 m sections of deactivated tubing can be seen in Figure 3.8. The retention time for the total PCBs was 1.78, 1.11, and 0.75 min for initial oven temperatures of 75, 125 and 150°C, respectively. The total PCB peak was focused onto the analytical column by the retention gap. This occured because the retention gap allows complete evaporation of the injected liquid without interaction with a stationary phase. The vapourized components then focus as a narrower band onto the stationary phase of

the analytical column. The effect of this improvement in peak width is illustrated in Figure 3.7. The peak widths were reduced to 1.54, 1.23, and 1.07 min for initial oven temperatures of 75, 125 and 150°C, respectively. The optimal initial oven temperature was determined to be 125°C. At this temperature the total PCB peak occurs at 1.23 min. This provides a fast analysis with some retention of the PCBs to reduce the potential of interference form lower boining halogenated compounds. The use of a retention gap and transfer line provided the best total PCB peak shape and was used for the remainder of this research.

Table 3.7: Peak width comparison for the MXT-1 analytical column equipped with a 0.5 m retention gap and a transfer line at the end for initial oven temperatures of 75, 125 and 150 °C.

	Retention Gap Preceding MXT-1 Analytical Column			**Retention Gap and Transfer Line connected to MXT-1 Analytical Column**		
Initial Oven Temperature (°C)	75	125	150	75	125	150
Peak Start Time (min)	1.76	1.09	0.43	1.17	0.68	0.21
Peak End Time (min)	5.06	3.19	4.01	2.71	1.91	1.28
Peak Width (min)	3.30	2.10	3.58	1.54	1.23	1.07

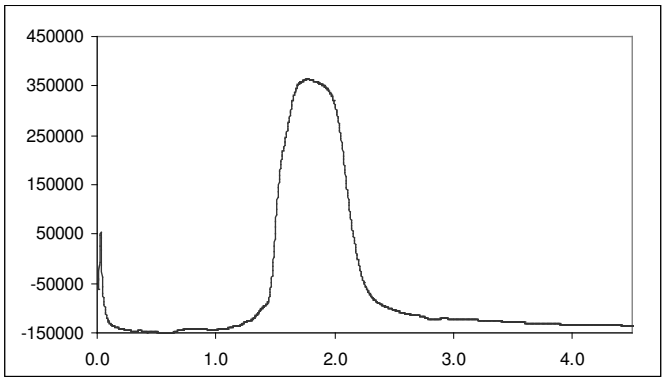
Table 3.8 summarizes the GC conditions and column selection providing optimum separation and sample turnaround time for the analysis of total PCBs as discussed in this section.

Table 3.8: Gas chromatographic condition for the analysis of total PCBs in soil extracts

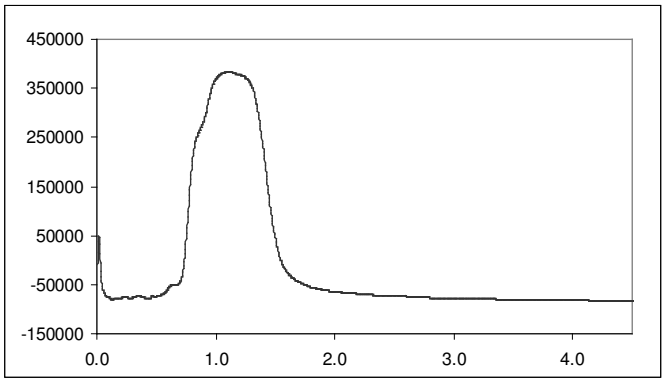
Injection	1 µL On-column
Retention gap	0.5m 0.53mm I.D. deactivated Silcosteel tubing
Analytical Column	0.5m 0.53mm I.D. 5µm MXT-1 Silcosteel column
Transfer line	0.5m 0.53mm I.D. deactivated Silcosteel tubing
Carrier Gas	N_2: flow rate 20 mL/min
Oven Temperature Program	Initial Temp: 125°C, hold 0.5 min; ramp 75°C/min to 275°C, hold 3 min
Detector	Dry Electrolytic Conductivity Detector (DELCD)
Detector Make-up	Ambient Air: flow rate 10 mL/min
Detector Heater Temperature	300°C
Detector Reactor Temperature	1000°C
Detector Attenuation	Medium

Figure 3.8: Chromatogram of 536 µg/mL total PCBs separated using a 0.5 m long, 0.53 mm I.D. MXT-1 Silcosteel column between using both a retention gap before the column and a transfer line after the column.

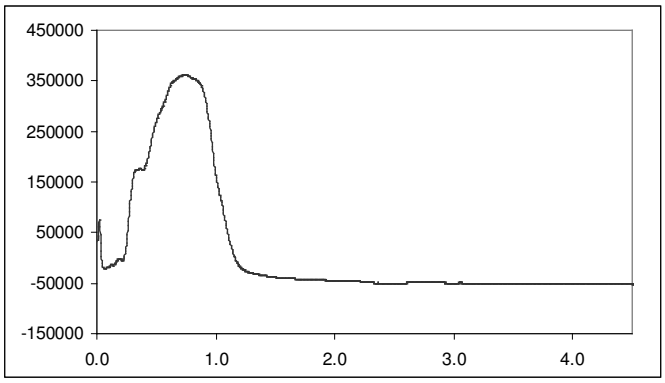
(a) Total PCB retention time 1.78 min, at initial oven temperature of 75 ℃



(b) Total PCB retention time 1.11 min with a shoulder at 0.83min, initial oven temperature of 125 ℃



(c) Total PCB retention time 0.75 min with a shoulder at 0.33min, initial oven temperature of 150 ℃



3.3.2 Dry Electrolytic Conductivity Detector Response to Total PCBs

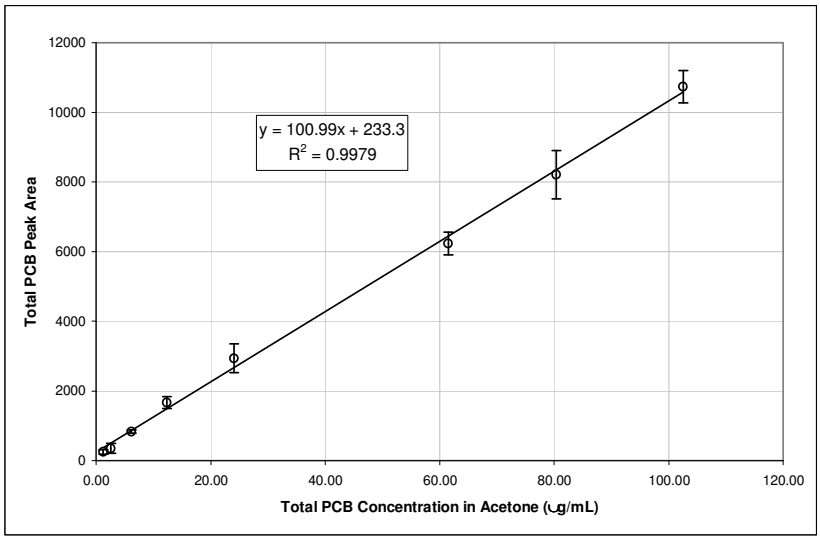
The dry electrolytic conductivity detector was developed for the determination of halogen ions in the gas phase. A reaction cell within the detector oxidizes vapourized organic molecules eluting from a GC column in a 1000°C oxygen-rich environment[7]. Under these conditions all eluting organic molecules are mineralized, with the residual halogens retaining a negative charge as gas phase ions. Detection of these ions allows for selective analysis of molecules such as organochlorine pesticides and PCBs without interferences from non-halogenated compounds that would occur with an electron capture detector[1].

The response of the DELCD to total PCBs was determined using a 0.5 m long, 0.53 mm I.D. MXT-1 Silcosteel column placed between two sections of deactivated Silcosteel tubing (0.5 m by 0.53 mm I.D.) with an oven temperature program of 125°C held for 0.5 min, increased at 75°C/min to 250°C and held for 3 min, with N_2 column flow rate of 20 mL/min and ambient air detector make-up gas at 10 mL/min. Using these conditions, 1µL of each total PCB solution was injected a minimum of three times from lowest to highest concentration. The peak areas were determined for each injection using Peak Simple software. Table 3.9 provides the average response for total PCBs in acetone, raw data for this table is presented in Appendix 3

Table 3.9: DELCD response to total PCBs

Total PCB Liquid Standard Concentration (µg/mL)	Average Peak Area	Peak Area STD
1.23	250.08	68.885
2.56	403.90	23.895
6.15	836.05	51.994
12.30	1667.56	172.655
24.10	2938.04	409.883
61.50	6232.89	328.136
80.40	8211.82	690.144
102.50	10740.50	463.948

Figure 3.9: Dry electrolytic conductivity detector response to total PCBs



The total PCB peak area for each standard was averaged, and the standard deviation (STD) was calculated. The results are presented in Table 3.9. The DELCD showed linear response for a range of total PCBs in acetone between 1.23 and 102.50 µg/mL as illustrated in Table 3.9.

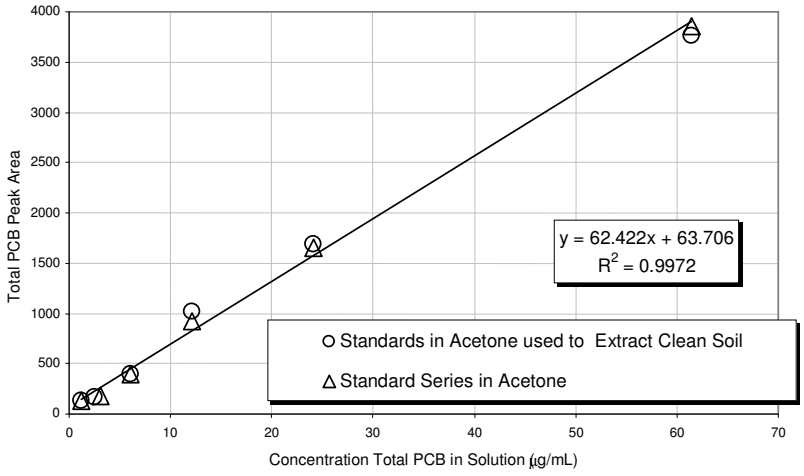
Prepared reconstituted clean soil extract spiked with PCBs to levels equivalent with the acetone standards were analyzed in triplicate by GC. GC results for total PCB peak areas are presented in Table 3.10. The results are also illustrated graphically in Figure 3.10.

Table 3.10: Detector response for total PCB peak areas determined for standards in pure acetone and extracted clean potting soil spiked to the same concentration.

Liquid Standard Concentration (µg/mL)	Acetone	Soil Extract	Confidence Interval for Spiked Soil Extracts
1.23	129.52	133.06	2.45
2.46	175.88	166.73	2.16
6.12	394.90	395.07	2.45
12.18	923.64	1021.07	2.45
24.12	1656.79	1685.70	2.45
61.50	3857.88	3763.20	2.45

The data in Table 3.10 indicates that the total PCB peak areas obtained for the two sets of solutions were very similar The confidence intervals for the triplicate PCB spiked soil extracts were within the Student's *t*-value at the 95% confidence level of 4.303 This indicates that the soil matrix components extractable with acetone did not interfere with the analysis of total PCBs by this method. Figure 3.10 illustrates the comparison of these two sets of standards.

Figure 3.10: Comparison of the detector response to total PCBs in pure acetone with the same concentration standards prepared by spiking the acetone extract of clean potting soil.



3.3.3 Limit of Detection

Table 3.11 provides the average peak height and standard deviation based on the raw peak height data for seven repeat injection of the 1.23µg/mL liquid standard. The limit of detection was estimated based on these data. The standard deviation was multiplied by the student t-test value[1] for the number of degrees of freedom (n). In this case n was equal to 6, making the t-test value equal to 2.447[1]. The resulting limit of detection was 0.511 µg/mL of the liquid standard. This LOD indicates that approximately 70 ng/g total PCBs can be detected by this method in soil when 10 g of contaminated soil is extracted with 15 mL acetone, with a concentration of the extract by a factor of 10. To detect PCB contamination in soils at levels lower than 70 ng/g, either a larger soil amount needs to be extracted, or a larger concentration factor should be used. For example, the 5 mL aliquot of the soil extract could be taken to dryness and reconstituted in 0.25 mL of fresh solvent. This would give a concentration factor of 20 and allow analysis of contaminated soils at levels as low as 45 ng/g total PCBs.

Table 3.11: Data and calculated limit of detection of total PCBs as Aroclor 1260 in acetone based on seven repeat injection of a 1µL of 1.23 µg/mL solution.

n	Total PCB Peak Height	Calculated LOD as Concentration Total PCBs (µg/mL)
1	14.88	
2	11.30	
3	16.86	
4	11.42	
5	13.77	
6	13.89	
7	10.63	
Average	13.25	
STD	2.251	
C.I.	2.082	
LOD	5.51	0.51

3.3.4 Extraction of Spiked Soils

The choice of a solvent for the extraction of an analyte depends in part on the solubility of the analyte in the solvent. The analyte must be soluble in the solvent, and the solvent must be able to come in contact with all surfaces of the media onto which the analyte is bound. PCBs are readily soluble in any number of organic solvents, including polar solvents such as acetone and non-polar solvents like hexane. However, soil has numerous crevices that provide pockets where solvents may not easily penetrate. In addition, even dry soil contains trace amounts of moisture. These two considerations must be addressed when choosing a solvent to be used in soil extraction.

Three solvents were used for the investigation of the extraction time and efficiency of solvent extraction of potting soil spiked with known quantities of total PCBs. These solvents were 99.9 % pure hexane, 99.9 % pure acetone and a solution of 1:1 acetone in hexane by volume. For each solvent extraction test, triplicate spiked levels of total PCBs in potting soil were prepared, extracted, concentrated and reconstituted as described in Section 3.2.5. The calculated concentrations for total PCBs in soil extracts are presented in Table 3.12.

The initial extraction trial was conducted using hexane. The clean potting soil used for this experiment was spiked to a concentration of 0.492 µg total PCBs per gram of soil. The reconstituted soil extract would have a concentration of 6.15 µg/mL assuming 100% recovery. Figure 3.11 illustrates the extraction time profile for total PCBs from potting soil. Table 3.12 provides the calculated concentrations of total PCBs determined by GC/DELCD analysis with comparison to an external standard at 6.15 µg/mL total PCB in acetone. The calculated concentration for total PCBs (µg/mL) as determined in the

solvent extract varied from 5.50 ±3.15 µg/mL for an extraction time of 5 min to 7.25 ±1.74 µg/mL for an extraction time of 60 min with a minimum extracted concentration of 3.61 ±1.24 µg/mL for a 20 min extraction. However as seen in Figure 3.11 the large variations observed for triplicate extractions of spiked potting soil suggest a poor contact of hexane with all surfaces of the soil. To improve solvent/soil contact, hexane was mixed with acetone (50% v/v) and the experiment was repeated.

Table 3.12: Calculated total PCB concentration extracted from 10 g of spiked clean potting soil (0.492 µg total PCB /g soil) for various solvents at as a function of extraction duration using ultrasonication.

Solvent	Extraction Time (min)	Average Total PCB Concentration (µg/mL)	STD
Hexane	5	5.5	3.15
	10	6.1	2.11
	20	3.6	1.24
	27	4.4	2.27
	30	6.0	1.41
	35	6.6	0.53
	45	7.1	1.74
	60	7.3	2.58
50 % Hexane in Acetone	5	4.8	na
	10	3.2	1.07
	15	2.3	0.85
	25	1.5	1.01
	35	3.3	0.52
	45	3.5	3.49
	60	1.6	0.48
	90	1.1	0.96
Acetone	5	5.1	0.51
	10	5.2	0.75
	15	4.7	1.19
	25	5.3	1.87
	35	8.2	0.75
	45	9.8	0.29
	60	8.5	1.83

na: only one result was available

Acetone, a more polar solvent than hexane, has been used to improve the extraction efficiency of organic compounds from soil [3,4,5,6] The use of a 50 % v/v mixture of acetone with hexane was anticipated to improve the solvent contact with the soil by reducing the surface tension between the soil and the solvent. Figure 3.12 illustrates the effect the 50

% v/v acetone/hexane solution has on the extraction time of total PCBs from spiked clean potting soil.

Figure 3.11: Hexane extraction of total PCBs from spiked clean potting soil for various extraction times

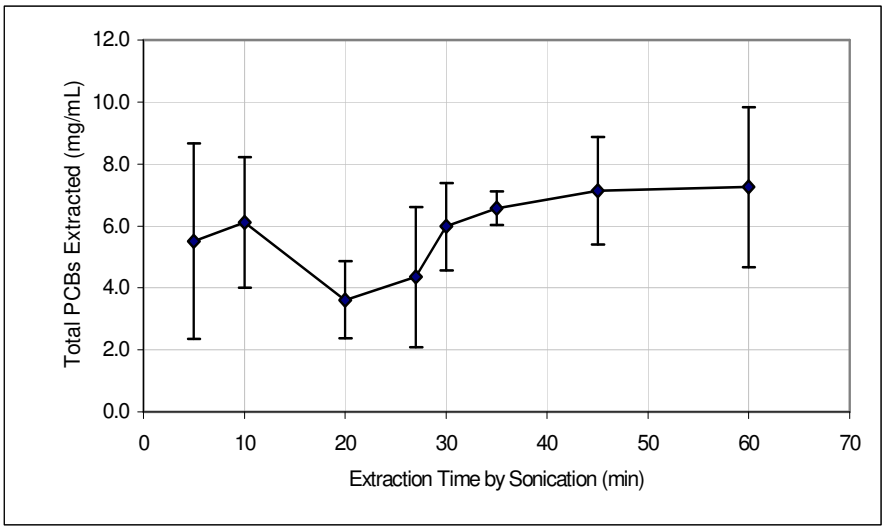
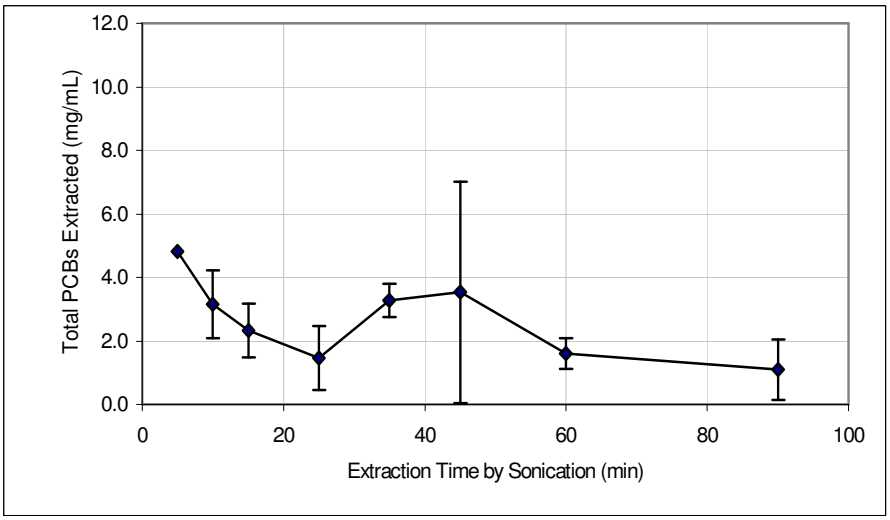


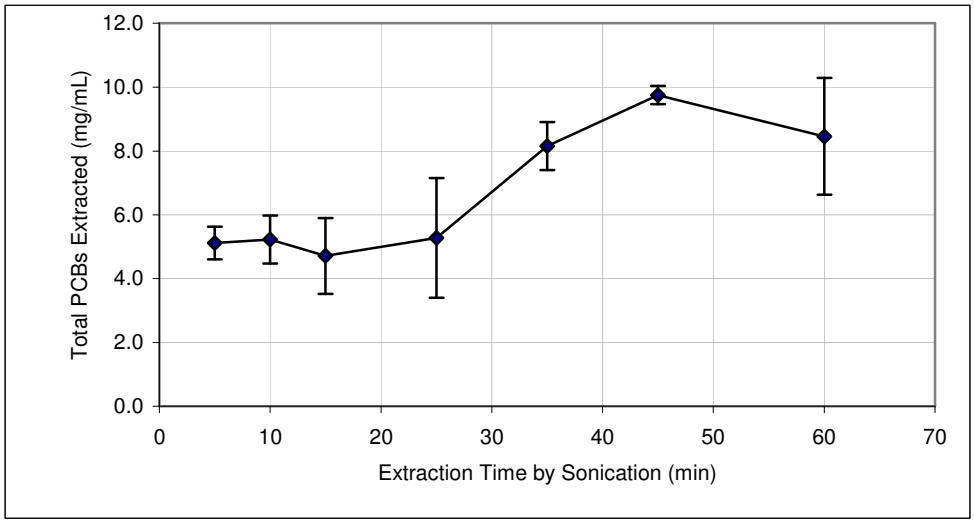
Figure 3.12 Extraction of total PCBs with 50 % acetone in hexane from spiked clean potting soil for various extraction times



When a solution of 50 % acetone in hexane was used to extract total PCBs from spiked clean potting soil, the concentration of total PCBs extracted appeared to decrease with increasing extraction time. Further, as extraction time increased an increasing number of extracts showed two separate liquid phases. This was caused by extraction of moisture

from the soil by the acetone. The increased water content in acetone resulted in formation of a layer of water/acetone that was no longer miscible in hexane. Secondly, it was observed that the quantity of hexane and acetone/water layers that could be drawn off of the soil varied despite extraction time. No attempt was made in this study to quantitatively determine the relationship between extraction time and volume of the acetone/water layer. However, it can be seen from Figure 3.12 that the increased volume of the acetone/water layer generated with increased extraction time resulted in reduced extraction of total PCBs from the spiked soil. The presence of water in the acetone may have acted as physical barrier between the soil and the hexane limiting the extraction of PCBs from the soil.

Figure 3.13: Acetone extraction of total PCBs from spiked clean potting soil for various extraction times



The potting soil and peat moss used to prepare humus-rich soil for spiking were taken directly out of the manufacture's packaging. No attempt was made to determine the moisture content of the soil nor was the soil oven dried. This procedure was followed to keep the sample preparation as simple as possible for use as an on-site analysis technique.

Acetone as a single solvent for extraction was expected to be able to remove the PCBs from the soil despite the presence of trace moisture. The efficiency of acetone as an extraction solvent for total PCBs from spiked clean potting soil is presented in Figure 3.13. Acetone was found to be the most effective solvent. The average amount of total PCBs extracted between 5 and 25 min was found to be 5.1±0.26 µg/mL, as compared to 6.15 µg/mL expected assuming 100% extraction efficiency. After 25 min, the average amount of total PCBs determined in acetone was found to increase to 8.8±0.84 µg/mL. The increse in total PCB concentrations seen in extraction conducted for more than 25 min may be due to loss of solvent as the sample temperature increased with increasing extraction times. In general, the extraction of total PCBs from soil with acetone provided a simple and easy to use technique. The extraction time profile for total PCBs from soil indicates that extraction times as low as 5 min may be used to obtain an effective extraction. However extraction times based on spiked soils may be used only as a guideline as native samples may behave differently.

3.3.5 Extraction Efficiency and Precision

Acetone (99.9 % pure) was used in the determination of PCB extraction efficiency from clean potting soil. The clean potting soil was spiked at four concentration levels: 0.00, 0.492, 0.820, and 1.640 µg total PCBs per gram of soil, and extracted with acetone as per Section 3.27. Table 3.13 provides the calculated concentration of total PCBs determined by GC/DELCD analysis.

Total PCB concentration determined by the extraction of a 0.492 µg/g spiked soil was calculated to be 0.411±0.127 µg/g for triplicate extractions with a recovery of 83.5 %. As

the spiked concentration increased, the extraction recovery decreased to 0.580±0.228 µg/g total PCB in the 0.820 µg/g spiked soil and 0.911±0.585 µg/g total PCB in the 1.64 µg/g spiked soil. The recovery for these last two spiked soils was determined to be 70.7% and 55.6%, respectively. The decrease in extraction recovery with increasing PCB soil concentration may be a result of partitioning of the PCBs between the soil and the solvent. As the concentration of PCBs increases, a greater percentaget of PCBs stay in the soil. Use of an internal standard will help compensate for the reduced extraction efficiency. Careful selection of a compound for use as the internal standard will result in a similar patitioning of the internal standard between the soil and the solvent in a manner similar to that of the PCBs.

Analysis precision was evaluated using the standard deviation for the repeat analyses of each extracted soil and calculated as %RSD (see Equation 3.4). The average %RSD for soils spiked between 0.492 and 0.820 µg total PCB per g of soil was 35.1%. At the higher spike concentration of 1.64 µg/g, the %RSD was calculated to be 57.7%. The high relative standard deviation can be attributed to variations in the extraction conditions. The use of 60 min extraction time resulted in warming of the sample during extraction. Even though the spiked soil samples were all extracted at the same time, some vial caps may have loosened during the extraction allowing for the loss of acetone and thus causing variations in the extract concentration. For this reason it is advisable to utilize an internal standard during extraction.

Both accuracy and recovery should be improved by the addition of an internal standard to the extraction solvent. The use of an internal standard would account for changes in

detector sensitivity over the duration of the analysis and account for any variations in extraction conditions.

Table 3.13: Calculated concentrations and % recovery for the extraction of total PCBs from soil as determined by GC/DELCD

Concentration Total PCBs Spiked into Soil (µg/g)	Calculated Total PCB Concentration by GC/DELCD (µg/g)
0.000	0.030
0.000	0.028
0.000	0.020
Average	0.026
STD	0.005
%RSD	19.23
% Recovery	NA
0.492	0.317
0.492	0.555
0.492	0.360
Average	0.411
STD	0.127
%RSD	30.93
% Recovery	83.457
0.820	0.280
0.820	0.660
0.820	0.497
0.820	0.563
0.820	0.970
0.820	0.509
Average	0.580
STD	0.228
%RSD	39.32
% Recovery	70.682
1.640	0.633
1.640	0.779
1.640	0.538
1.640	1.281
1.640	0.378
1.640	1.919
1.640	0.573
Average	0.911
%RSD	57.71
STD	0.585
% Recovery	55.566

3.4 Conclusions

A method for on-site analysis of total PCBs using a field portable SRI model 310 gas chromatograph was successfully developed. This method can be used for PCB screening

in humus-rich soils found in environmentally contaminated areas. The soil was extracted by sonication to provided a portable method of extraction for field use. The concentrated extract was chromatographed on a 0.5m 0.5µm MXT-1 column and detected using DELCD. Peak shape was improved by the use of a retention gap and transfer line. This method was found to have a limit of detection of 0.4 µg/ml in the reconstituted soil extract. This translates to a total PCB concentration of ~70 ng/g PCB in soil. For ease of use at field sites, a nitrogen generator can be used to provide carrier gas. This would eliminate the need for transportation of compressed gas cylinders.

Use of a DELCD detector provided selective quantitation of the PCBs without the need for extensive separation by gas chromatography. Use of a 0.5 m long MXT-1 column provided adequate separation of the PCBs from the matrix, while allowing for rapid sample turnaround time. The analysis time for this method was 7 min, followed by a 5 min cool down time for the oven to return to the initial temperature. The use of the field portable GC for this method will allow on-site soil analysis of total PCBs at any field location where a power source (e.g. a portable generator) is available.

3.5 References

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4 Analysis of Field Samples

4.1 Introduction

The analysis of environmental contaminants is usually conducted in laboratories located in populated centers while the originating contaminated site may be miles away or even remotely located in far northern regions. This distance adds to the cost and time required for completion of analysis as samples must be shipped to the laboratory for analysis. Shipping costs for large numbers of soil samples are high due to the weight of the samples involved. Therefore, limited numbers of samples may only be taken for analysis. This limited number of analyses is then used to delineate large contaminated sites. Basing the clean-up on limited data may increase the costs as excessive amounts of contaminated soil must be removed for treatment to provide a margin of safety. Providing a fast on-site analysis for the determination of environmental contaminants would provide readily accessible information for site delineation and decrease the cost of site clean-up.

To validate the on-site method developed during the research for this thesis, soil samples were obtained from a contaminated landfill in Norway. This landfill had been in use since the 1930's for waste disposal, including domestic household items such as china and furniture, industrial wastes such as transformer oils, cleaning solvents and unidentified chemicals, plus buried unexploded military ordinance leftover from World War Two. This landfill has been closed and the shrubs and grasses above the landfill have been allowed to reestablish. This has provided the soil with a rich source of humus from the decomposition of fallen vegetation.

The PCBs used in Norway during the operation of the landfill were formulated as Chlophen. The formulation of Chlophen was similar in composition to Aroclor 1260 [1]. Therefore Aroclor 1260 was used as the standard for the analysis of soil samples taken from the landfill.

Soil samples were taken during the remediation of this landfill according to the site remediation protocol by Akvaplan-niva of Norway. The samples were split and sent to UniLab, Norway, and the University of Waterloo for analysis. The soil samples received at the University of Waterloo were analyzed using the IMS thermal desorption of soil extracts as outlined in Section 2.2.3 and GC analysis using the field portable GC equipped with a DELCD detector as outlined in Section 3.2.5. Analysis results using the IMS and the GC/DELCD were compared to laboratory results obtained from UniLab, Norway.

4.2 Soil Sampling Procedure

Soils samples were taken at varying depths as outlined in the site remediation protocol by staff from Akvaplan-niva. Samples were transferred to labeled polyethylene bags secured by zippered type closures. Selected samples were mixed to ensure even distribution of any PCBs and divided into two portions. One portion was transferred to UniLab for analysis. The other was returned to the Akvaplan-niva laboratory where the soil was dried at 30°C overnight in a conventional laboratory oven. The dried samples were then shipped to the University of Waterloo for analysis in labeled polyethylene bags secured by zippered type closures.

4.3 Field Soil Analysis Procedure by IMS

4.3.1 Equipment

A model 350 IonScan (available from Smiths Detection, Mississauga, Ontario) was used for all IMS analyses. The model 350 IonScan included self-contained integration software. Instrument operating conditions are given in Appendix 1.

A vortex type mixer (available form Fisher Scientific) equipped with one touch variable speed control capable of 100 to 3200 rpm was used for mixing solutions and dissolving dried extract in reconstitution solvent. An ultrasonic water bath (manufactured by Crescent Ultrasonic Corporation) equipped with a digital timer, heater, and degas function, capable of ultrasonic frequency sweep from 50 to 60 Hz, was used for sample extraction.

4.3.2 Preparation of Liquid PCB Standards

Liquid standards were prepared in acetone using a certified 1000 µg/mL Aroclor 1260 standard solution available from Supelco. Five standard solutions were prepared over the range of 0.1 to 10 µg/mL. The 10 µg/mL standard was used to prepare the lower two concentration (0.1 and 0.5 µg/mL) analytical standards. The dilutions used to prepare the analytical standards are provided in Table 4.1.

Table 4.1: Preparation of liquid standards for the analysis of total PCBs by IMS

Volume of Stock Standard Used (µL)	Concentration of Stock Used (µg/mL)	Volume of Acetone for Dilution (µL)	Final Solution Volume (µL)	Final Concentration of Analytical Standard (µg/mL)
10	9.90	1000	1010	0.10
55	9.90	1000	1050	0.52
1	1000	1000	1001	1.00
5	1000	1000	1005	4.98
10	1000	1000	1010	9.90

4.3.3 Preparation and Extraction of Field Samples

Any large clumps found in the oven dried soil samples received from Akvaplan-niva were crushed by hand to provide fairly uniform consistency. A 10 g sample of soil was weighed into labeled 20 mL vials, extracted for 60 min using ultrasonication, concentrated and reconstituted prior to IMS analysis as outlined in Section 2.2.3.

4.3.4 IMS Analysis

4.3.4.1 Analysis of Standards

A new Teflon sample card was thermally desorbed in the IMS inlet to remove any trace contamination prior to use. A 1 g sample (±0.01g) of coarse clean sand was weighed onto the Teflon sample cards. At each concentration level, 100 µL of the liquid standard was applied to the sand on the sample card. One minute was allowed for the solvent to evaporate prior to analysis. The sample card was covered with two 2 µm Whatman glass fiber filters to prevent fine particles from entering the IMS inlet. The sample card was desorbed in the IMS inlet for 20 sec at 330°C in negative ion mode (explosives mode). Appendix 1 provides operating conditions for the IMS. The drift tube and inlet temperatures were set to 115°C and 230°C, respectively. Desorptions were repeated 5 consecutive times to ensure all PCBs were removed from the standard. The 5 µg/mL

analytical standard was used as a quality control standard to identify and correct for potential instrument drift. For this purpose, the 5 µg/mL standard was repeated after every fifth soil sample. The 5 analytical standards were repeated again at the end of the soil analysis.

IMS integration provided cumulative amplitude (Cum Amp) values for tetra-CB, penta-CB, hexa-CB, and hepta-CB in the IMS scan. These values were recorded in an Excel spreadsheet. Consecutive desorptions of the same standard were conducted until all analyte was removed from the sample card. Cum Amp values for PCB homologs in each of the consecutive desorptions were recorded and summed to provide a value for the total amount of tetra-CB, penta-CB, hexa-CB, and hepta-CB, which were then summed to determine the Cum Amp for total PCBs found as a result of all consecutive desorption. This procedure was repeated for each of the standards.

4.3.4.2 Analysis of Field Samples

An aliquot (100 µL) of the reconstituted field sample extract was added by a syringe to a 1 g portion (±0.01g) of clean coarse sand on a new Teflon sample card. The solvent was allowed to evaporate from the sample for approximately 1 min. Two 2 µm Whatman glass fiber filters were used to cover the sample card as before. Each sample was consecutively desorbed in the same manner as the liquid standards on clean sand, see Section 2.2.1.2. The integration values for the PCB homologs from each consecutive desorption were tabulated and summed to obtain a value for total PCBs for the soil sample. This value was used to calculate the concentration of total PCBs (see Equation 4.1) using the QC standard as the external standard.

Equation 4.1:

$$C_{sample} = \left(\frac{CumApm_{Sample} \times C_{Std}}{CumAmp_{Std}} \right) \times \frac{DilutionFactor}{W_{Sample}}$$

Where:

C_{Sample}	=	Calculated concentration of total PCBs in the soil sample
$CumAmp_{Sample}$	=	Total cumulative amplitude determined for a minimum of 5 consecutive desorption of a 100 µL aliquot of the reconstituted sample soil extraction.
$CumAmp_{Std}$	=	Total cumulative amplitude determined for a minimum of 5 consecutive desorption of a 100 µL aliquot a standard solution.
C_{Std}	=	Concentration of the standard used for quantitation (µg/mL)
Dilution Factor	=	see Equation 11
W_{Sample}	=	Weight of soil sample used in extraction

Equation 11:

$$DilutionFacor = \frac{V_{Solvent}}{V_{Ext}} \times V_{\text{Recon}}$$

Where:

$V_{Solvent}$	=	Volume of solvent used for extraction (mL)
V_{Ext}	=	Volume of soil extract used for concentration (mL)
V_{Recon}	=	Volume of solvent used to reconstitue the dried sample extract (µL)

4.4 Field Soil Analysis Procedure by GC/DELCD

4.4.1 Equipment

An SRI Instruments model 310 field portable GC equipped with a dry electrolytic conductivity detector (DELCD) was used for the separation and detection of total PCBs. The GC system was fitted with a direct injection port that permitted on-column injections. Total PCB separation was conducted using 5 m, 0.53mm I.D. Silcosteel megabore column coated with 0.5 µm MXT-1 stationary phase and mounted between two 0.5 m segments of 0.53 mm I.D. Silcosteel tubing.

Peak integration was conducted using Peak Simple Chromatographic Data System installed on a 486 personal desktop computer. The raw data and integration results were automatically stored by Peak Simple software on this computer.

4.4.2 Liquid PCB Standards

A stock solution of Aroclor 1260 was prepared from neat Aroclor 1260 stock standard (available from Supelco) as per Section 3.2.1. The stock standard was stored in 1.5 mL vials sealed with Teflon-faced silicon septa and hole top screw caps. All vials of stock standard were stored at 4°C until required. This solution was used to prepare a series of solutions to be used in the GC/DELCD analysis.

The PCB dilution series was prepared in two steps to provide a range of concentrations of total PCBs (as Aroclor 1260). Intermediate level standards (1230 – 4100 µg/mL) were prepared from the stock standard solution as provided in Section 4.3.2 of this thesis. Low range standards (1.23 – 80.39 µg/mL) were prepared using standards from the intermediate standard series. Standards were stored in 1.5 mL vials sealed using Teflon-faced silicon septa and hole top screw caps.

4.4.3 Extraction of Spiked Soils

A sample of the dried soil (10 g) was weighed into a labeled 20 mL vial. To each vial, 15 mL of HPLC grade acetone was added using a 25 mL solvent dispenser. The vials were capped with aluminum foil-lined screw caps and extracted for 60 min using an ultrasonic bath. Extraction time was controlled using the timer on the ultrasonic bath. Each soil sample was extracted a minimum of three times to determine the average total PCB concentration.

After completion of the extraction, 6 to 8 mL of the solvent was removed to a second labeled 20 mL vial using a 2 mL disposable glass pipette. Any suspended solids were allowed to settle by gravity. A syringe was used to measure and transfer a 5 mL aliquot of

extraction solvent to a labeled 7 mL vial. The 7 mL vial was placed under a gentle air stream in such a manner as to ensure that no extract was lost. When the extract was concentrated almost to dryness, the remaining solution was transferred to a labeled 1.5 mL vial. The 7 mL vial was then rinsed with three aliquots (each not more than 0.5 mL in volume) of solvent. Each acetone rinse was transferred to the 1.5 mL vial containing the concentrated extract. The 1.5 mL vial was then placed under a gentle stream of air to evaporate all solvent from the extract.

After all solvent had been evaporated, the dried extract was reconstituted with 0.5 mL acetone delivered by a syringe. The vial was sealed using a Teflon-faced silicon septum and a hole top screw cap. Each vial was then mixed thoroughly using a vortex-type mixer. Reconstituted extracts were analyzed by GC or stored for future analysis at 4°C.

4.4.4 Chromatographic Analysis

Liquid standards and soil extracts were analyzed by GC/DELCD using the conditions outlined in Table 4.2. A 1 µL injection volume, using a typical 10 µL GC syringe, was analyzed for both liquid standards and soil extracts.

Table 4.2: Gas chromatographic conditions for the analysis of total PCBs in soil extracts

Injection	1 µL On-column
Retention gap	0.5 m, 0.53mm I.D. deactivated Silcosteel tubing
Analytical Column	0.5 m, 0.53mm I.D. 5µm MXT-1 Silcosteel column
Transfer line	0.5 m, 0.53mm I.D. deactivated Silcosteel tubing
Carrier Gas	N_2: flowrate 20 mL/min.
Oven Temperature Program	Initial Temp: 125°C hold 0.0 min, ramp 50°C/min. to 300 °C.
Detector	Dry Electrolytic Conductivity Detector (DELCD)
Detector Make-up	Ambient Air: flowrate 10 mL/min.
Detector Heater Temperature	300°C
Detector Reactor Temperature	1000°C
Detector Attenuation	Medium

A series of 5 liquid standards were analyzed at the beginning of each day's analysis followed by the soil extracts. To minimize the effect of possible detector drift, one liquid standard was analyzed after every tenth soil extract. The series of liquid standards analyzed at the beginning of the day were repeated at the conclusion of the day's run.

4.5 Results and Discussion

4.5.1 Soil Analysis by IMS

An attempt was made to determine the concentration of total PCBs using IMS despite the indication that IMS analysis would not be effective for this analysis. Soil samples obtained from the Norwegian landfill were extracted and analyzed by IMS. Two soil samples of different soil composition are used for illustration in this thesis. Soil sample 51 was composed of humus-rich soil and contained leaf, root and plant bark materials. This sample came from a section of the general landfill and was expected to contain any number of environmental contaminants. Soil sample 1S was taken from the site used to dispose of transformer oils outside of a maintenance shop. This soil was sandy and contained little humus. The primary contaminants expected at this site were products associated with equipment maintenance such as oils and degreasing products. For the purpose of this site remediation, only PCBs were being analyzed, as soil containing PCBs had to be removed for treatment in accordance with Norwegian government regulations.

Examples of the IMS scans obtained for two of the Norwegian landfill sites are provided in Figure 4.2and Figure 4.3. A comparison of these two figures with that of a liquid standard (Figure 4.1) illustrates the differences in the pattern of the PCB homologs. The scan of the PCB standard indicates that the Aroclor 1260 used in the preparation of this

standard contained 3 main components (tetra-CB, penta-CB and hex-CB) refer to Figure 4.1. These peaks formed a fingerprint that could be used to identify PCB mixtures containing Aroclor 1260 or PCB mixtures of similar composition, including Chlophen. The mixture of Chlophen used in Norway was found to have a similar make up to that of Aroclor 1260[1] Without evidence of this fingerprint pattern, the identification of peaks in the IMS scan could not be confirmed as that of PCBs.

In the desorption of landfill sample number 51(Figure 4.2 and Figure 4.2b), the IMS only identified 2 peaks (tetra-CB and penta-CB) as PCB homologs. These two peaks do not make up the complete fingerprint pattern for PCB homologs as seen in the desorption of Aroclor 1260 from a standard solution (Figure 4.1). The largest peak in the standard occured for penta-CB. In Figure 4.2, the penta-CB peak was smaller than the one for tetra-CB. This may have been a result of the presence of another compound eluting at the same drift time as the tetra-CB. However, the absence of a peak at hexa-CB would indicate the absence of PCBs in this sample, as hexa-CB should be present along with tetra and penta-CB if the sample contained Chlophen. A cursory inspection of Figure 4.2 would indicate the presence of PCB homologs indicative of Aroclor 1260 or Chlophen. However, once again the largest of these three peaks occurred at tetra-CB, not penta-CB as in the standard. Also, hexa-CB was absent indicating the sample did not contain Chlophen, while GC/ECD analysis provided by UniLab showed it to be present.

Quantitation based on the tetra-CB and penta-CB peaks for sample number 51 is provided in Table 4.3. Analysis of sample 51 by GC/ECD supplied by UniLab of Norway showed a total PCB concentration of 0.224 µg/g., while analysis by IMS showed the sample to have a concentration of 0.832 µg/g total PCBs (but with no positive

identification possible). Despite the fact that the calculated concentration of PCBs determined by IMS was within the same order of magnitude as found by GC/ECD, the lack of fingerprint verification raises doubt in this analysis.

This doubt is illustrated again in soil sample 1S. The IMS scan (Figure 4.3a) of this soil sample extract did not show the PCB fingerprint pattern. Only a peak at the tetra-CB position was present in any of the consecutive desorptions conducted of this extract. Subsequent IMS scans (Figure 4.3b) showed no indication of PCBs being present. Calculation of the PCB concentration in sample 1S by IMS indicated the sample to contain 5.672 µg/g PCB, while GC/ECD analysis provided a PCB concentration of 0.544 µg/g total PCBs. This difference in concentration points to the unreliability of IMS for the analysis of total PCBs in extracted soil samples.

Further comparison of soil samples tested is given in Table 4.3. Of the soils analyzed by IMS, only sample ML5 was comparable to results obtained by GC/ECD. The presence of PCBs in this sample could still not be verified using the PCB fingerprint. Without this fingerprint pattern, peaks seen in the IMS scan could not be verified in the field, leading to inaccurate results.

Table 4.3: Comparison of the total PCB concentrations (µg/g) as determined by IMS analysis with GC/ECD analysis conducted at UniLab in Norway.

Soil Sample ID	Total PCBs Determined by IMS (µg/g)	Total PCBs, UniLab, Norway using GC/ECD (µg/g)	% Difference, IMS Analysis to GC/ECD
1 S	5.67	0.54	1042.6
51	0.83	0.22	371.4
ML 5	0.17	0.29	57.14
5 S	3.92	0.25	1598.8
12 S	5.26	1.10	476.4
13S	9.46	0.73	1290.5

Figure 4.1: Desorption of 0.5µg total PCBs (as 100µL of the 5 µg/mL standard solution of Aroclor 1260 in acetone) from coarse sand

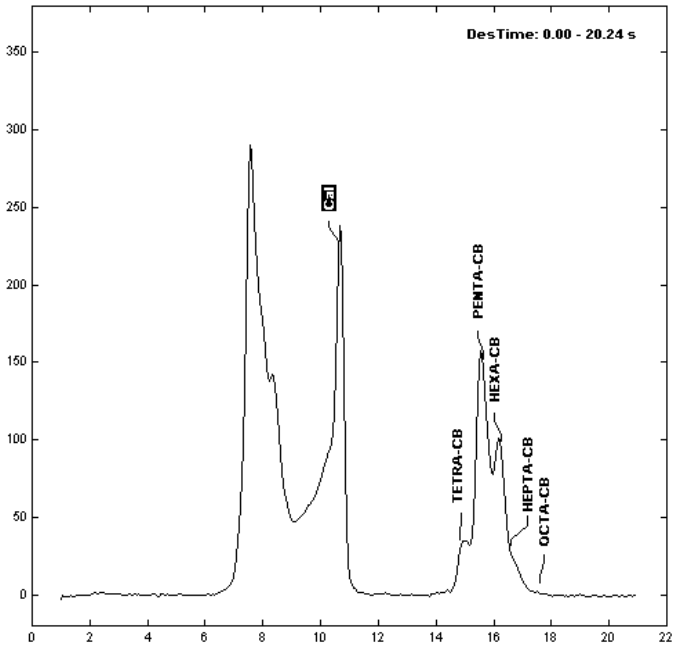
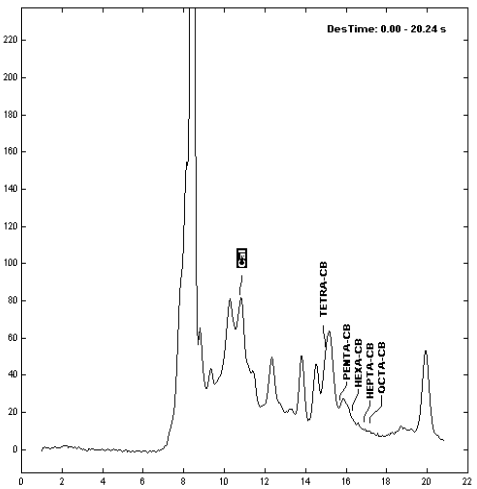


Figure 4.2: The first two consecutive desorptions (a and b) of Norwegian landfill sample 51.

a) First desorption of Norway landfill sample 51



b) Second consecutive desorption of Norway landfill sample 51.

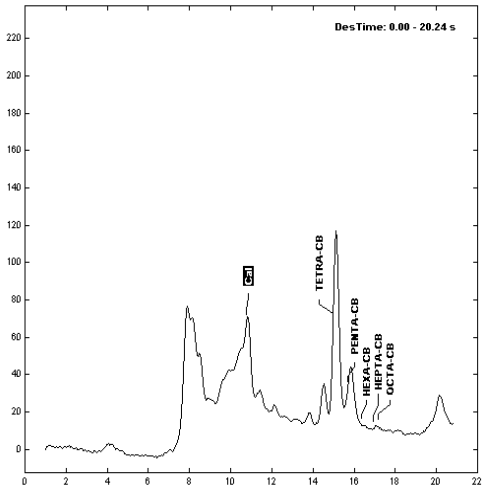
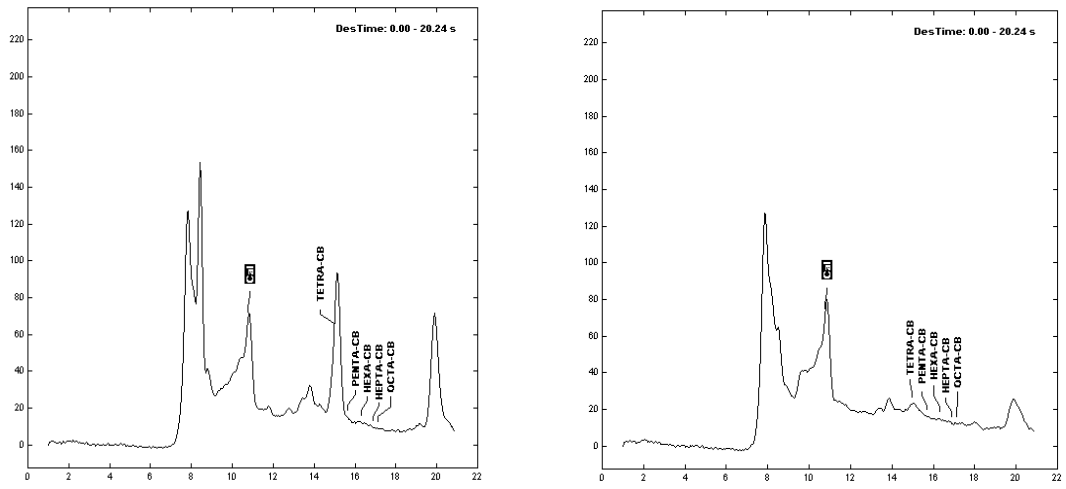


Figure 4.3: Fist two consecutive desorptions (a, and b) of Norwegian landfill sample 1 S

a) First desorption of Norway landfill sample 1S b) Second consecutive desorption of Norway landfill sample 1S landfill sample.



4.5.2 Soil Analysis by GC/DELCD

Calculated total PCB concentrations in Norwegian landfill samples as determined by GC/DELCD are provided in Table 4.5. Figure 4.4 and Figure 4.5 provide example chromatograms for the GC/DELCD analysis of soil samples 51 and 42. Due to the lack of soil sample results by GC/ECD available from Unilab, Norway, the only comparative data presented is for samples 50 and 51. Data for these two soil samples is provided in Table 4.4. The magnitude of the calculated total PCB concentration for these two soil samples was similar to that determined by GC/ECD by Unilab in Norway. However, the average calculated concentrations for both samples (based on triplicate extraction) were approximately twice as high as those determine by GC/ECD. This variation may have been due in part to variations in PCB concentrations in the soil sample. This hypothesis could not be verified, as UniLab only conducted one extraction and analysis for each soil sample, hence no variation data for repeat extractions were available.

Table 4.4 : Total PCB concentrations (µg/g) as determined by GC/DELCD analysis compared to GC/ECD analysis conducted at UniLab in Norway.

Sample ID	Extraction Number	Calculated Total PCBs Determined by GC/DELCD (µg/g)	Average Total PCBs Determined by GC/DELCD (µg/g)	Total PCBs, UniLab, Norway using GC/ECD (µg/g)	% Difference, IMS Analysis to GC/ECD
50	1	0.08	0.15	0.08	198.7
	2	0.14			
	3	0.23			
51	1	0.52	0.54	0.22	241.5
	2	0.50			
	3	0.60			

Table 4.5: Total PCB Concentrations in soil samples (µg/g) for Norway landfill as determined by GC/DELCD

Sample ID	Number of Repeat Extraction	Average Calculated Total PCB Concentration (µg/g)	Std	%RSD
42	3	0.38	0.06	16.34
43	3	3.48	0.69	19.91
44	3	1.96	0.40	20.36
45	3	10.14	4.28	42.22
46	6	0.21	0.02	10.26
47	3	0.67	0.16	23.95
50	3	0.15	0.08	50.59
51	3	0.54	0.06	10.25
MLP4 Red Kai*	3	0.08	0.10	124.5
ML STEIN 1	3	0.47	0.15	32.41
ML STEIN 2	3	12.39	2.79	22.53
		Average % RSD (excluding MLP4 Red Kai*)		24.88

* Reconstituted extract contained fine particulate that would not settle in the vial.

As illustrated in Table 4.5, the average percent relative standard deviation (%RSD) for this analysis was found to be 24.9%, with a range of 10.3 to 50.6 %. The highest standard deviation was found for soil sample MLP4 Red Kai. This sample, unlike all other sample extracts, contained fine particulate dispersed in the reconstituted extract solvent. This particulate did not settle completely and could be seen in the sample syringe prior to injection into the GC. The presence of this particulate is suspected to have affected the GC analysis of this set of sample extracts. For this reason, sample MLP4 Red Kai was not included in the calculation of the average percent relative standard deviation for this method.

Soil samples 45 and 50 both exhibited relatively high percent relative standard deviations. Sample 45 had an average calculated total PCB concentration of 10.1 µg/g, with a standard deviation of 4.3. Sample 50 showed an average calculated total PCB concentration of 0.15 µg/g, with a standard deviation of 0.075. The resulting percent relative standard deviations for these samples were 42.2 % for sample 45 and 50.6 % for sample 50. It is suspected that this variation in calculated concentrations is indicative of poor distribution of the PCBs throughout the soil. Use of a larger same size would reduce the sample to sample variation seen in this soil. Additionally, better mixing of the soil would also reduce the variation seen in these results.

Method precision might also be improved with the use of an internal standard. An internal standard would reduce variations that may occur during sample extraction steps of this method, thereby improving the precision. However, this method is intended for semi-quantitative screening analysis, and as such the average % RSD of 24.9 % was found to be acceptable.

Example chromatograms for the 6.15 µg/mL standard solution and soil samples 42 and 51 are shown in Figures 4.4, 4.5 and 4.6, respectively. The chromatogram of sample 42 provided in Figure 4.5 illustrates the total PCB peak occurring at 0.68 min with a peak width of 0.63 min. In this sample, the only peak seen was due to the PCB homologs. No other halogenated species were present in this sample. This indicates that the selectivity of the DELCD detector is well suited for rapid analysis of soil extracts where non-halogenated species are expected to complicate the chromatogram.

Figure 4.6 illustrates the total PCB peak occurring at 0.67 min in the chromatogram of soil sample 51. This peak is comprised of all PCB homologs present in the sample with

limited separation designed only to move the PCB components away from any lower molecular weight halogenated compounds. This separation was designed to make use of the DELCD detector, which is specific only for halogenated compounds, eliminating the need for longer analysis times to better separate the PCBs from other compounds. Thus, an analysis time of 6 min could be achieved. The presence of a large peak occurring after the elution of the PCBs indicates the presence of other halogenated compounds. During on-site analysis a sample such as this may require further analysis at a certified laboratory.

Figure 4.4: Chromatogram of the 6.15 µg/mL liquid standard used for the analysis of Norwegian landfill samples 51 and 42 as determined by GC/DELCD

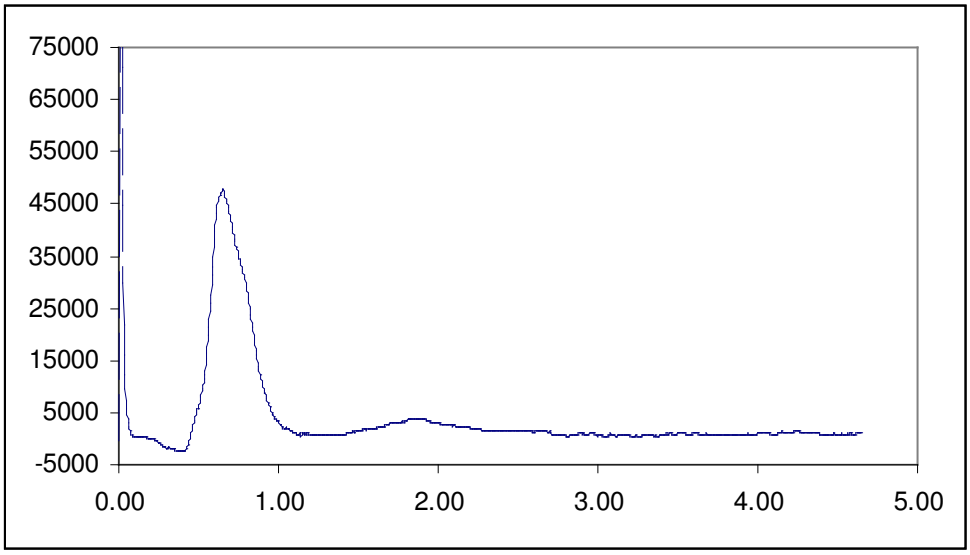


Figure 4.5: Example of GC/DELCD chromatogram for the analysis of Norwegian landfill sample 42 (Calculated concentration was 0.31 µg/g total PCBs).

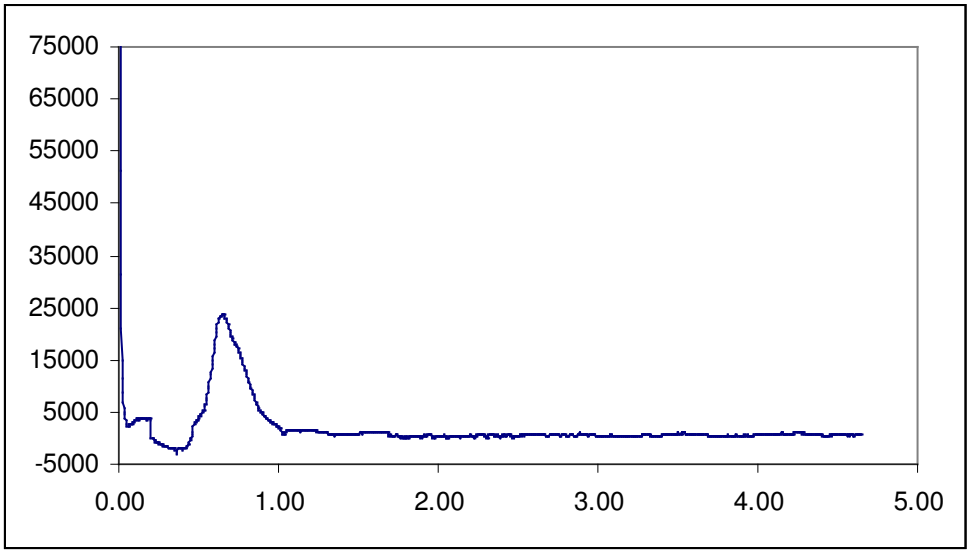
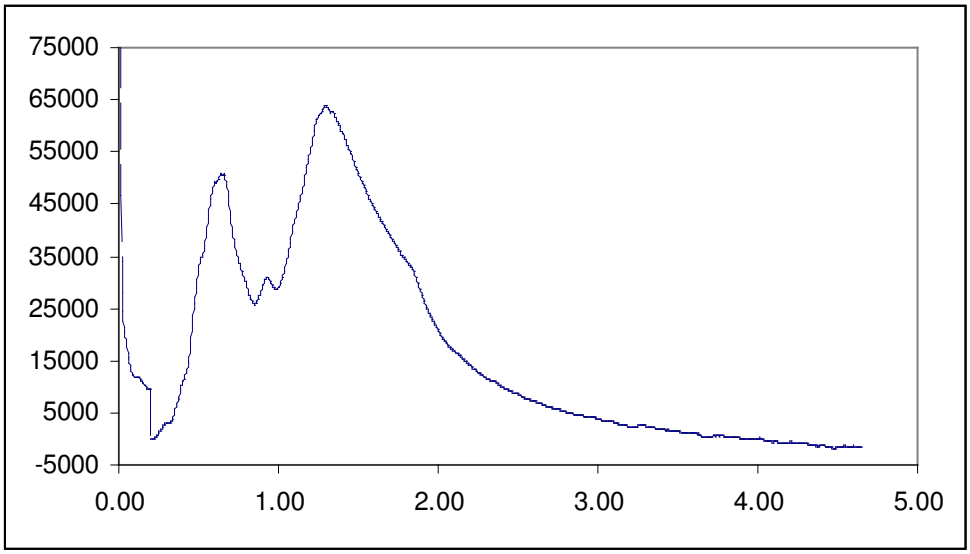


Figure 4.6: Example of GC/DELCD analysis of Norwegian landfill sample 51 (Calculated concentration was 0.15 µg/g total PCBs).



4.6 Conclusions

For this investigation, humus-rich soil was used for the extraction of spiked PCBs.

Previous analysis of coarse grain sand used direct thermal desorption of the soil into an IMS[2, 3]. The presence of humic matter was found to interfere with the analysis of soils

from forested areas. As a result, PCBs contained in this soil matrix required extraction with solvent prior to direct thermal desorption of the solvent extract for IMS analysis. The research conducted in this thesis provides a rapid method for the on-site analysis of total PCBs in soil after extraction with acetone. Instrumentation used for the development of a rapid on-site method included IMS and GC/DELCD.

Using IMS, a distinctive fingerprint pattern resulting form the ratio of PCB homologs present in PCB mixtures provided verification of the presence of PCBs in the soil. However, when humus-rich soils were extracted and analyzed by IMS, this fingerprint was missing. Without this confirmation, the sample could not be verified as containing PCBs. The IMS analysis results of field samples from Norway were compared to GC/ECD results obtained by an external laboratory (UniLab, Norway). The concentrations of total PCBs determined by IMS were up to an order of magnitude greater than the results of GC/ECD analysis. Futhermore, IMS did not show peaks for the PCB homologs known to be present in the sample resulting in a false negative result. This variation and the inability to verify the presence of PCBs in the sample indicates that IMS is not the optimum instrument for field analysis of PCBs.

However, GC/DELCD proved to provide rapid analysis practical for use as an on-site method plus selectivity for halogenated compounds. This method utilized the selectivity of the DELCD detector to reduce the time required for GC separation, as separation was only required for halogenated compounds. The DELCD detector oxidizes all compounds entering the reactor chamber producing CO_2 and water from most environmental contaminants. When a molecule contains a halogen atom, the creation of a halogenated ion increases the conductivity within the reaction chamber. This increased conductivity is

measured and is proportional to the number of halogen atoms in the eluting molecule. As a result, PCBs can be effectively measured in the presence of hydrocarbons normally present in contaminated landfills.

Sample preparation for this method required a 60 min extraction time plus time for sample concentration. The GC analyses of Norwegian landfill samples was conducted in 6 min using an SRI Instruments GC equipped with a DELCD detector. Parallel processing of multiple samples will reduce the sample preparation time thereby reducing the overall analysis time making it acceptable for on-site use. Repeat analysis of field samples gave an average percent relative standard deviation of 24.9 %.

The GC/DELCD method presented here provides a fast on-site analysis for total PCBs in soils. This analysis is intended to provide semi-quantitative measurements and screening of soil samples that may require more detailed analysis, such as GC/MS, for identification of more complex halogenated extracts are required during site remediation.

4.7 References

1. Personal communication with Dr. D. Gregor (CanDetec Inc.) and G. Christensen (Akvaplan-niva), August 2005

2. Orton, M.L., Gregor, D.J., and Weir, D., EnviroAnalysis 2002, Proceeding of the Fourth Biennial International Conference on Monitoring and Measurement of the Environment, Toronto, Canada, May, 517, 2002

3. Orton, M.L., and Gregor, D.J., Attachment 8 of Environmental Technology Verification: ToxSense™ Analysis of PCB Contaminated Soil for SNC Lavalin at Ramore, Ontario – Description and Verification of Selected Sample., CanDetec Inc. Confidential Report, June, 2004.

5 Appendix

Apendix1: Operating Conditions for IMS Analysis of PCBs in Soil

A: Windows Settings for Ionscan Manager

Windows Alarm Settings		Windows Channel Settings		
Alarm	Status	Channel	Ko	Amp Threshold
-	-	Cal	1.6540	-
Tetra-CB	On	Tetra-CB	1.2550	10
Penta-CB	On	Penta-CB	1.2030	10
Hexa-CB	On	Hexa-CB	1.1584	10
Hepta-CB	On	Hepta-CB	1.1065	10
Octa-CB	On	Octa-CB	1.0674	10
Nona-CB	On	Nona-CB	1.0386	10

B: DOS Settings for IM Manager Settings

1. Channel Control Parameters

Chn	ChanID	Usage D/L/A	Ko	Varblty (µs)	BlokTh	AmpTh (du)	FWHM	Consec	Ext AmpTh (du)
10	Tetra-CB	A	1.25500	200	1.5	10	600	2	4095
11	Penta-CB	A	1.20300	200	1.5	10	600	2	4095
12	Hexa-CB	A	1.15840	200	1.5	10	600	2	4095
13	Hepta-CB	A	1.10650	200	1.5	10	600	2	4095
14	Octa-CB	A	1.0674	200	1.5	10	600	2	4095
15	Nona-CB	A	1.0386	200	1.5	10	600	2	4095

2. Table of Defined Substances for Detection Purposes Mode: Explosive

Subst	Subst ID	Usage D/L/A	Subst	Subst ID	Usage D/L/A	Subst	Subst ID	Usage D/L/A
1	-	-	6	PENTA	A	11	-	-
2	-	-	7	HEXA	A	12	-	-
3	-	-	8	HEPTA	A	13	-	-
4	-	-	9	OCTA	A	14	-	-
5	Tetra	A	10	NONA	A	15	-	-

To create/update/display a substance definition, highlight the SubstID of the desired substance and press key F7. Usage: [D:Defined, L: Linked to inactive alarm, A: Alarm]

3. Table of Defined Alarms for Reporting Purposes Mode: Explosive

Subst	AlarmID	On/Off (1/0)	Subst	AlarmID	On/Off (1/0)	Subst	AlarmID	On/Off (1/0)
1			6	PENTA	1	11		
2			7	HEXA	1	12		
3			8	HEPTA	1	13		
4			9	OCTA	1	14		
5	TETRA	1	10	NONA	1	15		

To create/update an alarm definition, highlight the Alarm ID of the desired Alarm and press key F7.

4. Calibrant Control Parameters Mode: Explosives

SStart	10.2	Search interval start time (ms) after mid-point of shutter grid pulse
Swidth:	2.0	Search interval width (ms)
SBlokTh	1.5	Search mode Blok threshold
SAmpTh:	10.0	Search mode amplitude threshold (du)
Sdiscr:	50	Search mode discriminant (µs)
Ko	1.6540	Calibrant reduced mobility
Varblty:	50	Ready mode variability (us)
BlokTh:	2.5	Ready mode Blok Threshold

AmpTh	75	Ready mode Amplitude Threshold (du)
FWHM:	230	Full width at half maximum (µs)
RefPress:	101.33	
RefTime:	11220	Calibrant reference drift time (µs)
VarDTime:	200	
PkTrkSlp:	0.00	
PkTrkOff:	0.00	Peak tracking offset (/s) - used to estimate peak position

5. Miscellaneous Control Parameters — Mode: Explosives

Shut Wdth:	0.20	Shutter Grid Width
T:	22	Scan period (ms)
IDelay:	5.00	Drift time delay (ms)
IRefInt:	300	Duration (µs) of background reference interval
IPer:	50	Ionscan sampling period (us)
IScan:	20	Number of co-added scans per segment of analysis time
Drift Temp:	115	Drift Heater temperature set point (°C)
Inlet Temp:	238	Inlet heater temperature set point (°C)
Desorb Temp:	330	Desorber heater temperature set point (°C)
DriftFlow:	351	Drift flow set point (cc/min)
SampFlo:	300	Sample flow set point (cc/min)
ExhaustFlo:	663	Exhaust flow set point (cc/min)
StandyFlow:	51	Stand-by drift flow set point (cc/min)
MinATime:	20.000	Minimum analysis time (s)
MaxATime:	20.000	Maximum analysis time (s)
ADelay	0.200	Analysis delay (s) following start of desorption

6. PC Data Acquisition Parameters — Mode: Explosives

AcqOpt:	2	Acquisition options supported (0:PCDA; 1:serial; 2:both)
Wait:	2	Wait for IONSCAN Start command (0:don't wait; 1:wait; 2:automatic sampling, labeling and recording)
Sync:	1	Synchronize PC and IONSCAN sampling (0:no; 1:yes)
Scans:	20	Number of co-added scans per segment of analysis time
MinSegs:	14	Minimum number of segments to acquire per analysis
MaxSegs:	14	Maximum number of segments to acquire per analysis
Pts:	800	Number of sample points per scan
Per:	25.0	Sampling period (µs)
Delay:	1.000	Delay time (ms before start of sampling for each scan)

7. Plasmagram Format — Mode: Explosives

			Peak set:		Mode:
			Peak Labelling of Alarms For PeakSet 0		
				Alarm	LabSt
			1		
Drift time Axis			2		
Start Time:	13	ms	3		
Display width:	5	ms	4		
			5	TETRA-CB	2
Growth Curve Axis			6	PENTA-CB	2
Start Time:	0	ms	7	HEXA-CB	2
Display width:	20	ms	8	HEPTA-CB	2
			9	OCTA-CB	2
Plasmagram Display Paramenters			10	NONA-CB	2
Ref drift time:	3.5-4.0	X Amp Range	LabSt= 0:Off; 1:On Alarm only; 2:On		
Zero Ref:	0.05				
Amplitude Rng:	421 du	Auto:0			

Normalization peak NormPk:	-1
Smoothing Coefficient:	0
Display algorithm Alg:	
Segment averaged:	

8. Peak Set Definitions NormPk: -1 Mode: Explosives

					Usage in Peak Set					
				ChanID/ Peak/D	Set 0	Show GC	Set 1	Show GC	Set 2	Show GC
Chn/ Peak	Dtime (ms)	Ko	Fix Ko	CAL	*	*	*	*	*	*
0		1.6520	*							
9		1.25500	*	Tetra-CB	*	*	*	*		
10		1.20300	*	Penta-CB			*	*		
11		1.15840	*	Hexa-CB			*	*		
12		1.10650	*	Hepta-CB			*	*		
13		1.0674	*	Octa-CB	*	*	*	*		
14		1.0386	*	Nona-CB	*	*	*	*		

Appendix 2: Raw temperature data for illustrating the effect of oven temperature on the temperature of SRI on-column injector.

Time (min)	Oven Temperature (°C)	Injector Temperature (°C)	Time (min)	Oven Temperature (°C)	Injector Temperature (°C)
0.0	51	58	4.0	255	181
0.5	51	58	4.1	260	188
1.0	52	58	4.2	266	193
1.1	59	58	4.3	274	201
1.2	66	59	4.4	279	209
1.3	73	61	4.5	284	213
1.4	80	63	4.6	288	218
1.5	89	65	4.7	292	224
1.6	97	68	4.9	300	232
1.7	103	70	5.0	300	237
1.8	109	73	5.2	300	242
1.9	117	77	5.4	300	248
2.0	126	81	5.5	300	250
2.1	133	84	5.6	300	253
2.2	140	87	5.7	300	257
2.3	148	92	5.8	300	261
2.4	155	97	5.9	300	264
2.6	173	107	6.0	300	267
2.7	179	112	6.1	300	270
2.8	185	117	6.2	300	272
2.9	191	121	6.3	300	275
3.0	198	127	6.4	300	278
3.1	207	133	6.5	300	281
3.2	213	139	6.6	300	283
3.3	218	145	6.7	300	285
3.4	223	148	6.8	300	287
3.5	229	154	6.9	300	290
3.6	235	159	7.0	300	291
3.7	240	164	7.1	300	294
3.8	245	171	7.2	300	296
3.9	250	176	7.3	300	297

Appendix 3: Raw data for detector response over the range from 1.23 µg/mL to 102.5 µg/mL of total PCBs as Aroclor 1260 in acetone.

Liquid Standard Concentration (µg/mL)	Total PCB Peak Area	Liquid Standard Concentration (µg/mL)	Total PCB Peak Area	Liquid Standard Concentration (µg/mL)	Total PCB Peak Area	Liquid Standard Concentration (µg/mL)	Total PCB Peak Area
1.23	249.80	2.46	383.56	6.12	750.45	12.18	1536.76
1.23	177.06	2.46	419.70	6.12	843.92	12.18	1863.26
1.23	316.43	2.46	370.83	6.12	882.82	12.18	1602.66
1.23	363.57	2.46	413.43	6.12	799.30	-------	-------
1.23	241.87	2.46	374.68	6.12	861.78	-------	-------
1.23	224.307	2.46	415.40	6.12	900.34	-------	-------
1.23	178.50	2.46	424.84	6.12	813.73	-------	-------
Average	250.08		403.90		836.05		1667.56
STD	68.885		23.895		51.994		172.655

Liquid Standard Concentration (µg/mL)	Total PCB Peak Area	Liquid Standard Concentration (µg/mL)	Total PCB Peak Area	Liquid Standard Concentration (µg/mL)	Total PCB Peak Area	Liquid Standard Concentration (µg/mL)	Total PCB Peak Area
24.12	2464.78	61.50	5854.01	80.39	7620.57	102.5	10228.68
24.12	3169.99	61.50	6418.76	80.39	8044.73	102.5	11133.43
24.12	3179.34	61.50	6425.89	80.39	8970.17	102.5	10859.38
Average	2938.04		6232.89		8211.82		10740.50
STD	409.883		328.1364		690.144		463.948