

THE DEVELOPMENT AND APPLICATION OF A HELIUM
DISCHARGE DETECTOR FOR GAS CHROMATOGRAPHY

A Thesis

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Margaret L. Ware

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This thesis is submitted in partial fulfillment of
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Master of Arts

Margaret L. Ware

Margaret L. Ware

Approved, August 1988

Christopher J. Abelt

Christopher J. Abelt

Robert J. Huggett

Robert J. Huggett

Virginia Institute of Marine Science

Stephen K. Knudson

Stephen K. Knudson

Gary W. Rice

Gary W. Rice

Dedication

This thesis is dedicated to my favorite relatives
and to my closest friends. They know who they are.

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Abstract

A description of the system and characteristics of an element-specific multi-element helium discharge detector for gas chromatography is given. This detector was further investigated through helium gas purification, infrared wavelength, and excitation temperature experiments. The detector was also applied to the identification and quantitation of individual polychlorinated biphenyl congeners through a newly-developed technique which correlates an experimental relative retention index to a similar index published by another laboratory.

A HELIUM DISCHARGE DETECTOR FOR GAS CHROMATOGRAPHY

Chapter I

Element-selective Detectors for Gas Chromatography

Interest in element-specific multi-element detectors for gas chromatography (GC) has increased greatly over the past two decades. Such a detector should ideally provide subnanogram limits of detection, a wide linear response to analytes, tolerance to the passage of microliter volumes of eluting solvent, minimum dead volume from the GC column to the detector to minimize band broadening, and simplicity of operation and construction.¹ Signals should inherently be stable, reproducible, and either similar in response to all analytes or predictable and selective in response to one or more groups of analytes.² A final desirable but often unfeasible attribute is that the detector be nondestructive to the sample.

Certain terms need to be defined before a description of a specific detector can be satisfactorily given. These terms include sensitivity, noise, detectability, selectivity, linearity, response factor, and background current. Sensitivity is the slope of the instrument response with respect to the amount of analyte present. Noise generally refers to random, short term peak-to-peak signal perturbation. Determination of noise levels is important in finding the minimum measurable quantity of analyte and the

lower limit of the linear range.³ Detectability, or the limit of detection, is described by the minimum amount of analyte which can be detected above the noise level. In general, the smallest detectable signal above the noise level has been accepted as a factor of two although a more conservative and reasonable requirement is a factor of three. Selectivity, or specificity, is the ability to measure analytes or groups of analytes on the basis of some distinguishing physical property (e.g. atomic emission or electronegativity). Detector linearity is the range of sample concentration over which the detector sensitivity remains constant.³ The response factor for an analyte is the instrumental response measured against the response to an internal standard. Finally, background current or dark current is the continuous output signal generated by an ionization or emission detector during operation with no sample passing through.³

In giving an overview of the types of detectors available for GC, it is convenient to categorize them and to make generalizations about each group. There are, however, a number of ways to divide the various types. For instance, detectors can be divided into three groups solely on the basis of selectivity.⁴ Some detectors are rather non-selective such as the catharometer and flame ionization detectors. Others, such as the electron capture detector are selective for certain compound classes (e.g. electronegative functional groups). Finally, detectors such as the flame photometric detector, microwave induced plasma, and mass

spectrometer are both specific and widely applicable.⁴

There are a number of different element-selective detectors: thermionic, microcoulometric, flame photometric, direct current plasma, inductively coupled plasma, and microwave induced plasma detectors. Each of these detectors possesses certain of the desired characteristics to varying degrees.

The thermionic detector (TD) is selective toward nitrogen and phosphorus-containing organic compounds. In the detector assembly a hydrogen/air mixture flows past an electrically heated rubidium silicate bead, forming a flame with temperatures somewhere between 600-800°C.² This detector has been very useful in the analysis of phosphorus-containing pesticides but is not widely applicable to a variety of elements. Because all substances have a unique thermal conductivity, calibrated response factors are necessary for accurate quantitation.³

In a microcoulometric detector (MCD) the sample interacts with an electrochemically produced species, and the detector cell measures the amount of current needed to reestablish electrochemical equilibrium. The relationship between chromatographic peak area and the total number of coulombs required is used for quantitative analysis. Species containing sulfur, nitrogen, and the halogens can be selectively determined using this technique. Detection limits for this detector are usually in the nanogram range. Careful optimization is required for accurate quantitation. The coulometric reactions determine the selectivity.⁵

Flame photometric detectors (FPD) produce and excite atoms and molecular species in an H_2/O_2 flame similar to that of a flame ionization detector with the primary difference that subsequent emissions are monitored as excited species return to ground state energies. Detection limits are very good and are often in the subnanogram range. FPD has been used extensively for selective determination of phosphorus, sulfur, and to some extent, for tin and other metals. The detector's response to phosphorus-containing compounds is linear, but the presence of two sulfur atoms in S_2 makes the response to a compound with one S atom proportional to the square of the compound concentration. This square relationship can be a guide to determining how many sulfur atoms are present, although slopes have been observed ranging anywhere from one to two. Unfortunately, this detector is plagued by flame flicker and subject to flame extinction from large solvent volumes and high carrier gas velocities. In order to achieve maximum reproducibility, flow rates must be carefully monitored and controlled. Sometimes it is necessary to vent the solvent or even to reignite the flame.⁵

The inductively coupled argon plasma (ICP) is regarded as the method of choice for trace level multi-element analysis of a variety of metals and certain nonmetallic elements.⁶ Long residence times of analytes in the plasma and high temperatures, generally on the order of 5000K, usually result in detection limits at nanogram levels or less. GC-ICP has been found useful in the determination of

boron, carbon, hydrogen, iodine, phosphorus, silicon, and sulfur. Vacuum ultraviolet atomic emission can be used to detect bromine, chlorine, fluorine, nitrogen, and oxygen. In addition, the ICP's ability to measure relative ratios of elemental components in a sample makes it useful for the determination of empirical formulas.^{6,7} ICP detectors are rather expensive (50-100K) and may not be the most cost effective choice, particularly in a routine laboratory setting. There is a great deal of similarity between direct current plasma detectors (DCP) and ICPs. In fact, they have comparable multielement capabilities, precision and similar sample size requirements.⁸ Both of these detectors are also susceptible to plasma extinction if large volumes of solvent are introduced.

The microwave induced plasma detector (MIP) has been demonstrated to be selective for over 30 elements in GC applications.⁹ Excitation of a flowing carrier gas (usually argon or helium) through a high energy microwave tuned cavity produces a high temperature plasma which effectively leads to fragmentation of compounds and excitation of atomic species. Detection limits are quite good, generally at nanogram to picogram levels. Unfortunately, the MIP has a number of serious disadvantages. Spectral interferences arising from CN, C₂, and CH are problematic. Large solvent volumes may extinguish the plasma. Frosting of the discharge tube or devitrification caused by intense heat reduces sensitivity. In addition, a number of parameters (e.g. flow rate, power, observation area) should necessarily be

optimized for each element, thus the MIP's multielement capability is somewhat overshadowed by its inability to switch rapidly from the detection of one element to another.⁵ MIPs, at this point, are still limited primarily to research applications and are not commercially available.

The detectors discussed above have proven to be quite useful in certain applications, but each one has drawbacks or limitations which detract from widespread analytical acceptance, especially with regard to multi-element detection. With these problems in mind, we have continued development of a helium discharge detector which satisfies a good many of our requirements for a suitable element-selective, multi-element detector for GC. This detector has already been demonstrated to have equal or superior limits of detection to the MIP for a number of elements without the aforementioned problems.¹

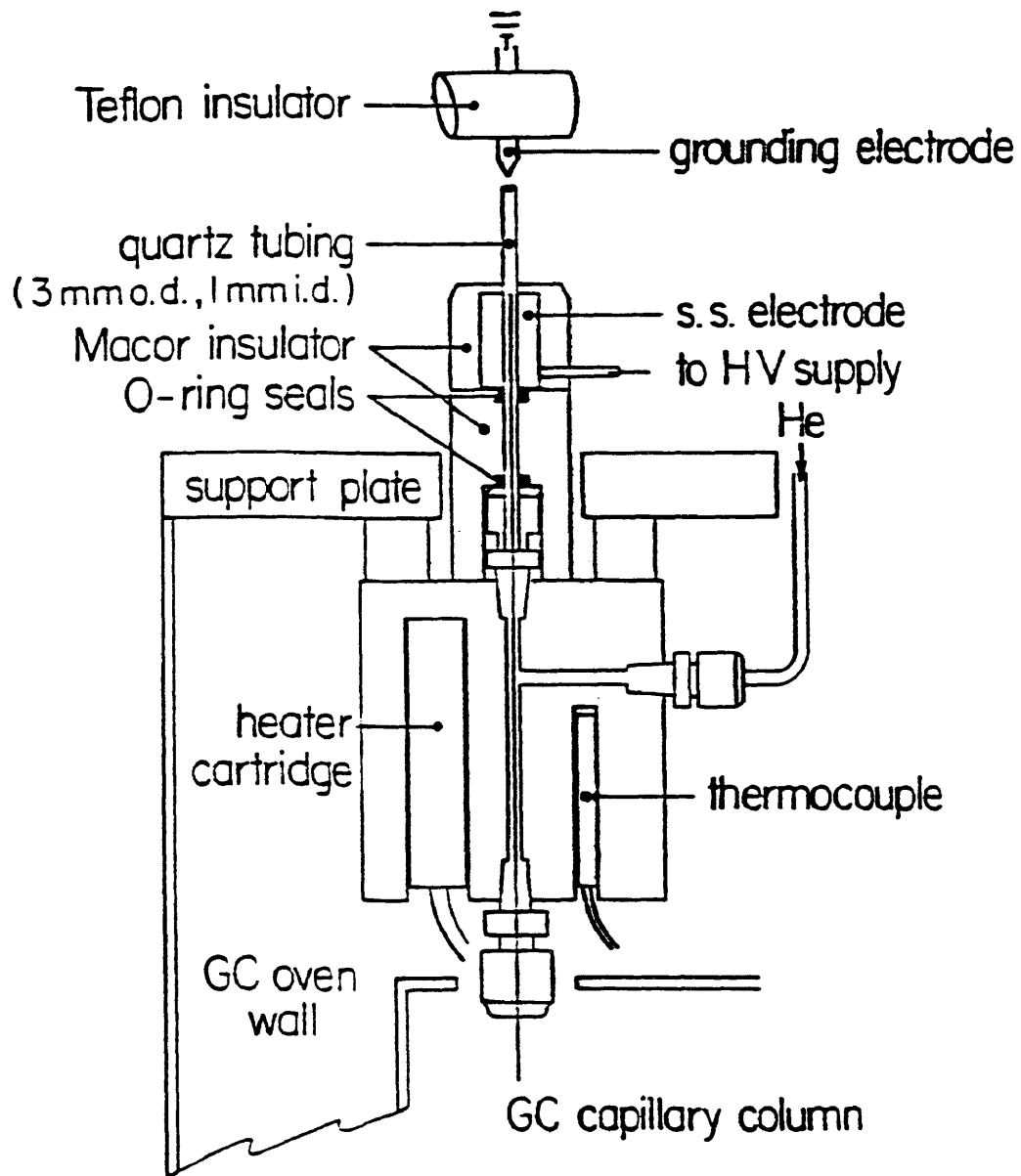
Chapter II

Helium Discharge Detector

i. System Description

A schematic diagram of the helium discharge assembly is shown in Figure 1. The electrodeless discharge is formed inside a 3 mm o.d. by 1 mm i.d. quartz tube which extends from just below the support plate to approximately 2 cm above a cylindrical stainless steel electrode which is connected to an AC high voltage supply. A second stainless steel electrode at the tip of the tube provides an ion path for the discharge. The region of the tube between the two electrodes is where emissions are monitored and is considered the secondary or analytical discharge region. The remaining part of the discharge surrounded by the cylindrical electrode is the primary discharge. The quartz tube is mounted on a stainless steel heater block which serves to maintain GC column temperatures at the interface between the GC oven and the discharge tube to reduce the risk of band broadening.¹⁰ The helium which sustains the discharge enters through an inlet perpendicular to the discharge tube in the heater block. Each Swagelok fitting connected to the heater block has been arc welded to prevent the entrainment of atmospheric gases into the helium stream.¹

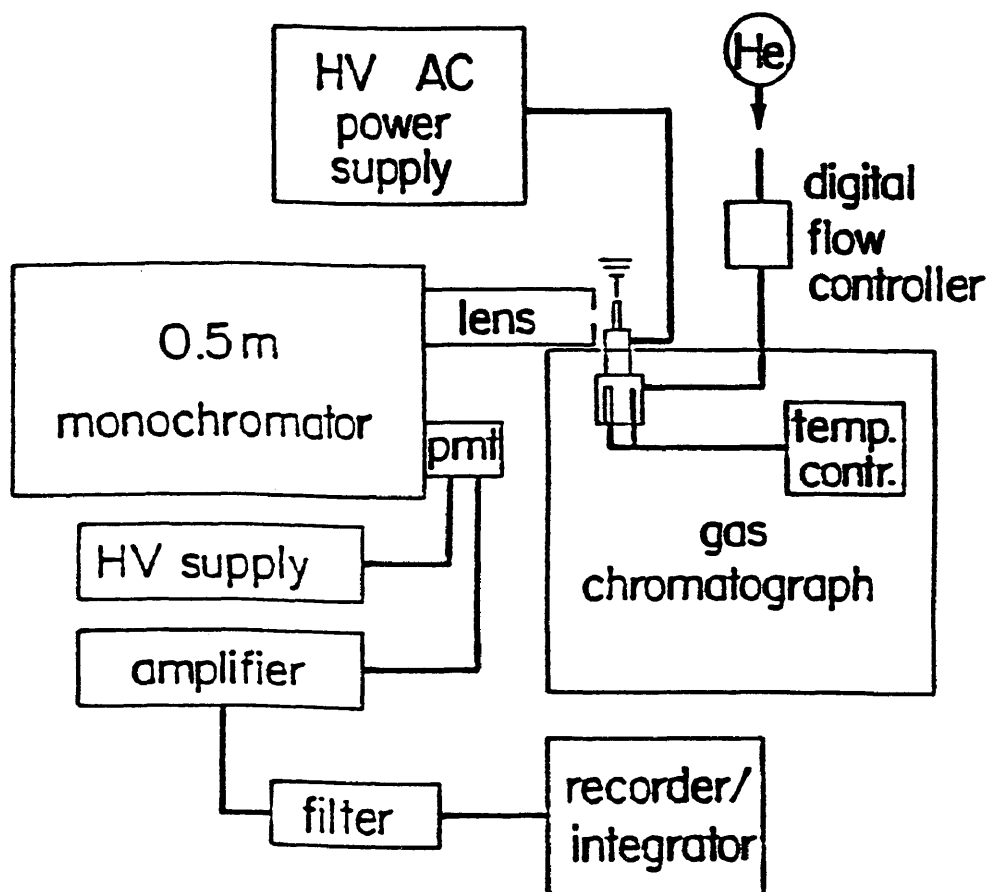
Figure 1
Schematic diagram of Helium Discharge Assembly



Approximately 10 cm of the GC capillary's polymeric coating must be stripped off with hot sulfuric acid to prevent the formation of polymeric deposits on the walls of the quartz tube. The GC capillary column is fed through the discharge tube until the end of the capillary is even with the top of the primary discharge region. Placement of the capillary column exit at this point is a very important feature of this detector.¹¹ The analyte stream is not introduced into the primary discharge and hence cannot affect the various excitation processes that produce energetic species of helium. This method of sample introduction is in direct contrast with that employed in other detectors such as the DCP, ICP, and MIP in which the solvent and analytes are introduced directly into the area where the plasma is generated, resulting in possible plasma extinction.^{9,12,13} The secondary discharge is perturbed by the introduction of samples and may undergo some quenching during the passage of solvent; however, this condition is only temporary due to continuous replenishment from the primary discharge region.

A schematic diagram of the entire GC-HDD system is shown in Figure 2. Optical emissions occurring in the secondary discharge are focussed through a calcium fluoride lens onto the collimating mirror of a 0.5m Czerny-Turner type monochromator. Dispersed radiation from the monochromator could be detected either by a photomultiplier tube or a silicon photodiode detector, depending on the spectral region under study. The photomultiplier tube utilized gives

Figure 2
Schematic Diagram of GC-HDD



a uniform response from 250 to 800 nm. On the other hand, the silicon photodiode detector functions well from the ultraviolet to near infrared regions (200-1100 nm) but is not as sensitive in response as the PMT. Typical operating conditions and parameters for the discharge, spectrometric, and gas chromatographic systems are outlined in Table 1. The discharge power supply has been frequency tuned to 176 kHz to minimize reflected power.

Table 1
Overview of Operating Parameters

A. Helium Discharge Detector

Helium flow rate	60 mL/min
Voltage	6500 V (RMS)
Frequency	176 kHz
Load Power	65 W

* Model HPG-2 (ENI Power Systems)

B. Spectrometric System

Monochromator	0.5m (Minuteman, Model 305M)
Bandpass (fwhm)	0.22 nm (100 micron slits)
Photomultiplier tube	R758 (Hamamatsu)
PMT voltage	1060 V (Keithley Model 247)
Amplifier	Keithley Model 485 picoammeter
Integrator	Shimadzu Model CR3A

C. Gas Chromatographic System

GC	Carlo Erba Model 4180
Injection mode	On-column
Carrier gas	Helium
Column	DB-5, 30m x 0.25 i.d. (J&W Scientific)

ii. Excitation Processes

Excitation processes in the discharge are not completely understood at this point. For the most part it is believed that as the current passes through the helium in the quartz tube, helium atoms may be excited by energy transfer from electrons with sufficient energy to produce metastable helium species. These metastable species can remain for a considerable time in the excited state (lifetimes up to 0.1 sec at atmospheric pressure)¹⁴ unless some collisional event causes the species to lose energy prematurely. Collisions of the metastable species with analyte molecules lead to fragmentation and excitation.¹⁵ Through the monitoring of atomic emissions at a particular analytical wavelength, elements of interest may be detected. From the standpoint of serving as an effective energy carrier in excitation mechanisms, helium has an advantage over other gases in that its ionization potential is 24.46 eV.¹⁶ In addition, two of the metastable helium states have excitation energies of 19.73 and 20.53 eV.¹⁴ In contrast, argon has an ionization potential of only 15.76 eV with metastable states of 11.50 and 11.67 eV.¹⁴ Thus, the helium discharge is a more appropriate choice for reactions requiring higher excitation energies to populate particular excited states.

Chapter III

Spectral Characteristics and Multi-element Detection

In the ultraviolet region of the electromagnetic spectrum there is considerable background emission observed in the helium discharge. Between 190 and 450 nm emissions are observed for a number of species including CO^+ , OH, NH, and N_2^+ . In addition, CN and C_2 emissions can be observed when carbon-containing species are introduced into the discharge. Because these molecular species lead to enhanced background emissions, selectivity ratios are calculated to evaluate the utility of the analytical wavelengths for a given element. In this case, the selectivity ratio is the ratio of the amount of carbon necessary to give a signal equivalent to a fixed amount of analyte. The selectivity relative to carbon was observed to be poor for elements with analytical wavelengths in the ultraviolet region. Interfering emissions arise because of inherent impurities in the helium gas stream. Such spectral interferences result in observations of emissions at virtually any wavelength in the ultraviolet region. Between 600 and 900 nm interferences are primarily from atomic emissions (H, He, N, Ne, and O) which can readily be resolved from analyte emission signals. Figures 3 and 4 show the type and extent of background interferences from 200-900 nm¹. Attempts to either correct

Figure 3
Background Emission in 190-600 nm Range¹

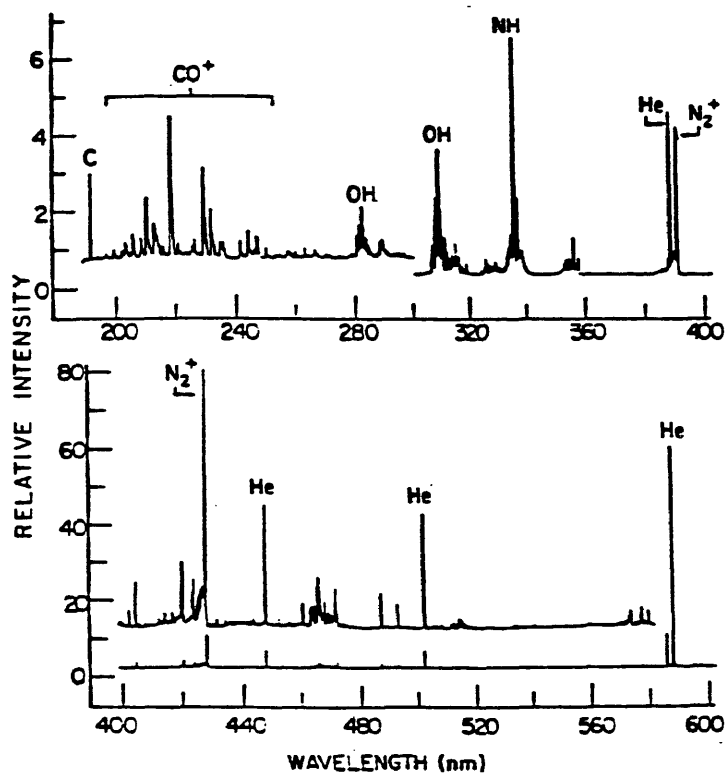
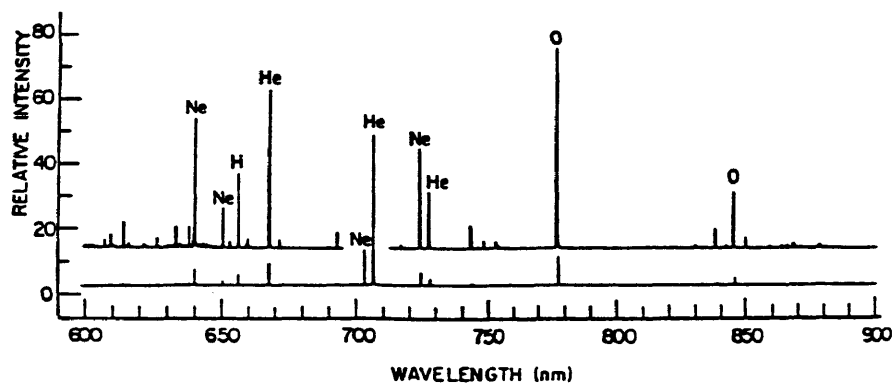


Figure 4
Background Emission in 600-900 nm Range¹



or circumvent these problems were made in the following experiments.

i. Gas Purification

Experimental Procedure: Because impurities in the gas stream are the major contributors to background emission, attempts were made to purify the helium as much as possible. Junctions of the gas line were sealed using graphite ferrules and Swagelok fittings to prevent entrainment of atmospheric gases into the system. The gas transfer lines were thoroughly heated to remove a film of moisture which was suspected to exist on virtually all surfaces in the system. A heated catalytic trap (Supelco Carrier Gas Purifier #2-3800) was incorporated to remove water and oxygen. Additional traps (American Scientific #G5301-36 and G5301-4) intended to remove oxygen, moisture, and trace hydrocarbon impurities were also incorporated. Copper tubing (0.25" o.d.) packed with molecular sieves and immersed in liquid nitrogen was also investigated as a possible means of gas purification. Emissions were monitored at common wavelengths for hydrogen, oxygen, nitrogen, and helium after each method of purification was given sufficient time to stabilize.

Results and Discussion: The wavelengths and relative intensities of the monitored emissions are listed in Table 2 under headings which indicate the conditions employed. Table 2 also compares the intensity ratios for a number of element

Table 2
Relative Intensities Under Various Conditions

<u>Element</u>	<u>Run 1</u> ^a	<u>Run 2</u> ^b	<u>Run 3</u> ^c	<u>Run 4</u> ^d
He ₇₂₈	2180	3080	3360	3080
He ₆₆₈	11100	15200	16200	16000
N ₈₆₈	1340	94	111	354
O ₇₇₇	12100	2030	1010	3380
O ₈₄₅	4100	700	290	1020
H ₆₅₆	890	1610	585	770

Intensity Ratios Under Various Conditions

<u>Wavelength pair</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>
He ₇₂₈ to N ₈₆₈	1.6	32.8	30.3	8.7
He ₇₂₈ to O ₇₇₇	0.2	1.5	3.3	0.9
He ₇₂₈ to H ₆₅₆	2.5	1.9	5.7	4.0
O ₇₇₇ to H ₆₅₆	13.6	1.3	1.7	4.4
O ₈₄₅ to N ₈₆₈	3.1	7.4	2.6	2.9
He ₆₆₈ to He ₇₂₈	5.1	4.9	4.8	5.2

^aLiquid nitrogen trap

^bHeated catalytic trap (initial startup)

^cHeated catalytic trap (overnight purge)

^dGC capillary column attached (w/catalytic trap)

pairs under the conditions mentioned above.

The changes in the gas lines were successful in significantly lowering the signals from impurities. Unfortunately, some of the improvements were not as effective upon inclusion of the GC capillary column, which invariably increased the oxygen signal. Thus, while it is possible to purify the helium to the point that impurity levels are substantially lowered, the methods are of limited utility due to gas flow from the GC. The intensity ratios reveal that while the helium to impurity intensity levels change dramatically, helium line ratios indicate that the helium metastable composition of the discharge is not being significantly altered by purification procedures. A marked increase (50%) in the He line intensities was also observed upon purification of the gas.

Conclusions: Research has proven that carefully controlled levels of oxygen and nitrogen prevent carbon deposits in the MIP assembly.^{17,18} Trace amounts of oxygen and nitrogen appear to scavenge carbon, especially during the passage of solvent, and prevent the deposition of carbon on the inner walls of the quartz tube. Although this occurrence has not been thoroughly investigated for the HDD, a "natural" level of contamination may be preventing carbon deposits from occurring on the quartz tube during elution of the solvent in GC processes.

ii. Alternative Analytical Wavelengths

Introduction: Because interfering emissions in the ultraviolet region appear to be problematic, analytical wavelengths in the near infrared region were investigated for a number of elements to determine which wavelengths might correspond to emissions which could prove useful as analytical wavelengths and improve selectivity over non-analyte emissions.

Experimental Procedure: Volatile compounds containing elements of interest were placed in small glass vials and pressurized to allow a constant flow of vapor to enter the discharge through a capillary transfer line. The compounds used for the corresponding element were tetrachloroethylene (Cl), dibromomethane (Br), iodopropane (I), trimethyl phosphite (P), and carbon disulfide (S). Nitrogen present as an impurity in the helium was also monitored. As the vapors were swept through the discharge, atomic emission was monitored until a constant signal was observed. Wavelengths were subsequently scanned with the monochromator from 600 to 1100 nm. Signals were detected with a silicon photodiode detector (Model 7183, Oriel Corporation). Pivonka et. al did a similar study for the microwave induced helium plasma and compiled lists of wavelengths for a variety of elements.¹⁹

Results: A typical scan for chlorine is shown in Figure 5 with the most intense chlorine emission wavelengths labeled. The ten most intense wavelengths for chlorine, bromine, iodine, nitrogen, phosphorus, and sulfur are listed in Table 3 with their relative intensities. The intensities given have been corrected for grating efficiency and detector response and have been normalized to the most intense wavelength in each group.

Conclusion: This portion of our research revealed that the analytical wavelengths being used for chlorine and bromine (837.6 and 827.2 nm respectively) corresponded to emissions which were only half as intense as those observed at 912.1 nm for chlorine and 889.8 nm for bromine. In all cases the most intense emissions in the HDD were the same as those observed in the MIP study. Further research needs to be conducted to test the analytical utility of these near infrared wavelengths, especially for elements which have been routinely detected in the ultraviolet region (C, P, S, and I) but have been susceptible to poor selectivity. The limiting factor in successfully conducting these experiments has been access to a viable near infrared detector for the HDD system.

Figure 5
Chlorine Wavelength Scan

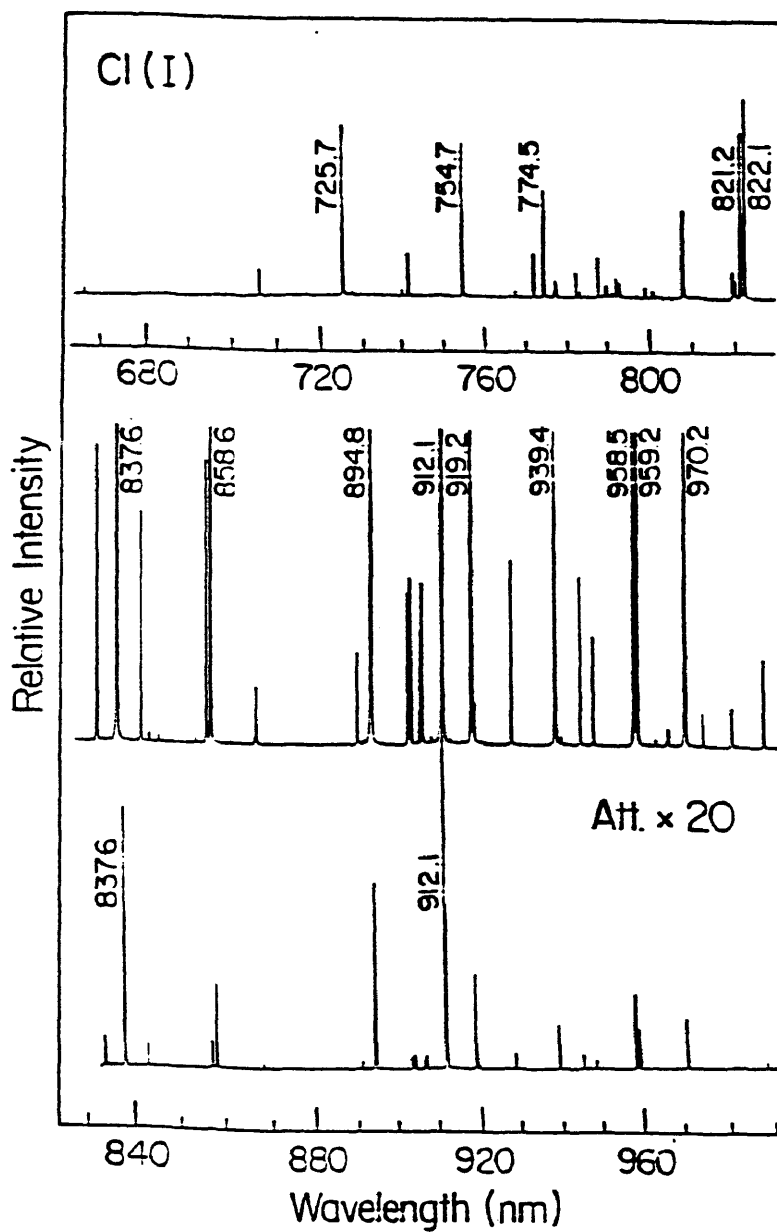


Table 3
Ten Most Intense Wavelengths for Elements
Scanned in the Near Infrared Region

CHLORINE		BROMINE		IODINE	
λ (nm)	REL. INT.	λ (nm)	REL. INT.	λ (nm)	REL. INT.
837.597	43.4	655.980	11.5	804.374	1.0
842.827	1.9	734.851	10.6	889.850	1.1
857.527	2.4	827.244	54.6	905.833	64.4
858.599	12.5	834.370	8.3	911.391	3.2
894.801	32.5	847.745	13.1	933.505	2.0
912.112	100.0	863.866	31.0	965.306	43.7
919.167	17.3	882.526	35.2	973.173	100.0
939.381	8.7	889.762	100.0	980.089	1.7
958.477	15.7	917.816	21.0	1023.882	8.9
970.235	14.7	926.542	19.0	1046.654	23.6

Table 3 (continued)
Ten Most Intense Wavelengths for Elements
Scanned in the Near Infrared Region

NITROGEN		PHOSPHORUS		SULFUR	
λ (nm)	REL. INT.	λ (nm)	REL. INT.	λ (nm)	REL. INT.
744.230	10.5	952.578	11.3	868.047	1.7
746.831	16.4	956.345	7.4	869.471	2.6
859.400	15.3	959.354	13.4	921.291	100.0
862.924	34.8	973.47	100.0	922.811	74.1
868.03	100.0	975.073	12.5	923.749	47.1
868.36	61.0	979.679	29.3	941.346	1.3
868.64	27.1	1008.422	15.6	942.193	1.1
870.34	26.0	1045.590	23.4	964.994	1.1
871.18	28.3	1052.945	9.1	1045.679	9.5
871.90	20.6	1059.692	24.1	1045.946	5.4

Chapter IV

Determination of Discharge Excitation Temperature

Introduction: In the evaluation of the discharge detector, a knowledge of the magnitude of the excitation temperature can be informative with respect to comparisons to other excitation sources and to the formulation of excitation mechanisms. The discharge consists of helium gas enclosed in a quartz tube in the presence of an electric field which causes diffusion and migration of the species present in the direction of the grounding electrode. This moving gas stream is energized by the current passing through it. Because of the ionized character of some of the species, the vapor is often referred to as a plasma. Collisions within the plasma result in the excitation and relaxation of atoms, ions, and molecules. A portion of the excited species may undergo non-radiative processes but a significant population is observed in the secondary discharge.²⁰

There are several temperature parameters which can be examined. Electron temperature is dictated by the kinetic energy of the electrons within the discharge. The gas temperature is defined by the kinetic energy of the neutral atoms. Ionization temperature dictates the various ionization equilibria.²⁰ The fourth type of temperature, the

one of concern in this research, is the excitation temperature. The excitation temperature gives an estimate of the populations of the different energy levels for a given species in the discharge medium.²⁰ If the discharge inside the quartz tube is in thermal equilibrium with the inner walls, then each particle type follows a Boltzmann distribution:

$$\frac{n_q}{n_o} = \frac{g_q}{g_o} \exp(-E_q/kT) \quad (1)$$

where n_q is the concentration in the excited state q , n_o is the concentration of ground state atoms, g_q and g_o are the statistical weights of the corresponding levels, E_q is the excitation energy of the state q , k is the Boltzmann constant, and T is the absolute temperature.²⁰ The statistical weight is the probability of populating a given state under the same conditions. The experimental section which follows outlines the two methods used to study the excitation temperature of the discharge.

Slope method: An estimate of the excitation temperature can be made by observing the spectral-line intensities of a number of transitions for a given species. Assuming that the excited state populations of a given species at the various energy levels follow a Boltzmann distribution, an expression may be written for the intensity of emission for a transition from upper state a to lower state b as

$$I_{ab} = \frac{d}{4\pi} A_{ab} h\nu_{ab} n \frac{g_a \exp(-E_a/kT)}{Z} \quad (2)$$

in which d represents the depth of the source (usually in cm), A is the transition probability, ν is the frequency of the transition, h is Planck's constant, and Z is the sum over states or the partition function, i.e.,

$$Z = \sum_0^j g_m \exp(-E_m/kT). \quad (3)$$

Upon rearranging and taking logarithms, it follows that

$$\ln \frac{I_{ab}}{g_a A_{ab} \nu_{ab}} = \ln \frac{d}{4 \pi} h + \ln \frac{n}{Z} - \frac{E_a}{kT}. \quad (4)$$

By using relative intensities and a relative transition probability, the above expression can be simplified to

$$\ln \frac{I'_{ab}}{g_a A'_{ab} \nu_{ab}} = \ln \frac{n}{Z} - \frac{E_a}{kT}. \quad (5)$$

If the simplified expression is applied to a collection of spectral lines arising from either atomic, ionic, or molecular emissions for a given species, a linear relationship can readily be obtained.²⁰ A plot of $\ln (I'_{ab}/g_a A'_{ab} \nu_{ab})$ versus E_a results in a line with a slope which can be used to calculate the excitation temperature, as long as self-absorption is assumed to be negligible. The values of n and Z are constants and unnecessary for the calculation. In our temperature experiments, plots of $\ln (gA/\lambda I)$ versus the energy of the upper state were obtained. The only consequence of this choice is the orientation of the line, which in this case yields a slope of $1/kT$. Table 4 lists the wavelengths used and their corresponding tran-

sitions, upper state energies (cm^{-1}), transition probabilities, upper state statistical weights, and relative intensities. Figure 6 is the Grotrian diagram for helium, which shows the origin of many of the prominent He transitions used in this study. The intensities used in these calculations were adjusted both for grating efficiency and for silicon photodiode detector response.

Two-line method: A second method of temperature determination is known as the two-line intensity method. The ratio of the intensities from two emissions can be expressed using equation 2, which upon rearrangement gives

$$\frac{I_a}{I_b} = \frac{(gA)_a}{(gA)_b} \cdot \frac{v_a}{v_b} \exp[-(E_a - E_b)/kT] \quad (6)$$

where the a and b designations refer to the two spectral lines in question. Upon taking the log of equation 6 and rearranging, the following expression is obtained for calculating the temperature from the intensities of two emissions at wavelengths a and b.

$$T = \frac{(0.434)(E_a - E_b)/k}{\log(gA)_a / (gA)_b - \log(\lambda_a / \lambda_b) - \log(I_a / I_b)} \quad (7)$$

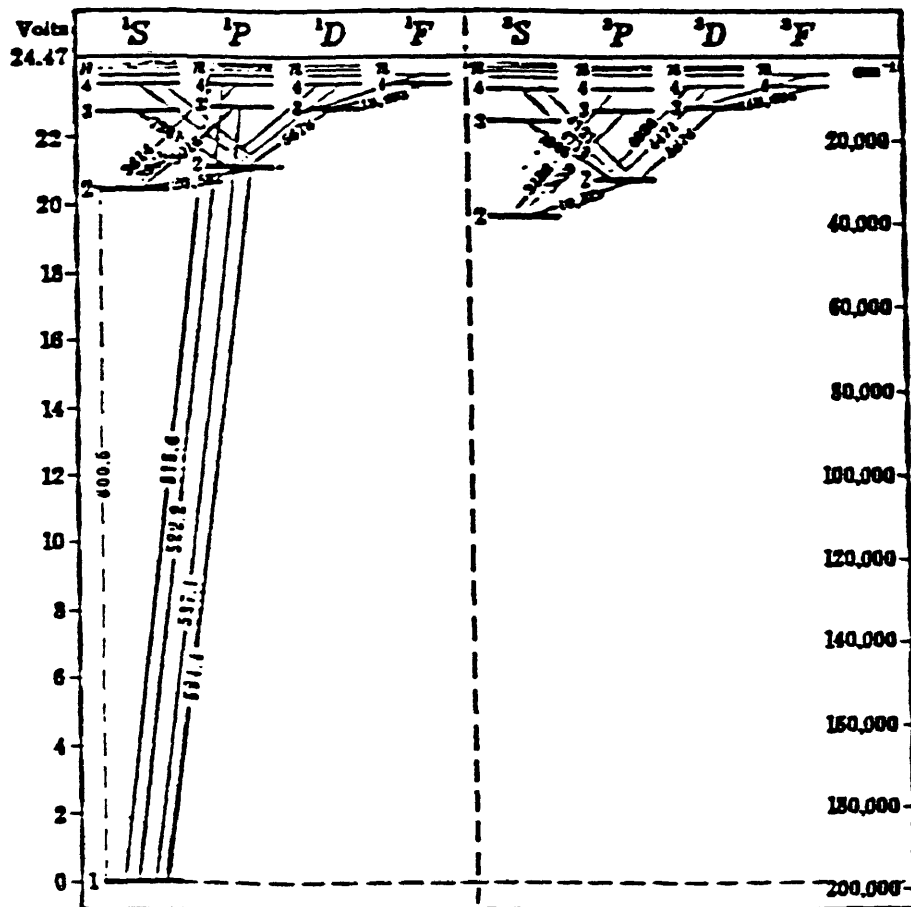
There are certain factors which must be taken into consideration in choosing wavelengths to use in the calculation. The relationship between (dT/T) and (dI/I) , the relative errors associated with the temperature measurement and intensity ratios (I_a/I_b) respectively, can be written

Table 4
Helium Wavelength Information for Slope Method

WAVELENGTH (nm)	TRANSITION	E_u (cm^{-1})	A ($\times 10^{-8} \text{s}^{-1}$)	g_u	RELATIVE* INTENSITY
388.87	$3^3\text{P} - 2^3\text{S}$	185565	0.0948	9	45
396.47	$3^1\text{P} - 2^1\text{S}$	191493	0.0719	3	0.4
402.62	$5^3\text{D} - 2^3\text{P}$	193917	0.116	15	0.7
447.15	$4^3\text{D} - 2^3\text{P}$	191465	0.246	15	6.0
471.32	$4^3\text{S} - 2^3\text{P}$	190298	0.0955	3	1.0
492.19		191467	0.198	5	1.0
501.57	$3^1\text{P} - 2^1\text{S}$	186210	0.134	3	4.6
587.57	$3^3\text{D} - 2^3\text{P}$	186102	0.705	15	91
667.82	$3^1\text{D} - 2^1\text{P}$	186105	0.634	5	20
706.52	$3^3\text{S} - 2^3\text{P}$	183237	0.279	3	100
728.14	$3^1\text{S} - 2^1\text{P}$	184865	0.183	1	52

* At 70 W; 60 mL/min He flow

Figure 6
Grotrian Diagram for Helium¹⁶



$$\frac{dT}{T} = \frac{T}{(E_a - E_b)/k} \cdot \frac{dI}{I},$$

which suggests that there should be a large difference in the excitation potentials of the two lines.²⁰ Also, enhanced precision may be achieved by using a pair of lines whose wavelengths differ very little, eliminating the necessity for changes in instrument response. Finally, the ratio $(gA)_a/(gA)_b$ should be large so that extreme values for the intensity ratio, I_a/I_b , will not be produced. The two lines being considered should also come from the same species, i.e. atomic or ionic.

The wavelength data in Table 5 were used to calculate temperatures with the two-line method. Various wavelength pairs were chosen with the aforementioned requirements in mind, and temperatures from three wavelength pairs: 4921.9/5015.7, 6678.2/7065.2, and 7065.2/7281.4 (in angstroms) were calculated and compared. Next, temperatures were determined for the first two wavelength pairs after a number of observations to check the reproducibility of the methods.

Table 5
Helium Wavelength Information for the
Two-line Intensity Method

<u>Wavelength(A)</u>	<u>g_{upper}</u>	<u>A(x10⁸s⁻¹)</u>	<u>Intensity*</u>	<u>E(cm⁻¹)</u>	<u>V(ev)</u>
4921.9	5	0.198	60.0	191447	23.74
5015.7	3	0.1338	12.0	186210	23.09
6678.2	5	0.6339	95.0	186105	23.07
7065.2	3	0.2786	180.0	183237	22.72
7281.4	1	0.1829	96.0	184865	22.92

*Intensities corrected for grating efficiency

Results: In the slope method, plots of $\ln (gA/\lambda I)$ versus E_u were obtained at a fixed flow rate of 60 ml/min of helium at input powers of 30, 40, 50, 60, and 70 W. If all eleven wavelengths were used in the calculations, a cluster of three points consistently fell above the plotted line. Figure 7 shows a representative graph for such data obtained at 70 W. When these three points were arbitrarily discarded, the correlation coefficients for the lines improved markedly as demonstrated by Figure 8. Removal of the points also affected the numerical value of the temperature, but because this temperature-determination method should be regarded as accurate to within no more than about $\pm 200\text{K}$, the excitation temperature during operation at standard conditions is probably somewhere between 2500 and 2700K. All subsequent temperature measurements were made with the eight-point slope. Table 6 presents the results of this phase of the experiment, and Figure 9 shows graphically the dependence of temperature on power. It should be noted that at low powers, approximately 30 W and lower, the discharge is difficult to maintain and gives off an extremely faint glow compared to its appearance under normal operating conditions. Next, the power was held fixed at 70 W, and the flow rates 50, 80, 110, and 140 ml/min were used. As Table 7 demonstrates, there does not appear to be any significant flow rate dependence for the excitation temperature. It was also noted that the temperature was fairly uniform throughout the viewing region of the discharge from measuring cross sections of the tube from the top of the primary discharge to

Figure 7
Eleven-point Temperature Plot at 70 W

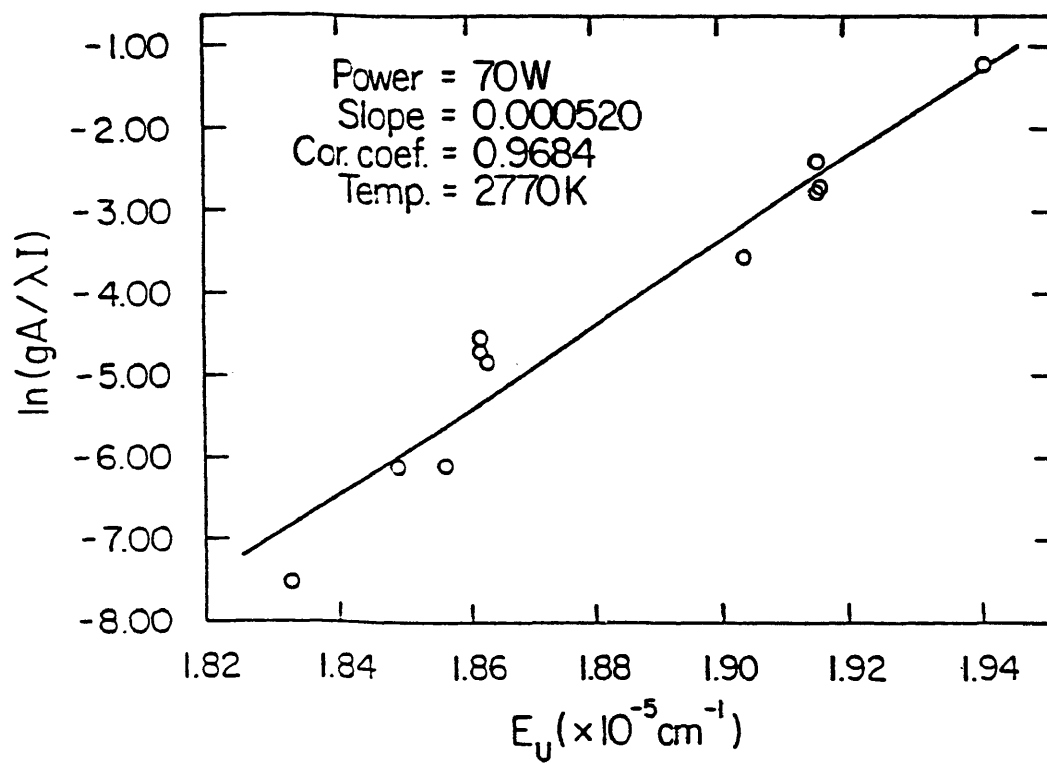


Figure 8
Eight-point Temperature Plot at 70 W

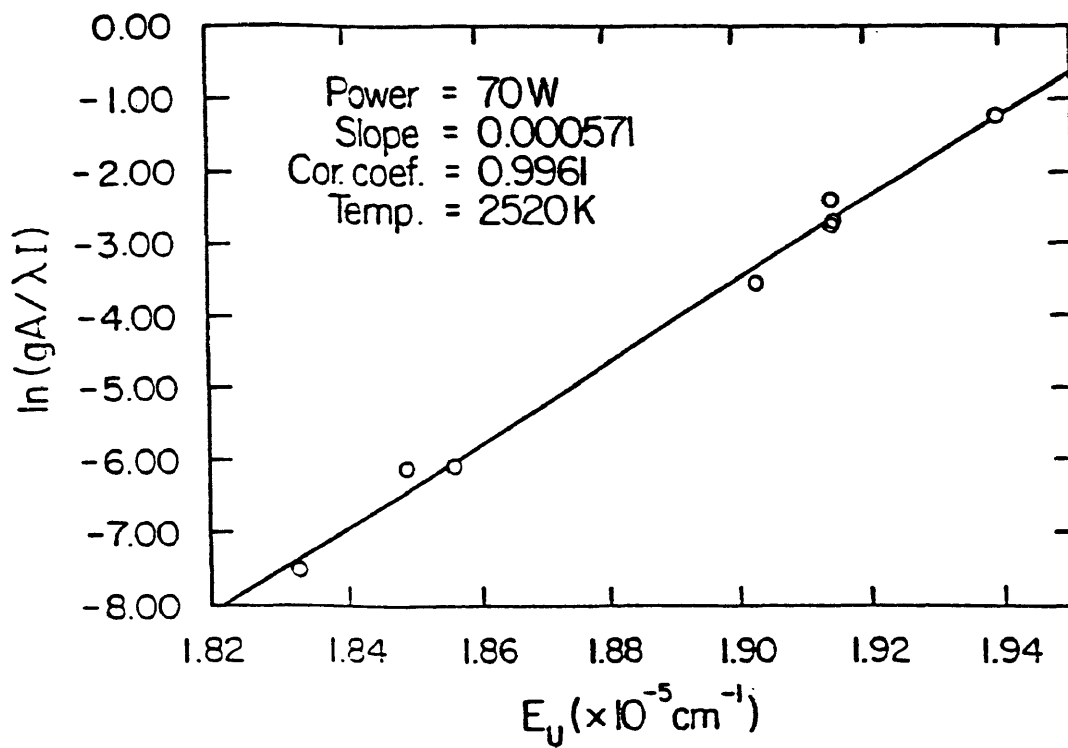


Table 6

Power Effect* on Excitation Temperature (K)

<u>Power (W)</u>	<u>Eleven-point Temperature</u>	<u>Slope x 10⁵</u>	<u>Correlation Coefficient</u>
30	2572	55.926	0.932
40	2632	54.674	0.938
50	2679	53.715	0.967
60	2728	52.738	0.965
70	2767	51.997	0.968

<u>Power (W)</u>	<u>Eight-point Temperature</u>	<u>Slope x 10⁵</u>	<u>Correlation Coefficient</u>
30	2324	61.904	0.996
40	2328	61.811	0.995
50	2430	59.196	0.997
60	2496	57.655	0.996
70	2517	57.130	0.996

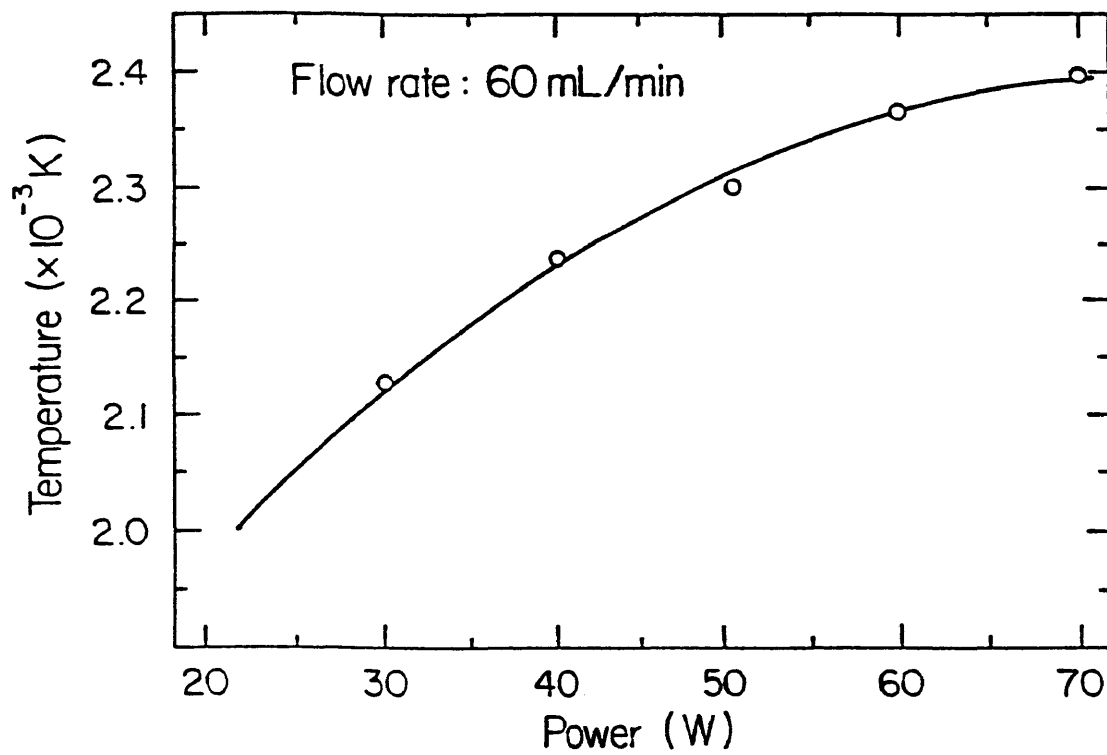
* Flow rate = 60 ml/min

Table 7
Flow Rate Effect* on Excitation Temperature (K)

<u>Flow Rate</u> <u>(ml/min)</u>	<u>Eight-Point</u> <u>Temperature</u>	<u>Slope x 10⁵</u>	<u>Correlation</u> <u>Coefficient</u>
50	2505	57.431	0.997
80	2549	55.474	0.989
110	2510	57.315	0.996
140	2543	56.581	0.994

*Power = 70 W

Figure 9
Power Dependence of Temperature



the grounding electrode.

Unfortunately, the two-line method appeared to be unsatisfactory compared to the slope method. The results of this phase of the experiment provided no conclusive information about the temperature whatsoever, and the experiment's total lack of reproducibility, with temperatures ranging from approximately 860 to 1430K, is even more damaging evidence of the method's failure.

Conclusion: Based on the stringent requirements for wavelength selection outlined earlier, the poor results obtained by the two-line method may be attributed to the difficulty of finding suitable wavelength pairs to give an accurate reliable result. For this reason we concluded that the slope method was indeed the method of choice for the determination of the excitation temperature of helium in the HDD.

Workman et. al studied the excitation temperature of a microwave-induced helium plasma formed inside a laminar flow torch by using the method of plotting $\log(I\lambda/gA)$ versus E_u .²¹ The results of the MIP experiments differed from the HDD results in a number of ways. In their results temperatures ranging from 5700-6700K were obtained at various power and flow rate combinations. In addition their determinations were made at five different positions across the plasma's equator. According to their findings, intensity measurements were found to be significantly flow rate dependent. Many of the helium lines incorporated in their

study were used in our research. It is interesting to note that while the HDD has considerably lower excitation temperatures than the helium MIP, the limits of detection are comparable or better for a number of elements, possibly indicating that the excitation mechanisms involved in the two plasmas are not the same.

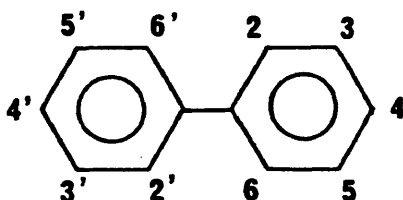
Chapter V

Analysis of Polychlorinated Biphenyls

Introduction: Of particular interest and concern to environmental analytical chemists today is the study of polychlorinated biphenyls (PCBs). Polychlorinated biphenyls are produced commercially by chlorinating biphenyl with anhydrous chlorine in the presence of a catalyst such as ferric chloride or iron filings to yield a variety of PCB mixtures. These mixtures are marketed under commercial trade names such as Phenoclor, Clophen, and Aroclor. Each mixture in the Aroclor series has a four-digit numerical designation, the first two numbers of which denote the molecular type. The number 12 represents chlorinated biphenyls; 54 indicates terphenyls. There are also biphenyl/terphenyl blends designated by 25 and 44 (75% and 60% biphenyl respectively).²² Trace amounts of chlorinated terphenyl may also be present in mixtures which are intended to be primarily composed of chlorinated biphenyls. The second pair of numbers in the designation gives the weight percent of chlorine in the mixture. As an example, Aroclor 1221 is a combination of polychlorinated biphenyls which is 21% chlorine by weight. Various mixtures of PCBs can be obtained with 21%, 32%, 42%, 48%, and so on. The viscosity of the sample increases directly with an increase in the chlorine

content so that mixtures may exist as liquids, resins, and even solids.

There are ten substitution sites on the biphenyl ring, as shown below, giving rise to 209 possible congeners, ranging from monochlorobiphenyls to decachlorobiphenyl. Each



congener has been assigned a number according to a system devised by Ballschmiter and Zell (Appendix A), thus the option exists for listing the congeners numerically (1-209) rather than by the more complicated and cumbersome substitution patterns.

PCBs, until recently, were widely used in industry because of their excellent physical properties including good thermal stability, strong resistance to acids, bases, and corrosive chemicals, general inertness, and insolubility in water.²³ In general, the Aroclors are very high boiling, with boiling points ranging from 278°C for 1221 to 415°C for 1268. Because of their electrical properties PCBs were widely used by the electrical industry in capacitors and transformers as coolant insulation fluids. The electrochemical properties of the PCBs have not been thoroughly investigated, however, since the stability of the molecules makes the determination of oxidation/reduction potentials difficult.²³ Other applications have included use

as plasticizers, heat transfer fluids, solvent extenders, lubricants, and flame retardents.

Annual production of PCBs in the Western world was estimated to have peaked at 100 million pounds in the late 1960s.²² Their inherent and extreme resistance to degradation has thus led to the persistent presence of PCBs in the ecosystem as environmental contaminants. Although commercial production of PCBs has been greatly curtailed, these reductions do not offset the detrimental effects which improper disposal techniques and spills have had on the environment in recent years. PCBs have been detected at significant levels in such a variety of matrices that they are now regarded, along with DDE [1,1-dichloro-2,2-(bis p-chlorophenyl)-ethane], as the most prevalent chlorinated aromatic pollutants in the world.²² PCBs have even been detected in humans, particularly in the adipose tissue²⁴, and the hazardous nature and mutagenic properties of some of the congeners are only beginning to surface.^{25,26,27}

The difficult task of quantitating PCBs as environmental contaminants is compounded by matrices in which the PCBs are present such as soil, oil, water, fish tissue, blood etc . . . which also present challenges with respect to sample cleanup and isolation of the PCBs. A number of methods have been developed over the years for the determination and quantitation of PCBs. Quantitative methods can be divided into non-selective and congener-selective categories.

Among the non-selective techniques are derivatization

and pattern recognition. Two extremes have been demonstrated for the derivatization technique. Cooke et.al described the on-column catalytic reduction of PCBs to biphenyl before determination by GC coupled with mass spectrometry (GC-MS).²⁸ This method reportedly allows detection of polychlorinated species at nanogram levels. A second method, the perchlorination technique, is based on the conversion of all PCB congeners present to decachlorobiphenyl. One disadvantage of this technique is that biphenyl is also chlorinated, giving rise to artificially high quantitation values.^{29,30,31} Neither of these techniques yields any information on PCB composition or Aroclor identity.

Pattern recognition, on the other hand, is based on the premise that a gas chromatogram is a fingerprint of the PCB sample. Dunn and coworkers used chromatograms of Aroclors 1242, 1248, 1254, 1260 as models to categorize chromatograms of "real" samples on the basis of similarities between their peak profiles.³² Such an approach is an oversimplification and, in many cases, is not applicable to accurate quantitation because the PCBs originate from partially decomposed Aroclors, mixtures of Aroclors, or non-Aroclor sources.³³

Congener-selective methods have primarily utilized the GC/ECD and GC/MS combinations. The most widely used and most sensitive technique involves separation through high resolution capillary gas chromatography and subsequent electron capture detection. The primary disadvantage of the ECD for quantitative purposes is that the signals generated

are not directly proportional to the mole quantities present. Chlorine substitution patterns significantly affect the magnitude of the signal observed using electron capture detection.³⁴ Cairns and Siegmund illustrated the problem of disproportionate responses by comparing ECD signals for a series of homologs. The differences in signals for a group of dichlorobiphenyl isomers were especially noteworthy. One figure showed peak heights for 1-ng samples of five different dichlorobiphenyls chromatographed under the same conditions. Comparison of the peak heights gave a ratio of 1:1:4:4:2 for the five isomers.³⁴ In order to quantitate PCBs by GC-ECD the system must be calibrated either for all 209 congeners, using relative response factors to an internal standard, or for some significant subset (i.e. 80 congeners) from which conclusions about the remaining compounds must be drawn.³⁴ In either case the groundwork for the procedure is tedious, costly, time consuming, and largely instrument specific. Even after all this work is carried out there is still the possibility that response factors may change for a given instrument over time, resulting in a need for re-calibration to ensure optimum accuracy.

PCB mass spectra are distinctive because of the peak clusters typical of chlorine-containing compounds. If PCBs are present in sufficient quantity to yield a complete spectra, unknowns may be identified upon comparison with spectra obtained from standards.^{35,36} While natural isotopic abundance ratios do not vary, instruments and interferences

may. For this reason ratios compared to standards are sometimes more reliable than isotope ratios.³⁷ GC-MS may be used for a quantitative peak-to-peak comparison of a PCB sample to Aroclor reference standards. While the disproportionate responses observed with ECD are not a problem in MS, detection with GC-MS is weight dependent; therefore, molar sensitivity tends to decrease with increased molecular weight.³⁴

The helium discharge detector has been shown to be highly viable for selective quantitation of individual PCB isomers.³⁸ Its application to the analysis of solutions containing PCBs was the focus of the next phase of this research.

i. Overview of Published HDD Results for
PCB Determinations

Previous work in our laboratory (Appendix B) has demonstrated that the HDD could be applied to a more direct approach for quantitating individual PCB congeners. Congener peak areas were converted to concentrations with the following equations:

From the internal standard peak area:

$$\text{Cl unit area} = \frac{\text{Peak area}}{\text{Concentration (}\mu\text{g/ml)}}$$

From the congener peak area:

$$\text{Concentration (}\mu\text{g/ml)} = \frac{(\text{PCB Area})}{(\text{Cl unit area})} \cdot \frac{(\text{g PCB/mol PCB})^*}{(\text{g Cl /mol PCB})}$$

* Congener identity or number of chlorines must be known

Solutions containing known concentrations of twenty-nine congeners were tested using tetrachlorobenzene (TCB) and hexachlorobenzene (HCB) as internal quantitative standards. Table 8 contains the results of this experiment. An average error of $\pm 3.2\%$ was obtained for the congeners studied.

Table 8
PCB Congener Concentrations Determined by HDD³⁸

<u>BZ#</u>	<u>Substitution Pattern</u>	<u>Concentration</u> ($\mu\text{g/ml}$)		<u>%Error</u>
		<u>Known</u>	<u>Found</u>	
1	2	7.32	7.14	-2.44
3	4	5.96	5.59	-6.17
15	4,4'	4.55	4.56	0.22
18	2,2',5	1.74	1.77	1.54
21	2,3,4	6.02	5.97	-0.84
24	2,3,6	6.82	6.88	0.92
31	2,4',5	1.23	1.32	7.45
33	2',3,4	4.44	4.49	1.20
40	2,2',3,3'	5.25	4.98	5.20
49	2,2',4,5'	0.98	1.00	2.00
50	2,2',4,6	3.62	3.56	-1.64
52	2,2',5,5'	1.12	1.11	-1.16
54	2,2',6,6'	6.43	6.67	3.69
60	2,3,4,4'	3.80	3.75	-1.35
61	2,3,4,5	6.36	6.11	-3.88
65	2,3,5,6	5.38	5.09	-5.31
66	2,3',4,4'	2.96	2.97	0.65
70	2,3',4',5	2.13	2.04	-4.38
77	3,3',4,4'	0.912	0.933	2.33
88	2,2',3,4,6	4.03	3.72	-7.73
97	2,2',3',4,5	4.80	4.79	-0.28
101	2,2',4,5,5'	5.91	5.90	-0.14
105	2,3,3',4,4'	1.98	1.90	-3.87
116	2,3,4,5,6	5.58	5.35	-4.16
136	2,2',3,3',6,6'	5.00	4.72	-5.64
153	2,2',4,4',5,5'	3.62	3.82	5.51
171	2,2',3,3',4,4',6	4.34	4.58	5.68
183	2,2',3,4,4',5',6	3.98	3.68	-7.55
209	2,2',3,3',4,4',5,5',6,6'	1.00	1.02	2.00

The total area generated in Aroclor chromatograms could also be correlated to the area of the internal standards to give the weight percent of chlorine present without any prior knowledge of the identity of the individual congeners. These results were compared to a potentiometric procedure³⁹ developed in our laboratory for the determination of halogen content in organic compounds. (Appendix C) The Aroclors' chlorine percentages agreed well with the nominal percentages as shown in Table 9.

The primary advantage of the HDD for PCB quantitation is the fact that chromatographic peak areas are directly proportional to the relative moles of chlorine present.⁴⁰ Consequently, relative response factors can be eliminated. Furthermore, only chlorine-containing compounds will be detected, further simplifying the potentially complex chromatography associated with real samples.

Table 9
Chlorine Composition Determined for Aroclors^{38,40}

<u>Aroclor</u>	<u>% Cl</u>	<u>Titration</u> <u>expt. %Cl</u> ^a	<u>GC-HDD</u> <u>expt. %Cl</u> ^a
1221	21	21.5(0.4)	21.7(0.4)
1232	32	31.9(0.6)	32.0(0.3)
1242	42	42.6(0.2)	42.3(0.5)
1248	48	47.6(0.4)	48.1(0.2)
1254	54	53.8(0.4)	53.4(0.4)

^aMean from three determinations (\pm average deviation)

ii. Identification and Quantitation of Individual PCB Congeners

The primary disadvantage of quantitating the individual congeners by this method, as shown in the aforementioned formulas, is that the congener identity must be known. At the very least, the number of chlorine atoms on the biphenyl ring must be known so that the mole amount of chlorine determined for a given peak, through comparison with the internal standard, can be converted to moles of PCB congener.

The most common method of identification by GC is the use of a relative retention index where the PCB retention times are converted to a relative scale dictated by internal retention standards. Such a procedure, in this case, would be very tedious and expensive if all 209 congeners were evaluated. Nevertheless, Mullin et. al completed the synthesis of all 209 congeners and compiled a relative retention index (Appendix D) based on the PCB retention time in relation to octachloronaphthalene (OCN).⁴¹ They were able to separate 187 PCBs using a 50m narrow-bore, SE-54 fused silica capillary column, leaving eleven pairs incompletely resolved. The following discussion demonstrates how Mullin's relative retention data base could be correlated to our experimental conditions for the separation, identification, and quantitation of individual PCB congeners in Aroclor samples.

Experimental Procedure: Solutions containing a subset of thirty-six congeners, covering the entire range of chlorination, were spiked with TCB and OCN as retention markers. Relative retention times were calculated from the ratio

$$\frac{\text{PCB time} - \text{TCB time}}{\text{OCN time} - \text{TCB time}} .$$

TCB elutes well before any of the PCB congeners, and OCN elutes after all of the congeners except octachlorobiphenyl 206 and decachlorobiphenyl. Chromatograms were obtained using a temperature program of 65°C-6°Cmin⁻¹-280°C(15min). Averages were calculated for relative retention times of duplicate runs.

Results and Discussion : Reproducibility of the retention index was very good with an average deviation of 0.0005 retention units and no deviations greater than 0.003 units. Table 10 shows the congeners studied along with experimental and literature relative retentions.

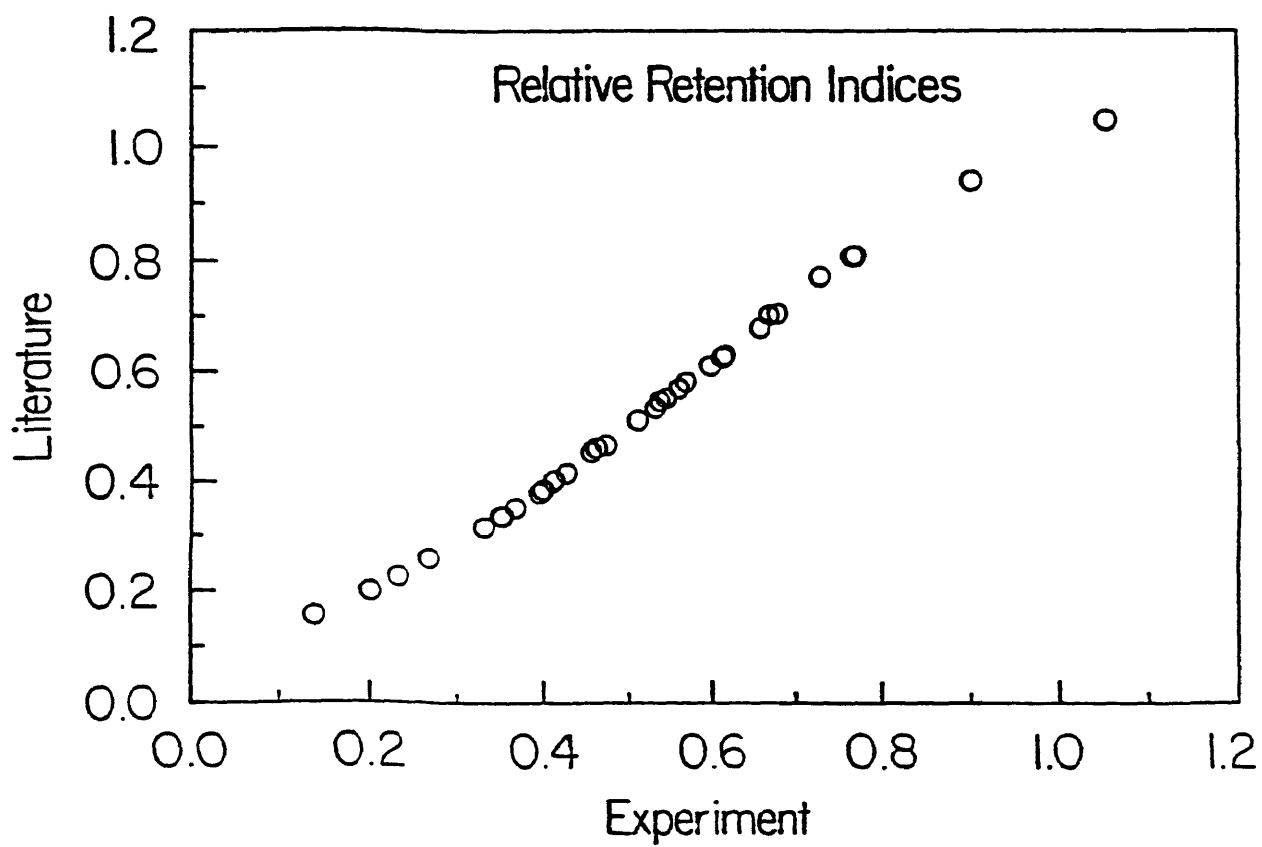
The thirty-six congeners used can easily be identified, but the results themselves give no information about the remaining 173 PCBs. A plot of the literature values as a function of the experimental data is shown in Figure 10. The correlation appears linear over a portion of the curve, however, significant deviations from linearity were observed in both the upper and lower ends of the graph, giving it the appearance of an elongated S. The fact that the plot contained virtually no random scattering of points suggested that some mathematical expression could be formulated to approximate the curve and allow interpolation of experimental/literature values. Thus, the function could be used to calculate a predicted literature value from which the experimental data would reveal the identity of the unknown congener.

Table 10

PCBs and Relative Retention Times

BZ#	Experiment	Literature
1	0.1386	0.1544
3	0.1996	0.1975
10	0.2316	0.2243
7	0.2671	0.2566
30	0.3299	0.3165
18	0.3480	0.3378
15	0.3514	0.3387
24	0.3646	0.3508
54	0.3930	0.3800
26	0.3995	0.3911
31	0.4085	0.4024
50	0.4095	0.4007
33	0.4236	0.4163
21	0.4238	0.4135
52	0.4551	0.4557
49	0.4612	0.4610
65	0.4722	0.4671
40	0.5096	0.5102
61	0.5303	0.5331
70	0.5321	0.5408
66	0.5376	0.5447
88	0.5431	0.5486
60	0.5596	0.5676
101	0.5676	0.5816
97	0.5949	0.6100
116	0.6024	0.6132
136	0.6098	0.6257
77	0.6125	0.6295
143	0.6546	0.6789
153	0.6660	0.7036
105	0.6765	0.7049
183	0.7273	0.7720
171	0.7621	0.8089
202	0.7652	0.8089
207	0.8991	0.9423
209	1.0496	1.0496

Figure 10
Correlation of Experimental and Literature
Relative Retention Indices



First attempts at finding a function involved using a linear least squares analysis. Predicted values were exceptionally poor at the ends of the graph. The deviations at each end also affected predictions in the linear region and gave poor results.

A Hewlett-Packard regression analysis routine was then utilized which builds a polynomial regression model of the form

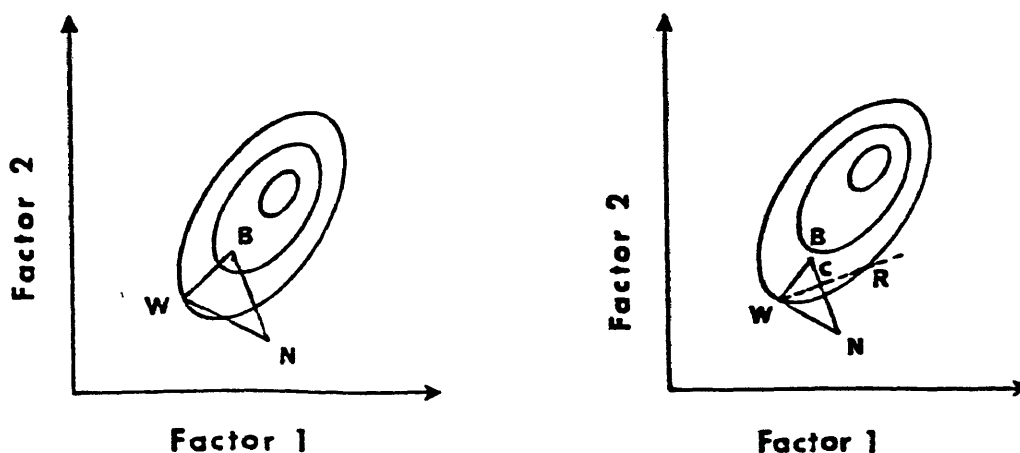
$$y(x) = a_0 + a_1x + a_2x^2 + \dots + a_nx^n$$

where n is less than or equal to six and coefficients are computed using the Cholesky method which factors the sum of squares and cross-products matrix.⁴² Experimental values were used as the independent variable and literature values as the dependent variable to obtain coefficients for a fourth degree polynomial. This method worked fairly well in the central portion of the graph, however, unacceptable differences were still found at the ends.

A third method which appeared to have a strong potential for successfully identifying a useful function for the curve was a simplex optimization method. This simplex method is a sequential optimization technique that involves repeated observations of a system response to selected variables, selection of new values for the variables, followed by further observation, and so on.⁴³ For a two variable problem the procedure can be described as one of tracking on a response surface whose three axes correspond to variable 1, variable 2, and the response. This method of tracking is called the simplex, a geometric figure with one

more vertex than the number of variables. Figure 11 shows a typical simplex in two dimensions.⁴³

Figure 11. Simplex on Response Surface⁴³



A new simplex may be constructed next to an existing one by rejecting one of the three original vertices and creating a new vertex to replace it. Thus the simplex moves about the factor space and samples response values as it progresses. Because the simplex must move toward a better region of the factor space, in a step-wise manner individual vertices corresponding to the most undesirable responses are rejected and replaced with their mirror images through reflection across the face formed by the remaining two vertices. The simplex continues tracking about in this fashion until the best coefficients are obtained for the function being studied.

The graph, previously shown in Figure 10, bears some resemblance to both hyperbolic tangent and inverse tangent functions. A Fortran simplex program by Jurs⁴³ (Appendix E), was processed on an AT&T 3B2 microcomputer for coefficient determinations in the simplex optimization. Estimated coefficients for the target functions were substituted into the program as starting points. For example, in the case of the inverse tangent, the function

$$y - a = c [\arctan (x-b)]$$

was employed in which the parameters being optimized were a and b, the offset values, and c the amplitude. The expressions resulting from optimization again provided good agreement except at the ends of the graph. An alternative method was attempted in which the data set was divided into two segments at about 0.6 relative retention units along the experimental axis where a point of inflection occurred. Coefficients for a third degree polynomial were approximated for each segment of the graph. The polynomial equations obtained, in which y is the predicted literature value and x is the experimental relative retention index, were as follows:

Experimental Relative Retention Index < 0.6:

$$y = 0.08809 + 0.2691x + 1.618x^2 - 1.004x^3$$

Experimental Relative Retention Index > 0.6:

$$y = 0.2710 - 0.6117x + 2.905x^2 - 1.549x^3$$

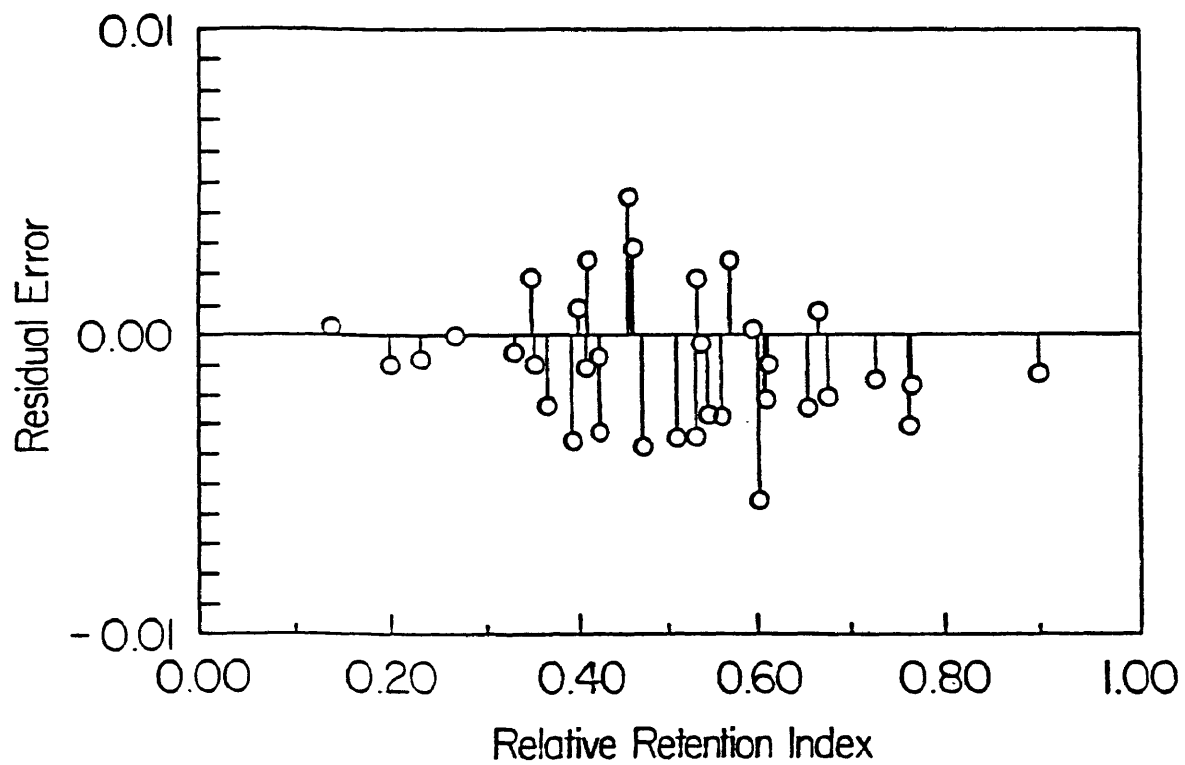
Table 11 lists the PCBs studied, the literature values, corresponding polynomial predictions, and residuals. Figure 12 shows a plot of these residuals as a function of the experimental relative retention index. Predicted relative retention values agreed well with literature values for most of the congeners studied. an average residual error of ± 0.0023 units, or an average relative error of $\pm 0.44\%$ was obtained. Considering that the average residual error is less than the index differences for most of the PCB congeners (see Appendix D), we felt that the curve-fitting equation developed was adequate for fairly reliable identification of PCB congeners in complex samples.

Table 11

**Comparison of Literature Relative
Retentions and Polynomial Predictions**

BZ#	Literature	Prediction	Residual	% Error
1	0.1544	0.1541	-0.0003	0.19
3	0.1975	0.1985	0.0010	0.51
10	0.2243	0.2251	0.0008	0.36
7	0.2566	0.2566	0.0000	0.00
30	0.3165	0.3171	0.0006	0.19
18	0.3378	0.3359	-0.0019	0.56
15	0.3387	0.3397	0.0010	0.30
24	0.3508	0.3532	0.0024	0.58
54	0.3800	0.3836	0.0036	0.95
26	0.3911	0.3902	-0.0009	0.23
50	0.4007	0.4018	-0.0011	0.27
31	0.4024	0.3999	-0.0025	0.62
21	0.4135	0.4168	0.0033	0.80
33	0.4163	0.4170	0.0007	0.17
52	0.4557	0.4511	-0.0046	1.01
49	0.4610	0.4581	-0.0029	0.63
65	0.4671	0.4709	0.0038	0.81
40	0.5102	0.5137	0.0035	0.69
61	0.5331	0.5366	0.0035	0.66
70	0.5408	0.5389	-0.0019	0.35
66	0.5447	0.5450	0.0003	0.06
88	0.5486	0.5513	0.0027	0.49
60	0.5676	0.5704	0.0028	0.49
101	0.5816	0.5791	-0.0025	0.43
97	0.6100	0.6098	-0.0002	0.03
116	0.6132	0.6188	0.0056	0.91
136	0.6257	0.6279	0.0022	0.35
77	0.6295	0.6305	0.0010	0.16
143	0.6789	0.6814	0.0025	0.37
153	0.7036	0.7028	-0.0008	0.11
105	0.7049	0.7070	0.0021	0.30
183	0.7720	0.7735	0.0015	0.19
171	0.8089	0.8120	0.0031	0.38
202	0.8089	0.8106	0.0017	0.21
207	0.9423	0.9436	0.0013	0.14
209	1.0496	1.0380	-0.0116	1.11

Figure 12
Plot of Residual Error versus Experimental
Relative Retention Indices



iii. Aroclor Analysis

Experimental Procedure: Solutions containing a series of Aroclors (Alltech Associates) were prepared in hexane at concentrations of 25.0 µg/ml and spiked with HCB and TCB, each at a concentration of 1.00 µg/ml. OCN was also added as an internal standard for the retention index. The solutions for Aroclors 1221, 1232, 1242, 1248, and 1254 were chromatographed using the same temperature program employed previously [$65^{\circ}\text{C}-6^{\circ}\text{Cmin}^{-1}-280^{\circ}\text{C}(15\text{min})$]. Congeners were tentatively identified by a polynomial fit to Mullin's retention index as previously described.

Results and Discussion: Identification of the PCBs present in each Aroclor made it possible to determine the amounts and weight percents of each congener present. The results of this study are given in Tables 12-16. Figure 13 shows representative chromatograms and the characteristic shifts of the peak clusters. In each chromatogram a majority of the peaks were identified by the polynomial fit to Mullin's data for each Aroclor. Only a few peaks gave polynomial predictions which did not match literature values. In these cases unknown compounds were considered to be impurities. Results of calculations of the total chlorine weight percentage for each sample agreed with the nominal Aroclor percentages, indicating that quantitation could be undertaken successfully. A ± 0.003 index-unit window was used on the polynomial prediction relative retention times

for matching to literature values. In some cases several congeners were considered in the identification for one peak due to very similar retention indexes. In most cases the congeners were in the same homolog group, thus variances in percent compositions were not applicable. In a few cases the multiple peak identities gave congeners in different homolog classes, which gave slight variations in the overall weight percent composition of the Aroclors. Numbers given in parentheses were not used in homolog weight percent calculations and were eliminated primarily because literature data did not confirm their presence.

Figure 13
Comparison of Aroclor Chromatograms

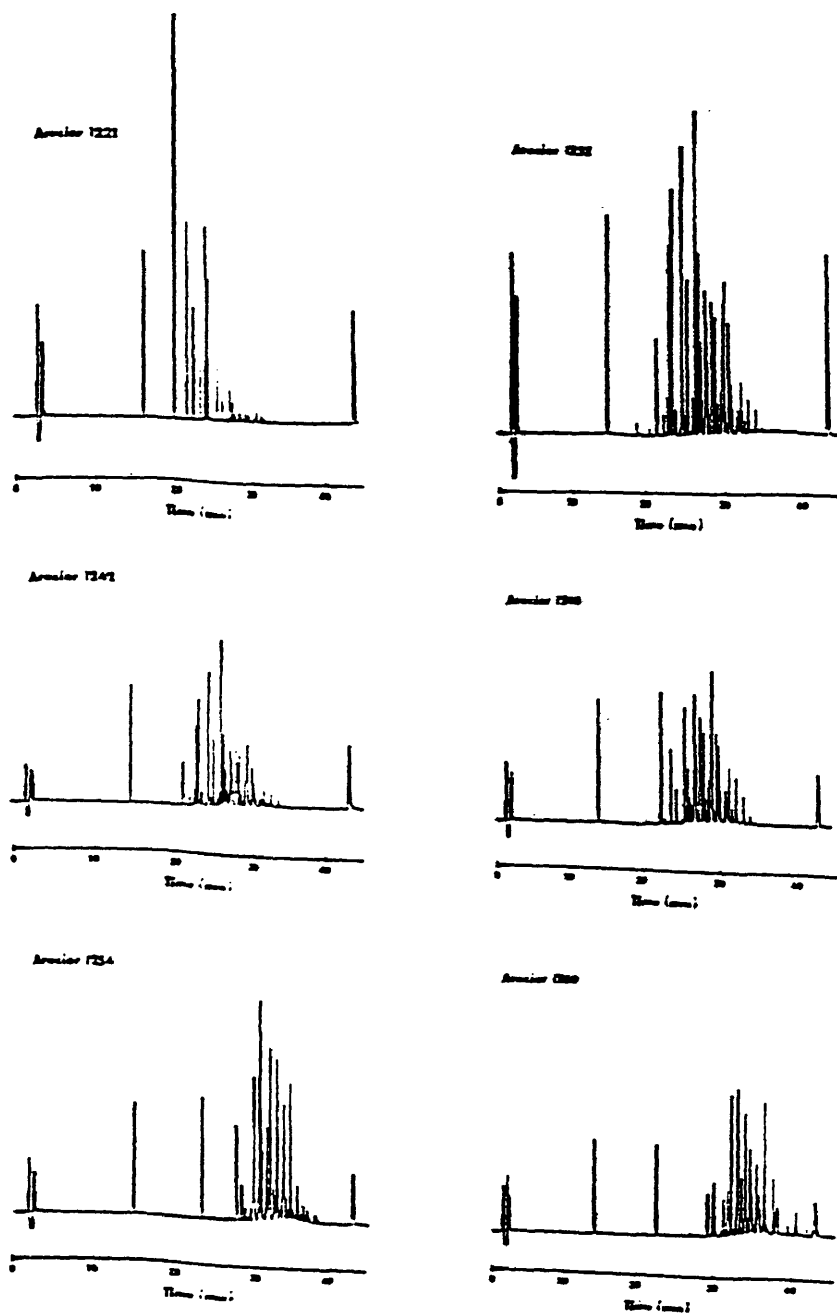


Table 12
Analysis of Aroclor 1221

Peak	Average Retention Time (min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
1	18.225	0.1386	0.1538	0.1544	1	34.5
2	19.753	0.1935	0.1934	0.1937	2	3.3
3	19.913	0.1990	0.1980	0.1975	3	17.3
4	20.798	0.2310	0.2242	0.2243	10	6.2
				0.2245	4	
5	21.793	0.2666	0.2564	0.2566	7	2.8
				0.2570	9	
6	22.210	0.2816	0.2697	0.2709	6	3.1
7	22.450	0.2902	0.2779	0.2783	8	10.6
				0.2785	5	
8	23.965	0.3446	0.3319	0.3319	13	1.1
9	24.175	0.3521	0.3396	0.3387	18	4.0
				0.3398	15	
10	24.813	0.3750	0.3636	0.3636	32	0.9
11	25.820	0.4112	0.4025	0.4024	31	1.9
				0.4031	28	
12	26.198	0.4247	0.4173	0.4170	20	0.9
13	26.470	0.4345	0.4281	0.4267	22	0.4
14	27.095	0.4569	0.4531	0.4510	69	0.4
15	27.840	0.4537	0.4831	0.4832	44	0.3
16	28.288	0.4997	0.5013	0.4999	64	0.3
17	29.238	0.5369	0.5401	0.5407	70	0.3
				0.5408	76	
18	29.378	0.5388	0.5457	0.5447	66	0.4
				0.5464	80	
				0.5464	95	

Table 13
Analysis of Aroclor 1232

Peak	Average Retention Time(min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
1	18.260	0.1384	0.1537	0.1544	1	17.9
2	19.803	0.1938	0.1937	0.1937	2	1.7
3	19.965	0.1996	0.1983	0.1975	3	10.3
4	20.840	0.2310	0.2242	0.2243	10	4.9
				0.2245	4	
5	21.843	0.2670	0.2562	0.2566	7	1.9
				0.2570	9	
6	22.250	0.2817	0.2698	0.2709	6	2.3
7	22.493	0.2904	0.2781	0.2783	8	9.5
				0.2785	5	
8	23.288	0.3189	0.3059	0.3045	19	0.4
9	24.013	0.3449	0.3322	0.3315	13	0.8
10	24.155	0.3508	0.3383	0.3378	18	(8.8)
				0.3387	15	11.5
11	24.538	0.3638	0.3518	0.3521	27	0.3
12	24.855	0.3751	0.3637	0.3636	32	3.0
13	25.538	0.3997	0.3900	0.3911	26	0.6
14	25.865	0.4114	0.4027	0.4024	31	7.3
				0.4031	28	
				0.4035	21	
15	26.253	0.4253	0.4180	0.4170	20	3.5
				0.4187	53	(3.0)
16	26.520	0.4349	0.4286	0.4267	22	1.7
17	26.705	0.4415	0.4359	0.4334	45	(0.5)
				0.4375	36	0.6
18	26.985	0.4516	0.4471	0.4450	46	0.2
				0.4488	39	(0.2)
19	27.130	0.4568	0.4530	0.4510	69	1.9
				0.4554	73	

Table 13
Analysis of Aroclor 1232 (continued)

Peak	Average Retention Time (min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
20	27.298	0.4628	0.4596	0.4593	38	1.8
21	27.433	0.4677	0.4651	0.4651	48	1.0
22	27.880	0.4837	0.4832	0.4832	44	1.9
23	28.005	0.4882	0.4883	0.4870	42	1.7
24	28.323	0.4996	0.5012	0.4999	64	1.8
25	28.623	0.5104	0.5134	0.5142	103	0.4
26	29.145	0.5291	0.5347	0.5341	74	0.7
27	29.280	0.5340	0.5403	0.5407	70	1.9
				0.5408	76	
28	29.413	0.5387	0.5456	0.5464	80	1.8
				0.5464	95	
29	30.000	0.5598	0.5697	0.5676	56	1.5
				0.5676	60	
30	30.213	0.5675	0.5774	0.5779	89	0.6
31	30.413	0.5747	0.5865	0.5862	113	0.2
32	30.990	0.5954	0.6100	0.6100	97	0.1
				0.6105	86	
33	31.163	0.6016	0.6171	0.6171	115	0.2
				0.6175	87	
34	31.518	0.6143	0.6324	0.6314	110	0.3
				0.6349	154	(0.3)
35	32.370	0.6449	0.6692	0.6693	118	0.3
36	33.290	0.6779	0.7088	0.7078	127	0.1

Table 14
Analysis of Aroclor 1242

Peak	Average Retention Time(min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
1	18.265	0.1384	0.1537	0.1544	1	0.6
2	20.853	0.2313	0.2245	0.2243	10	3.5
				0.2245	4	
3	21.848	0.2671	0.2562	0.2566	7	0.8
4	22.260	0.2819	0.2700	0.2709	6	1.4
5	22.498	0.2904	0.2781	0.2783	8	7.1
6	23.285	0.3187	0.3057	0.3045	19	0.8
7	24.000	0.3444	0.3317	0.3315	13	0.2
8	24.165	0.3508	0.3383	0.3378	18	12.8
				0.3387	15	(16.6)
9	24.540	0.3637	0.3517	0.3508	24	0.5
				0.3521	27	
10	24.868	0.3755	0.3642	0.3636	32	5.2
11	25.518	0.3989	0.3892	0.3911	26	1.2
12	25.613	0.4023	0.3928	0.3937	25	0.7
13	25.865	0.4114	0.4027	0.4024	31	13.1
				0.4031	28	
14	26.263	0.4256	0.4183	0.4170	20	6.4
				0.4187	53	(5.4)
15	26.523	0.4350	0.4287	0.4267	22	3.0
16	26.710	0.4417	0.4361	0.4375	36	1.2
17	27.015	0.4527	0.4483	0.4488	39	0.4
18	27.148	0.4574	0.4536	0.4510	69	3.7
				0.4554	73	
				0.4557	52	
19	27.313	0.4634	0.4603	0.4593	38	(3.5)
				0.4610	49	3.0
20	27.443	0.4680	0.4655	0.4651	48	2.3

Table 14
Analysis of Aroclor 1242 (continued)

Peak	Average Retention Time (min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
21	27.900	0.4844	0.4840	0.4832	44	3.6
22	28.025	0.4889	0.4891	0.4870	42	3.1
23	28.333	0.5000	0.5016	0.4999	64	3.7
24	28.640	0.5110	0.5142	0.5142	103	0.7
25	29.005	0.5241	0.5292	0.5290	63	0.1
26	29.168	0.5300	0.5357	0.5341	74	1.8
27	29.285	0.5342	0.5405	0.5407	70	3.8
				0.5408	76	
28	29.430	0.5394	0.5465	0.5464	80	4.3
				0.5464	95	
29	29.675	0.5482	0.5565	0.5562	55	0.3
30	30.025	0.5608	0.5708	0.5676	60	3.2
31	30.233	0.5682	0.5792	0.5779	89	1.4
				0.5814	90	
32	30.428	0.5752	0.5871	0.5862	113	0.6
				0.5880	99	
33	30.990	0.5954	0.6099	0.6100	97	0.5
				0.6105	86	
34	31.163	0.6016	0.6171	0.6171	115	0.5
				0.6175	87	
35	31.320	0.6073	0.6240	0.6243	148	0.3
36	31.508	0.6140	0.6320	0.6314	110	1.2
37	31.913	0.6286	0.6496	0.6499	151	0.3
38	32.380	0.6454	0.6698	0.6693	118	0.8
				0.6707	139	(0.7)
				0.6707	140	
39	33.330	0.6784	0.7094	0.7078	127	0.6

Table 15
Analysis of Aroclor 1248

Peak	Average Retention Time (min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
1	20.915	0.2277	0.2214	0.2243	10	0.3
				0.2245	4	
2	22.571	0.2865	0.2745	0.2709	6	0.8
				0.2783	8	
3	24.219	0.3447	0.3320	0.3315	13	7.4
4	24.952	0.3706	0.3590	0.3625	16	2.1
5	25.952	0.4059	0.3967	0.3937	25	8.5
6	26.362	0.4207	0.4130	0.4135	21	3.8
7	26.530	0.4270	0.4199	0.4187	53	0.2
8	26.616	0.4293	0.4225	0.4242	51	1.4
9	26.820	0.4367	0.4304	0.4334	45	1.2
10	27.095	0.4463	0.4411	0.4450	46	0.4
11	27.247	0.4516	0.4471	0.4450	46	7.1
				0.4488	39	(8.4)
12	27.413	0.4575	0.4537	0.4510	69	5.3
				0.4554	73	
				0.4557	52	
13	27.554	0.4625	0.4593	0.4593	38	2.7
				0.4587	43	
14	28.006	0.4784	0.4773	0.4757	104	5.8
15	28.136	0.4830	0.4824	0.4832	44	2.5
16	28.444	0.4941	0.4950	0.4984	72	5.5
				0.4989	71	
				0.4990	41	
17	28.753	0.5048	0.5071	0.5057	96	1.0
18	29.289	0.5237	0.5286	0.5290	63	2.7
19	29.397	0.5276	0.5329	0.5331	61	7.2
				0.5331	94	(6.5)

Table 15
Analysis of Aroclor 1248 (continued)

Peak	Average Retention Time(min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
20	29.530	0.5323	0.5383	0.5407 0.5408	70 76	8.3
21	29.807	0.5420	0.5494	0.5486	88	0.8
22	30.163	0.5546	0.5637	0.5666	155	4.2
23	30.373	0.5620	0.5722	0.5742 0.5744	92 84	3.8
24	30.563	0.5687	0.5798	0.5779 0.5814 0.5816	89 90 101	1.5
25	30.934	0.5818	0.5946	0.5968 0.5969	119 150	0.2 (0.1)
26	31.140	0.5891	0.6029	0.6024 0.6029	78 83	1.4
27	31.302	0.5948	0.6093	0.6100	97	1.3
28	31.347	0.5953	0.6099	0.6105	86	0.9
29	31.467	0.6006	0.6159	0.6149 0.6149 0.6150	81 145 117	0.7
30	31.503	0.6008	0.6162	0.6171 0.6175	115 87	0.5
31	31.653	0.6072	0.6239	0.6243	148	2.9
32	32.373	0.6315	0.6531	0.6563 0.6563	135 144	0.1
33	32.547	0.6388	0.6619	0.6608 0.6626	147 108	2.2
34	33.304	0.6655	0.6940	0.6955	146	0.2
35	33.467	0.6713	0.7009	0.7016	184	1.5
36	34.265	0.6994	0.7342	0.7329	137	0.4

Table 16
Analysis of Aroclor 1254

Peak	Average Retention Time (min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
1	27.262	0.4527	0.4484	0.4488	39	3.1
2	27.429	0.4588	0.4551	0.4554	73	1.1
				0.4557	52	
3	28.020	0.4786	0.4774	0.4757	104	1.5
4	28.460	0.4953	0.4962	0.4984	72	0.7
				0.4989	71	
				0.4990	41	
5	29.289	0.5246	0.5295	0.5290	63	0.6
6	29.430	0.5295	0.5352	0.5341	74	3.6
7	29.576	0.5347	0.5411	0.5407	70	9.3
				0.5408	76	
				0.5415	98	(8.3)
8	29.818	0.5433	0.5508	0.5518	121	1.1
9	30.183	0.5562	0.5655	0.5666	155	1.8
10	30.384	0.5633	0.5736	0.5742	92	11.8
				0.5744	84	
11	30.580	0.5702	0.5815	0.5814	90	3.4
				0.5816	101	
12	30.966	0.5839	0.5970	0.5968	119	0.4
				0.5969	150	
13	31.157	0.5907	0.6046	0.6029	83	2.7
				0.6062	152	(2.4)
14	31.330	0.5968	0.6115	0.6105	86	4.8
15	31.492	0.6025	0.6182	0.6175	87	1.3
				0.6183	111	
16	31.646	0.6091	0.6261	0.6256	120	10.4
				0.6257	136	(9.4)
17	32.081	0.6233	0.6432	0.6453	82	1.8
18	32.262	0.6298	0.6511	0.6499	151	1.2
19	32.371	0.6336	0.6556	0.6563	135	0.3
				0.6563	144	

Table 16
Analysis of Aroclor 1254 (continued)

Peak	Average Retention Time (min)	Average Relative Retention	Average Polynomial Prediction	Comparable Literature Values	BZ#	Average Weight%
20	32.554	0.6401	0.6635	0.6628	107	12.1
21	32.917	0.6529	0.6788	0.6789	143	0.5
				0.6781	134	
22	33.120	0.6601	0.6875	0.6871	122	0.8
				0.6871	133	(0.8)
23	33.340	0.6679	0.6968	0.6968	161	4.5
24	33.471	0.6725	0.7023	0.7016	184	(5.0)
				0.7035	132	5.3
				0.7036	153	
25	33.763	0.6828	0.7146	?	--	--
26	33.809	0.6845	0.7166	?	--	--
27	34.012	0.6916	0.7250	?	--	--
28	34.071	0.6944	0.7283	0.7284	130	0.7
29	34.302	0.7019	0.7372	0.7396	160	8.1
				0.7396	163	
30	35.247	0.7353	0.7760	0.7761	128	1.8
31	35.675	0.7505	0.7934	0.7965	174	0.3
				0.7968	181	
32	36.037	0.7632	0.8076	0.8089	171	0.8
				0.8089	202	(0.8)
33	36.593	0.7830	0.8295	0.8293	197	0.4
34	36.639	0.7846	0.8312	?	--	--
35	37.732	0.8233	0.8720	0.8740	170	0.5
				0.8740	190	

Table 17 gives a comparison of the experimental homolog weight percent distributions for five of the Aroclors to an average distribution reported in the literature.²³ The average number of chlorine atoms per molecule, the chlorine weight percents, and the approximate molecular weight of the different Aroclors are also given. Experimental values are in parentheses. The agreement between experimental and average values in virtually all cases was good to excellent, indicating that the identification and quantitation methods used were appropriate.

Differences in experimental and average literature values are readily accounted for by the variations associated with PCB mixtures. Although peak patterns for a given Aroclor are generally very similar from one batch to another, the composition of the mixture can vary markedly from lot to lot, as well as from brand to brand, with respect to the amount of individual congeners present.^{33,44} For this reason PCB data in the chemical literature may be regarded as quite useful qualitatively but only as somewhat helpful quantitatively.⁴⁵ An example of this point is demonstrated in Table 18 which gives a comparison of literature data for analyses of Aroclor 1242 from three different literature sources, as well as data from our own laboratory.^{44,46,47}

Table 17
Average Molecular Composition (Weight%)^a
of Selected Aroclors

#Cl	<u>1221</u>	<u>1232</u>	<u>1242</u>	<u>1248</u>	<u>1254</u>
0	10	b			
1	50 (55.1)	26 (29.8)	1 (0.6)		
2	35 (27.8)	29 (30.9)	13 (12.9)	1 (8.5)	
3	4 (4.0)	24 (19.0)	45 (45.4)	21 (22.7)	1 (3.1)
4	1 (1.6)	15 (14.5)	31 (32.9)	49 (39.0)	15 (15.3)
5		(1.8)	10 (6.2)	27 (18.0)	53 (52.0)
6			(0.6)	2 (7.8)	26 (24.2)
7				(1.5)	4 (1.7)
8					(0.4)

Average # Cl/molecule:

1.15	2	3	4	5
(1.2)	(2.0)	(3.1)	(3.9)	(5.0)

Approximate Weight %Cl:

21	32-33	40-42	48	52-54
(22.0)	(31.7)	(42.6)	(48.8)	(54.5)

Approximate Molecular Weight:

193.7	223.0	257.5	291.9	326.4
(195.3)	(224.9)	(256.3)	(286.5)	(326.6)

^aReference 23 (Experimental values given in parentheses)
^b5% tentatively identified as biphenyl

Table 18
Comparison of Literature Analysis Results
Average Molecular Composition of Aroclor 1242

<u>Biphenyl Homolog</u>	<u>Experiment Mole %</u>	<u>Literature Values</u>		
		<u>Mole %^b</u>	<u>Mole %^a</u>	<u>Mole %^c</u>
Monochloro	1.4	0.9	0.8	1.3
Dichloro	15.5	17.2	23.0	19.2
Trichloro	47.3	51.7	39.9	44.5
Tetrachloro	30.2	24.7	32.9	24.5
Pentachloro	5.1	5.2	3.4	7.5
Hexachloro	0.5	0.2	---	2.9

^aReference 23

^bReference 46

^cReference 47

Finally, some consideration should be given to certain aromatic impurities which may be present within the PCB mixtures. The potential contaminants include polychlorinated terphenyls (PCTs), polychlorinated quaterphenyls (PCQs), polychlorinated naphthalenes (PCNs), and polychlorinated dibenzofurans (PCDFs). Erickson suggests that PCDFs present at microgram per gram levels may be responsible for some of the toxicological properties attributed to the commercial PCB mixtures.²³ Again, the literature available can be of limited utility on this point because the presence and levels of contaminants often vary widely from batch to batch.²³ Such impurities as the PCDFs appear to be more of a problem in the more highly chlorinated mixtures, i.e. 1248 and higher. In a gas chromatographic analysis, an impurity, present in a detectable quantity, could conceivably have a retention time which might cause it to be mistaken for a PCB. The impurity would probably have to be present at least at the part per thousand level.

An analysis of 1242 by Albro revealed that five PCDFs were present at ng/g levels and that PCNs might be present, but the amounts were so small that detection was difficult and quantitation was nearly impossible.⁴⁶ Based on these results, it seems reasonable to assume that the impurity levels are not high enough to interfere significantly with identification. Some peaks, however, whose relative retention indices do not match any of those in the literature could possibly be impurities of the types mentioned here.

While the Aroclors' propensity for quantitative

variation must be taken into account, a congener comparison is still informative. Table 19 is a compilation of the PCBs identified in Aroclor 1242 along with calculated mole percents. Also listed are results from a similar study conducted by Albro.⁴⁶ Overall agreement was good with regard to the major constituents, although a number of congeners appeared exclusively in either study. Again, this occurrence may be attributed to the variations in composition from lot to lot for a given Aroclor.

Table 19
Comparison of Aroclor 1242 Analysis to Literature⁴⁶

BZ#	Expt. Mole%	Albro Mole%	BZ#	Expt. Mole%	Albro Mole%	BZ#	Expt. Mole%	Albro Mole%
1	0.95	0.68	54		0.17	60		0.21
2		0.04	45		0.70	121		0.92
3		0.22	53	5.22	0.97	98		0.13
10,4	4.47	4.12	52		4.08	95		0.53
9		0.31	75		2.18	113	0.47	0.39
7	1.06	1.04	43		0.44	91		trace
6	1.83	1.24	46		0.31	84		0.38
8	8.92	8.97	48	2.24	1.33	108		0.46
14		0.35	49	2.87	3.28	85		0.40
12		0.09	44	3.43	1.06	87		0.09
13	0.25	0.12	42	3.03		105		0.25
15		0.99	41		1.67	92		0.12
19	0.89	0.97	64	3.52		99	''''''	0.55
18	14.01	9.36	40		0.15	97	0.40	
17		2.92	103	0.61		115	0.42	
16		3.25	63	0.10		87	''''''''	
27	0.59	0.54	56		0.60	111	0.27	
32	5.65	2.15	47		1.65	148	0.23	
26	1.27	0.55	74	1.77	2.02	110	1.01	
31	14.36	4.53	70	3.63	1.11	151	0.21	
28	'	13.30	76	'''	trace	108	0.06	
25	0.74	1.68	80	4.15		107	''''''''''	
20		3.64	95	''''		118	0.67	
22	3.33	2.64	55	0.28		127	0.52	0.05
36	1.27		89	1.22		158	0.07	
33		2.83	78		0.52	101		0.27
35		0.66	81		0.28	120		0.31
37		1.62	77		0.34	123		0.36
39	0.44	1.03	72		0.33	126		0.03
69	3.58		66		0.81	143		0.07
73	''		69		0.24	138		0.08
						158		0.02

Unresolved peaks:

' 31 and 28
 '' 69 and 73
 ''' 70 and 76
 '''' 80 and 95
 '''''' 113 and 99
 '''''''' 115 and 87
 '''''''''' 108 and 107

Conclusions: The HDD has performed very well in the analysis of individual PCB congeners in a variety of Aroclors by element selective detection of atomic chlorine emissions at ppb levels. Because the area/unit mass Cl ratio does not depend on the PCB substitution pattern, there is no need for precalibration or response factor adjustment. The total chlorine percentage can be determined for any PCB mix without a knowledge of the congeners contained in it.

Individual congener identification and quantitation provides much more complete information than pattern recognition and derivatization. As more is learned about the toxicological properties of the various congeners, specific knowledge about the types and quantities of PCBs will be increasingly valuable, especially in situations where an assessment of the extent of contamination is required.

The ability to correlate experimental data to published data has proven to be time saving and cost effective in this research. As long as the correlation can be adequately described by some mathematical formulation, there appears to be no reason interpolation cannot be used to identify unknown PCBs. The method may possibly be applied to other groups of compounds if reliable literature data is available. Caution should be exercised in the selection of a literature data base, however, because possible errors associated with literature will undoubtedly affect the performance of the technique.

Chapter VI

Summary and Suggestions for Further Research

The helium discharge has been described as a relatively simple and very reliable element-specific multi-element detector for GC. Signals are detected through the generation of atomic emissions as analyte molecules dissociate in the plasma. Construction and maintenance of the GC-HDD system is fairly simple. Important advantages of the HDD include low helium consumption, excellent reproducibility, and the elimination of solvent-induced plasma extinction.³⁸ Limits of detection are at picogram levels for a variety of elements, and the response to element concentrations is linear over three or four orders of magnitude.

While there are any number of areas where the HDD might be applied, certain specific opportunities for experiments are suggested by this research. As mentioned previously, the infrared wavelength study could be pursued to determine limits of detection and selectivities in that region. Secondly, the PCB analysis could be further investigated and confirmed by analyzing and quantitating standard samples such as the transformer and motor oils from the National Bureau of Standards. Once standards have been successfully

tested, the HDD could be used to examine real samples such as fish tissue, sediment, blood etc. . . . Finally, the data correlation technique, which provides a mathematical means of extending the experimental data base, could be used with two sets of experimental data from the same laboratory, particularly in cases where appropriate and reliable literature references are not available. Relative retention indices obtained using different columns, different temperature programs, or a combination of the two could confirm the reliability of compound identification.

Appendix B

Direct Quantitation of PCB Congeners Using a Helium Discharge Detector and Internal Standard Techniques

PETER J. McATEER, TOM B. RYERSON, MARK D. ARGENTINE,
MARGARET L. WARE, and GARY W. RICE*

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185

Individual PCB congeners have been quantitated at ppm levels, with an average error of $\pm 3.2\%$, with the use of a helium discharge detector (HDD) for element-selective detection of Cl emission. Chlorinated internal standards of known concentrations were added to each solution determined to establish the relative peak areas per unit concentration of Cl present. No detector recalibration or response factor determinations were required, since the detector response is based solely on the moles of Cl present. The same methodology was utilized to determine the % Cl in Aroclor samples without prior identification of the PCB congener present.

Index Headings: Element selective detector; GC; Atomic emission; Spectroscopic techniques; Internal standard techniques; PCB determinations.

INTRODUCTION

The widespread distribution of polychlorinated biphenyls (PCB) in the environment and food chain ecosystem has been well documented over the past twenty years.^{1,2} The number of possible congeners (209) and the complexity of PCB mixtures commonly observed have resulted in a number of methods for quantifying the total PCB content in a sample. These methods have included derivatizations,³⁻⁴ pattern recognition routines in gas chromatography,^{4,5} and mass spectrometry.⁶ Several PCB congeners have been found to possess greater mutagenic properties relative to other congeners.^{7,8} Thus, selective congener quantitation may be more pertinent for assessing the potential ecological impact of specific PCB contaminations.

Selective quantitation of individual PCB congeners has been studied in detail. The most widely used and sensitive techniques involve separation of the congeners by gas chromatography (GC), using an electron capture detector (ECD).¹¹⁻¹³ The primary disadvantage for quantitative purposes is that signals generated by each PCB congener are not directly proportional to the mole amount of eluent present. Substitution patterns on the biphenyl rings have a marked effect on the observed signals.¹⁴ The response from a known amount of each congener must then be related to one or more internal standards to develop response factors for quantitating solutions of unknown composition. In such cases, one also must rely on the long-term detector stability to maintain these values, as well as on whether other ECDs of different construction can validly use such response factors for accurate quantitative measurements.

We recently reported on the development of a helium discharge detector (HDD) as an element-selective, mul-

ti-element detector for GC.⁹ The detector functions by means of producing atomic emission from the respective elements dissociated from compounds through collisional energy transfer processes with He metastable species produced from the discharge.

We later observed that peak areas observed in chromatograms for a number of chlorinated or brominated aliphatic hydrocarbons were directly proportional to the relative moles of halogen present.¹⁰ Thus, one could directly quantitate a number of compounds using an internal standard containing the same element at a known concentration, without relying on relative response factors.

We now report on the applicability of the HDD as a device which possesses a reliable and attractive alternative for direct quantitation of individual PCB congeners and mixtures.

EXPERIMENTAL

PCB Reference Solutions. Seventeen PCB congeners of known concentrations in hexane were provided by the Virginia Institute of Marine Science, College of William and Mary. An additional twelve congeners (Analabs) were weighed and diluted in hexane to yield concentrations on the order of 1 to 8 $\mu\text{g}/\text{mL}$. Internal references were prepared from 1,2,4,5-tetrachlorobenzene (TCB) and hexachlorobenzene (HCB) (Aldrich). Both standards were purified through two successive sublimations. Standard solutions containing 1000 $\mu\text{g}/\text{mL}$ of each internal standard were prepared in hexane (HCB required initial dissolution in dichloroethane prior to dilution with hexane, ~10% V/V). The TCB and HCB were added to the PCB solutions at concentrations of 4 $\mu\text{g}/\text{mL}$ each.

Stock solutions of Aroclor samples (Alltech) were prepared in hexane at a concentration of 1000 $\mu\text{g}/\text{mL}$. Diluted solutions containing the Aroclors and internal standards were prepared at concentrations of 50 $\mu\text{g}/\text{mL}$ and 2 $\mu\text{g}/\text{mL}$, respectively.

Apparatus. The design and operation of the HDD utilized in these investigations have been previously described.¹¹ All major instrument components were changed in the present study; however, the overall configuration was similar in design to that of the previous system. Details of the operational characteristics of the HDD, spectrometric system, and GC parameters used for the present investigation are summarized in Table I.

RESULTS AND DISCUSSION

The helium discharge detector provides a simple and reliable means of element-selective detection for GC by

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* Author to whom correspondence should be sent.

TABLE I. Operating conditions for the GC-HDD system.

(A) Helium discharge detector	
He flow rate:	60 mL/min
Voltage:	6000 V (RMS)
Frequency:	178 kHz
Load power:	66 W
	Model HPG-2 (ENI Power Systems)
(B) Spectrometric system	
Monochromator:	0.5 m (Hammamam, Model 30580)
Bandpass (FWHM):	0.22 nm (100 nm slit)
Analytical wavelength:	837.8 nm
Photomultiplier tube:	R758 (Hammamam)
FMT voltage:	1000 V (Keithley Model 247)
Amplifier:	Keithley Model 485 preamplifier
Integrator:	Shimadzu Model CR3A
(C) GC system	
GC:	Cario Erba Model 4120
Injection mode:	On-column (10 μ L injections)
Carrier gas:	Helium
Column:	DB-5, 30 m \times 0.25 I.d. (J&W)
Temp. program:	65°C-5°C/min-250°C (15 min)
Detector interface temp:	300°C

generating atomic emission through the dissociation of analyte molecules present in the discharge. The system is relatively simple to construct and maintain. He gas consumption is low (60 mL/min), and day-to-day reproducibility is excellent. A significant advantage of the HDD is that GC effluents are introduced above the region where the primary He discharge is produced; thus the discharge region where solvents and analyte molecules are introduced is continually replenished by long-lived energetic He species from the primary discharge.¹³

Absolute limits of detection observed for individual PCB congeners ranged from 10 pg for decachlorobiphenyl to 35 pg for the monochlorobiphenyl, based on a signal-to-background scatter ratio of three. The signal response to Cl concentration was linear over approximately four orders of magnitude. Selectivity over signals generated by nonanalyte species at the Cl analytical wavelength was approximately 350:1.

The ability to quantitate individual PCB congeners, using TCB and HCB as the internal standards, is given in Table II. The number of chlorinated sites and substitution sites was varied as much as possible over the entire range of PCB congeners to validate the general applicability of the method. An average relative area per unit Cl concentration was used from the TCB and HCB peak areas to minimize possible integration errors. The average error observed for experimental concentrations was $\pm 3.2\%$ from the known values at congener concentrations ranging from 1 to 7.5 ppm (1-7.5 μ g/mL).

The unit area determined from the known Cl concentration of the internal standards could be directly correlated to each congener concentration, since the emission signal observed for each compound was solely dependent on the number of Cl atoms present. This assumption is well founded with respect to the low errors generally observed with the use of the chlorinated internal standards. Most of the resultant error observed may be associated with how accurately the standard solutions could be prepared (considering that only 5-10 mg of each congener was available), as well as the integrity of the parameters selected for the integrator in establishing the peak areas.

TABLE II. PCB-congener concentrations determined by the HDD with the use of internal standard techniques.

EC#	Chlorine substitution pattern	Concentration		
		Known (pp/mL)	Found (pp/mL)	% Error
1	2	2.32	2.14	-2.44
3	4	4.96	5.09	+0.17
16	4,6	4.65	4.96	+0.22
18	2,2,5	1.74	1.77	+1.54
21	2,1,4	6.02	5.97	-0.84
26	2,1,6	6.82	6.98	+0.92
31	2,4,5	1.23	1.32	+7.45
36	2,1,4	4.44	4.40	-1.20
40	2,2,3,5	3.23	4.96	-5.20
49	2,2,4,5	0.90	1.00	+2.08
50	2,2,4,6	3.62	3.56	-1.64
62	2,2,3,5	1.12	1.11	-1.18
84	2,2,6,6	6.43	6.67	+3.60
99	2,1,4,6	1.80	2.73	-1.25
101	2,1,4,5	6.26	6.11	-2.88
105	2,1,5,6	5.28	5.09	-5.31
106	2,2,4,6	2.96	2.97	+0.65
70	2,2,4,5	2.13	2.04	-4.38
77	3,3,4,6	0.912	0.933	+2.33
30	2,2,3,4,6	4.03	3.77	-1.73
39	2,2,3,4,5	4.80	4.79	-0.28
108	2,2,4,5,5	5.91	5.90	-0.14
109	2,1,3,4,6	1.90	1.90	-2.87
116	2,1,4,5,6	5.53	5.23	-4.16
136	2,2,3,3,6,6	5.08	4.72	-5.64
153	2,2,4,4,5,5	3.62	3.82	+5.51
171	2,2,2,2,4,4,6,6	4.34	4.58	+5.68
183	2,2,2,4,4,5,5,6	3.98	3.68	-7.55
200	2,2,2,2,4,4,5,5,6,6	1.00	1.02	+2.00

* Numbering nomenclature developed by Ballschmiter and Zell (Ref. 17).

One disadvantage of the technique is that, in order to perform a conversion from the Cl weight to PCB congener weights, one must know the number of Cl atoms present on the biphenyl ring; however, adequate resolution and accurate retention time identification of each congener could minimize such problems considerably.

We further confirmed the applicability of the technique by determining the Cl percentage in standard Aroclor samples; the results are presented in Table III. The % Cl determined with the use of the HDD was also compared with results obtained from a potentiometric titration method developed in our laboratory.¹⁴ The total peak area obtained from the PCB congeners in the Aroclor samples was compared with the average relative peak area per unit Cl concentration obtained from the TCB and HCB internal standards to assess the Cl/Aroclor

TABLE III. Percent chlorine determined in Aroclor samples.

Aroclor	% Cl	% Cl found by	
		Potentiometric titration*	GC-HDD
1221	21	21.5 (0.4)	21.7 (0.4)
1222	32	31.9 (0.6)	32.0 (0.3)
1242	42	42.6 (0.2)	42.3 (0.5)
1248	48	47.6 (0.4)	48.1 (0.2)
1254	54	53.8 (0.4)	53.4 (0.4)

* Means of triplicate determinations \pm average deviation.
* Ref. 18.

weight percentage. The % Cl determined in all the Aroclor samples was in close agreement with the nominal values expected, as well as the values obtained from the potentiometric method. An interesting aspect of these results is that the % Cl could be determined without prior identification of the individual PCB congeners, again indicating that the Cl emission observed was independent of the structure for each respective PCB congener present in the Aroclor samples. A primary concern was that several PCB congener peaks would overlap with the internal standards; however, no significant peaks were observed at the retention times of the internal standards (~ 15.6 min for TCB and ~ 24.4 min for HCB under the present experimental conditions).

Comparisons to chromatograms obtained with the use of a flame ionization detector indicated that there was no discernible loss of resolution or peak quality through the heated interface between the column and HDD. One advantage noted was the absence of detectable column bleed at the high GC column temperatures (230–310°C) necessary to elute the highly chlorinated PCB congeners. Even at the highest permissible gain setting (4 nA full scale) at temperatures of 300°C over a 30 min period, no greater than a 5% full-scale increase in the baseline was observed. This observation is in direct contrast to results from conventional nonselective GC detectors, in which the background signal can significantly increase over the course of a chromatogram, especially at low attenuations and high column temperatures. Such problems can result in integration errors for peak area determinations or in the need for greater signal attenuation to compensate for excessive background shifts.

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Appendix C

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Potentiometric Determination of Halogen Content in Organic Compounds Using Dispersed Sodium Reduction

Margaret L. Ware, Mark D. Arpatina, and Gary W. Rice*

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185

We recently became interested in assessing the percent Cl in commercial polychlorinated biphenyls (Aroclors) via classical methods for comparison to spectroscopic techniques being developed in our laboratory for the same purpose (1). A review of the literature revealed a number of classical methods (2), of which most involved tedious and time-consuming combustions, lengthy refluxing, or sodium fusion processes. The specialized equipment and/or glassware required for many of these procedures was not available in our laboratory.

A procedure first developed by Stepanow utilized nascent hydrogen, generated from Na in ethanol, to quantitatively displace the halides from organic compounds (3). Several modifications of this procedure have appeared over the years (4-7). A procedure which we thought might be applicable used a dispersed sodium reagent for complete conversion of the organohalogen to free halides (8). The method involved generating sodium alkoxide from a small amount of alcohol added to an inert solvent (e.g., benzene) containing the dispersed Na and organohalogen compound. After a 5-min reaction period, excess Na was reacted with additional alcohol, the solution acidified with nitric acid, and the halide titrated potentiometrically by using silver indicator and glass reference electrodes. The method was reported as being rapid, accurate, and reproducible for a number of aliphatic and aromatic halides.

We have been unsuccessful in duplicating these procedures for a number of similar halogenated compounds. The following discrepancies or observations were noted: (1) the aqueous layer (ca. 30 mL) created by the addition of 10% HNO₃ to neutralize and subsequently acidify the organic layer was insufficient for placement of standard electrodes, even in a tall form beaker; (2) reactions in benzene resulted in a bluish residue at the organic/aqueous interface, which upon stirring coated the electrodes to produce erratic voltage readings; (3) an alternative single phase procedure (concentrated HNO₃ for acidification) resulted in small amounts of water (where halides would preferentially solvate) clinging to the beaker surface, even with vigorous stirring; (4) results obtained by following the exact procedure were totally unsatisfactory, with poor reproducibility as well as inaccurate

Table I. Halogen Content Determined for Chloro and Bromo Organic Compounds

compound	% halide		
	theory	exptl ^a	% error
1-chloroethane	33.25	32.18 (0.16)	-0.30
trichloroethylene	80.96	81.11 (0.89)	+0.19
1,2,4,5-tetrachlorobenzene	65.69	65.49 (0.59)	+1.22
2,3-dichloroacetone	28.69	28.39 (0.57)	-1.05
2-chloropyridine	31.22	31.39 (0.12)	+0.28
p-chloroaniline	27.23	26.39 (0.28)	-6.04
2-chloroacetamide	37.91	38.05 (0.23)	+0.37
1,3-dichloro-2-propanol	54.97	55.98 (0.59)	+1.84
dichloroacetic acid	54.59	55.46 (0.32)	+0.85
1-bromoethane	48.48	48.13 (0.39)	-0.57
1,4-dibromobenzene	74.98	74.05 (0.39)	+0.05
1,4-dibromobenzene	67.74	67.23 (0.67)	-0.75
1-bromophthalene	38.59	38.59 (0.29)	+2.59
p-bromophthalene	46.45	47.25 (0.41)	+1.72

^aMean from three determinations (± average deviation).

values for halogen percentages.

This study incorporates several significant modifications of the aforementioned procedure. The halogen content for a number of compounds and complex mixtures has been successfully determined by using the techniques to be described.

EXPERIMENTAL SECTION

Reagents and Compounds. HPLC grade methanol (American Scientific) and a 40% (w/v) Na dispersion in light oil (Aldrich no. 21712-0), with anhydrous diethyl ether (Mallinckrodt) as the solvent, were used for the halogen displacement reactions. Silver nitrate solutions (0.15 M) were standardized with 99.999% NaCl (Aldrich). Compounds and Aroclor (polychlorobiphenyl (PCB)) mixtures (Aldrich Associates) tested for halogen content were used without further purification.

Apparatus. A syringe pump (Sage Instruments, Model 341A) was calibrated to give a fixed flow rate of AgNO₃ from 10- or 30-mL syringes (typically on the order of 1.5 mL/min). The potential generated from standard Ag wire and saturated calomel electrodes was recorded on a strip chart recorder (Fisher Series

Table II. Halogen Content Determined for Bromochloro Organic Compounds

compound	% Br		% Cl		Br/Cl atom ratio	
	theory	expt ^a	theory	expt ^a	theory	expt
1-bromo-2,3-dichlorobenzene	24.37	24.25 (0.46)	21.39	21.59 (0.28)	0.99	0.99
2-bromochlorobenzene	41.73	42.29 (0.24)	21.82	20.81 (0.31)	1.99	0.99
1-bromo-4-chlorobenzene	46.80	46.39 (0.83)	24.68	24.23 (0.64)	1.99	0.99

^aMean from three determinations (\pm average deviation).

Table III. Chlorine Compositions Determined for Polychlorinated Biphenyl Mixtures (Aroclors)

Aroclor no.	% Cl	expt ^a % Cl
1221	21	21.5 (0.4)
1232	32	31.5 (0.6)
1242	42	42.5 (0.2)
1248	48	47.8 (0.4)
1254	54	53.5 (0.4)

^aMean from three determinations (\pm average deviation).

800) and stored on a computer (Hewlett-Packard 85 series) interfaced to a digital voltmeter (Keithley Model 179).

Procedures. Organohalide samples on the order of 10–100 mg were accurately weighed and transferred into a 250-ml. tall form beaker with 50 mL of anhydrous diethyl ether. Approximately 2-ml. of the sodium dispersion was then added, with continuous stirring on a magnetic stirrer, followed by 30 drops of methanol from a disposable pipet. After 5 min, any excess sodium was reacted by the slow addition of 15 mL of 2-propanol. Approximately 100 mL of deionized water was then added with vigorous stirring for 30 s to ensure that all the halide produced was extracted into the aqueous layer. Several drops of methyl orange indicator were then added, followed by concentrated HNO₃ to the pinkish red methyl orange end point (pH ~3.5–4) for neutralization of base produced in the reaction and slight acidification to prevent AgOH formation. The electrodes were then lowered into the aqueous layer, a capillary tube from the syringe placed in the solution, the syringe pump turned on, and the potential change monitored. The end point(s) could be determined either by the method of bisectum from the recorder traces or by automatic means through an in-house titration program used on the HP-86 computer.

RESULTS AND DISCUSSION

The use of anhydrous diethyl ether as a solvent produced very clean reactions, the ether and aqueous phases being clearly separated with very little or no emulsion produced. The reacted solutions took on an orange color after complete removal of excess sodium, which could be due to the oil used for the Na dispersion. Although some compounds were obviously insoluble in ether, no problems were encountered in producing quantitative reactions to the respective halides. Stable and well-defined potential changes were generally observed during the course of the titrations in the aqueous phase as opposed to erratic signals generated from previous procedures.

Typical results for a number of chlorines and bromine containing organic compounds are given in Table I, and for several bromochloro compounds in Table II. All determinations were performed in triplicate. A small chloride blank (270 μ g), found in the reagents used, was corrected for in all chlorine determinations.

The experimentally determined halogen contents closely agreed with the theoretical values for the various compounds

arbitrarily tested. Discrepancies between theoretical and experimental percentages can probably be attributed in part to the purity of the compounds as well as possible halogen impurities in the samples. The precision associated with the technique was quite acceptable, as indicated by the average deviations from the mean values. The halogen content in sample sizes as small as 10 mg could readily be determined. The bromochloro composition of multihalogen compounds was readily determined with the same procedure and multiple end point determinations, to the extent that empirical ratios for the halogens could be reliably determined as demonstrated in Table II.

The applicability of the technique to complex mixtures is represented in Table III for a number of different Aroclor (PCB) samples. All values obtained were in close agreement to the nominal chlorine percentages designated by manufacturer specifications for Aroclor nonacidic mixtures.

A typical determination could be completed in 10 min when using automated end point detection and calculation routines. The titration can also be performed with a buret instead of a syringe pump, provided that the buret tip is of sufficient length to extend through the organic layer into the aqueous layer where the Ag titrant must necessarily be added. In addition, the method is sensitive and accurate, requires reagents and apparatus common to most laboratories, and only requires average analytical expertise.

Registry No. 1-Chlorobenzene, 543-89-9; trichloroethylene, 79-01-6; 1,2,4,5-tetrachlorobenzene, 95-94-3; 9,10-dichloroanthracene, 605-49-1; 2-chloropyridine, 103-09-1; *p*-chloroaniline, 106-47-8; 2-chloroacetamide, 79-07-2; 1,3-dichloro-2-propanol, 95-23-1; dichloroacetic acid, 79-43-4; 1-bromobenzene, 111-25-1; 1,4-dibromobenzene, 106-69-1; 1,4-dibromobenzene, 106-37-6; 1-bromonaphthalene, 50-11-9; *p*-bromonitrobenzene, 105-49-1; 1-bromo-2,3-dichlorobenzene, 5983-77-4; 2-bromochlorobenzene, 694-80-4; 1-bromo-4-chlorobenzene, 2949-78-9; bromine, 7726-95-6; chlorine, 7782-50-5; biphenyl, 92-52-4; xylene, 7446-21-5; methanol, 67-56-1; 2-propanol, 67-63-0; Aroclor 1221, 11184-28-2; Aroclor 1232, 11141-18-5; Aroclor 1242, 53469-21-9; Aroclor 1248, 12872-29-6; Aroclor 1254, 11097-09-1.

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Appendix D

Mullin OCN Relative Retention Index

BZ NUMBER	REL. RET. TIME	BZ NUMBER	REL. RET. TIME	BZ NUMBER	REL. RET. TIME	BZ NUMBER	REL. RET. TIME
1	.1544	42	.4873	148	.6243	128	.7761
2	.1937	72	.4984	123	.6221	147	.7814
3	.1975	71	.4989	126	.6207	182	.7848
10	.2243	41	.4998	77	.6275	174	.7965
4	.2245	64	.4999	118	.6314	181	.7968
7	.2566	63	.5048	154	.6349	177	.8031
9	.2578	96	.5057	82	.6403	171	.8089
6	.2709	48	.5182	151	.6499	292	.8089
8	.2783	102	.5142	132	.6563	156	.8102
5	.2785	57	.5123	144	.6563	173	.8122
14	.2973	100	.5212	124	.6584	157	.8184
19	.3045	87	.5214	147	.6688	288	.8197
30	.3163	53	.5267	188	.6626	284	.8217
11	.3233	65	.5298	187	.6628	192	.8269
12	.3298	61	.5331	123	.6628	172	.8278
13	.3315	94	.5351	149	.6672	197	.8292
18	.3373	74	.5341	184	.6688	188	.8362
15	.3387	70	.5487	118	.6693	192	.8377
17	.3398	76	.5488	139	.6787	191	.8447
24	.3538	98	.5415	146	.6787	199	.8494
27	.3551	102	.5431	143	.6789	149	.8622
16	.3625	92	.5437	134	.6796	170	.8744
32	.3656	66	.5447	114	.6823	198	.8748
23	.3770	80	.5484	142	.6848	198	.8848
34	.3782	92	.5464	131	.6853	251	.8872
34	.3800	88	.5484	122	.6871	194	.8938
29	.3829	121	.5518	133	.6871	283	.8938
26	.3911	91	.5549	160	.6929	189	.9142
25	.3937	22	.5562	188	.6929	288	.9229
50	.4007	122	.5664	144	.6922	192	.9321
31	.4024	56	.5676	161	.6948	287	.9423
28	.4051	60	.5676	184	.7816	194	.9622
21	.4152	92	.5742	132	.7832	282	.9678
33	.4163	84	.5744	153	.7836	286	1.8103
20	.4170	89	.5779	182	.7849	289	1.8496
53	.4187	90	.5814	148	.7868		
51	.4242	101	.5816	127	.7873		
22	.4267	112	.5862	141	.7203		
45	.4354	99	.5888	179	.7282		
36	.4375	79	.5894	138	.7284		
46	.4453	119	.5968	174	.7382		
39	.4488	120	.5969	137	.7329		
69	.4510	112	.5984	144	.7396		
73	.4554	109	.6016	165	.7396		
52	.4557	78	.6024	164	.7399		
43	.4587	82	.6059	138	.7483		
38	.4593	122	.6062	184	.7416		
49	.4610	97	.6188	128	.7429		
47	.4639	86	.6182	129	.7531		
72	.4643	116	.6132	126	.7512		
48	.4651	122	.6142	178	.7537		
65	.4671	81	.6149	146	.7572		
62	.4682	145	.6149	172	.7611		
35	.4738	117	.6158	182	.7623		
104	.4757	112	.6171	187	.7654		
44	.4832	87	.6175	159	.7622		
37	.4828	111	.6183	183	.7728		
59	.4860	82	.6224	142	.7737		

Appendix E

Fortran Program: Simplex Optimization

```

PROGRAM SIMPLX
C...
C...  SIMPLEX MINIMIZATION OF A FUNCTION
C...
      CHARACTER*1 ANS
      DIMENSION C(10),E(10),P(10,10),R(10),X(10)
      DIMENSION DATA(100,10)
C...
C...  ENTER INITIAL INFORMATION
C...
      MAXCNT=500
      ERRMIN=1.0E-03
      NOUT=6
      NINP=5
      NSIM=1
C...
      WRITE (NOUT,1)
1  FORMAT (' THIS IS PROGRAM SIMPLX',/)
      WRITE (NOUT,3) NOBS
3  FORMAT (' ENTER NUMBER OF OBSERVATIONS')
      READ (NINP,*) NOBS
      WRITE (NOUT,4) NV
4  FORMAT (' ENTER NUMBER OF VARIABLES (X+Y)')
      READ (NINP,*) NV
      WRITE (NOUT,5)
5  FORMAT (' ENTER X1,X2,...,XP AND Y')
      DO 6 I=1,NOBS
6  READ (NINP,*) (DATA(I,J),J=1,NV)
      IF (NOBS.GT.NV) GO TO 11
      WRITE (NOUT,9)
9  FORMAT (' NO. OF OBS. MUST BE GT NO. OF VARS. ')
      STOP
11 WRITE (NOUT, 12)
12 FORMAT (' ENTER NUMBER OF PARAMETERS')
      READ (NINP,*) NP
      NP1= NP + 1
      WRITE (NOUT,13)
13 FORMAT (' ENTER INITIAL ESTIMATES OF PARAMETERS')
      READ (NINP,*) (X(I),I=1,NP)
      E(1)=ERROR(X,DATA,NV,NOBS,KOUNT)
      WRITE (NOUT,15) E(1)
15 FORMAT (' STARTING ERROR FUNCTION VALUE',G12.4)
      WRITE (NOUT,17)
17 FORMAT (' WANT DEBUG LEVEL OUTPUT? (Y OR N?)')
      READ (NINP,18) ANS
18 FORMAT (A1)
      IDB = 0
      IF (ANS.EQ.'Y') IDB = 1
C...
C...  INITIALIZE THE SIMPLEX
C...

```

```

        KOUNT = 0
        DO 22 J=1, NP
22     P(1, J) = X(J)
        DO 28 I=2, NP1
            DO 26 J=1, NP
26     P(I, J) = X(J)
            P(I, I-1) = 1.1 * X(I-1)
            IF (ABS(X(I-1)) .LT. 1.0E-12) P(I, I-1) = 0.0001
28     CONTINUE
C...
C... FIND PLOW AND PHIGH/ BEST=PLOS/ WORST=PHIGH
C...
31     ILO=1
        IHI=1
        DO 34 I=1, NP1
            DO 32 J=1, NP
32     X(J) = P(I, J)
            E(I) = ERROR(X, DATA, NV, NOBS, KOUNT)
            IF (E(I) .LT. E(ILO)) ILO=I
            IF (E(I) .GT. E(IHI)) IHI=I
34     CONTINUE
        WRITE (NOUT, 36)
36     FORMAT (/, ' INITIAL SIMPLEX')
        DO 40 K=1, NP1
            WRITE (NOUT, 39) K, E(K), (P(K, J), J=1, NP)
39     FORMAT (3X, ' VERTEX', I2, ' ERROR AND PARAMETERS:', 5F8.3)
40     CONTINUE
C...
C... FIND PNHI THE NEXT HIGHEST NEXT=PNHI
C...
41     NHI=ILO
        DO 43 I=1, NP1
            IF (E(I) .GE. E(NHI) .AND. I.NE.IHI) NHI=I
43     CONTINUE
C...
C... COMPUTE THE CENTROID
C...
        DO 46 J=1, NP
            C(J) = -P(IHI, J)
            DO 44 I=1, NP1
                C(J) = C(J) + P(I, J)
44     CONTINUE
            C(J) = C(J) / NP
46     CONTINUE
51     CONTINUE
C...
C... PRINT CURRENT BEST VERTEX
C...
        WRITE (NOUT, 53) KOUNT, NSIM
53     FORMAT ('AFTER', I3, 'ERROR EVALUATIONS AND', I3, 'SIMPLEXES')
        WRITE (NOUT, 54) (P(ILO, J), J=1, NP)
54     FORMAT ('  PARAMETER ESTIMATES:', 5G12.4)
        WRITE (NOUT, 55) E(ILO)
55     FORMAT ('  ERROR FUNCTION:', G12.4)
C...
C... STOPPING CRITERION

```

```

C...
  IF (KOUNT.GT.MAXCNT) STOP
  IF (ABS(E(ILO)-E(IHI))/E(ILO).LT.ERRMIN) GO TO 56
  GO TO 61
56 WRITE (NOUT,57)
57 FORMAT (/, '==> ERROR CRITERION SATISFIED')
  WRITE (NOUT,54) (P(ILO,J),J=1,NP)
  STOP
C...
C... REFLECTION
C...
61 DO 62 J=1,NP
    R(J)=1.9985*C(J)-0.9985*P(IHI,J)
62 CONTINUE
  ER=ERROR(R,DATA,NV,NOBS,KOUNT)
  IF (IDB.GT.0) WRITE (NOUT,65) ER,(R(J),J=1,NP)
65 FORMAT (' REFLECTION VERTEX',3F10.5)
C...
C... REFLECT AGAIN IF SUCCESSFUL
C...
  IF (ER.LT.E(ILO)) GO TO 91
  IF (ER.GE.E(IHI)) GO TO 122
C...
C... REPLACE WORST VERTEX WITH NEW ONE
C...
79 DO 80 J=1,NP
    P(IHI,J)=R(J)
80 CONTINUE
  NSIM=NSIM+1
  E(IHI)=ER
  IF (ER.GT.E(NHI)) GO TO 51
  IHI=NHI
  GO TO 41
C...
C... EXPAND THE SIMPLEX
C...
91 ILO=IHI
  IHI=NHI
  DO 93 J=1,NP
    X(J)=1.95*R(J)-0.95*C(J)
93 CONTINUE
  EX=ERROR(X,DATA,NV,NOBS,KOUNT)
  IF (EX.LT.ER) GO TO 104
C...
C... R BETTER THAN X
C...
  DO 99 J=1,NP
    P(ILO,J)=R(J)
99 CONTINUE
  NSIM=NSIM+1
  E(ILO)=ER
  GO TO 110
C...
C... X IS BETTER THAN R
C...
104 DO 105 J=1,NP

```

```

        P(ILO,J)=X(J)
105 CONTINUE
    IF(IDB.GT.0) WRITE (NOUT,106) EX,(X(J),J=1,NP)
106 FORMAT (' EXPANSION VERTEX',3F10.5)
    NSIM=NSIM+1
    E(ILO)=EX
110 CONTINUE
    GO TO 41
C...
C... CONTRACT THE SIMPLEX
C...
122 DO 123 J=1,NP
    R(J)=0.5015*C(J)+0.4985*P(IHI,J)
123 CONTINUE
    ER=ERROR(R,DATA,NV,NOBS,KOUNT)
    IF (IDB.GT.0) WRITE (NOUT,124) ER,(R(J),J=1,NP)
124 FORMAT (' CONTRACTION VERTEX',3F10.5)
    IF (ER.LT.E(ILO)) GO TO 91
    IF (ER.LT.E(IHI)) GO TO 79
C...
C... SCALE
C...
    WRITE (NOUT,135)
135 FORMAT (' ENTER SCALE (<0 EXPANDS, >0 SHRINKS, 0=STOP):')
    READ (NINP,*) SCAL
    IF (SCAL.EQ.0.0) GO TO 999
137 DO 138 I=1,NP1
    DO 138 J=1,NP
        P(I,J)=P(I,J)+SCAL*(P(ILO,J)-P(I,J))
138 CONTINUE
    GO TO 31
999 STOP
    END
C
-----
    FUNCTION ERROR (X,DATA,NV,NOBS,KOUNT)
C... COMPUTES THE ERROR FUNCTION FOR THE DATA SET
C... SMALLER VALUE IS BETTER
    DIMENSION X(10),DATA(100,10)
    ERROR=0.0
    DO 10 I=1,NOBS
        YOBS=DATA(I,NV)
C... CHANGE THE NEXT STATEMENT TO CHANGE THE FUNCTION BEING FIT
        YCALC=X(1)*(1.0-EXP(-X(2)*DATA(I,1)))
C        YCALC=X(1) + X(2)*DATA(I,1) + X(3)*DATA(I,1)**2
C        1 - X(4)*DATA(I,1)**3 + X(5)*DATA(I,1)**4
        RESI=YOBS-YCALC
        ERROR=ERROR+RESI*RESI
    10 CONTINUE
        KOUNT=KOUNT+1
    RETURN
    END

```

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Vita

Margaret LaVerne Ware

Born in Richmond, Virginia on November 10, 1964. Graduated from Kenston Forest in Blackstone, Virginia, June 1983. Earned a Bachelor of Science degree with highest honors and a concentration in chemistry at the College of William and Mary, May 1987. Master of Arts candidate, College of William and Mary, 1987-88, with a concentration in analytical chemistry. The course requirements and thesis have been completed.