Effect of sampling parameters on analysis by tandem cell gas phase coulometry
by Robert Jerry Crawford

A thesis submitted in partial fulfillment of the requirments for the degree of Master of Science in Chemistry
Montana State University

Abstract:
In the initial testing of the theory for absolute quantitative analysis of halogenated methanes by tandem electron capture detector (ECD) gas phase coulometry (GPC), the result was found to vary with the frequency of the pulse applied to the BCD's. Several hypotheses developed that could cause this problem were: collection of negative ions at the central anode of the ECDf field induced dissociation of the analyte, associative electron capture by the initial dissociative electron capture products, the ECD not acting as a well-mixed reaction vessel, and thermal degradation of the analyte. These hypotheses were investigated by observing the effect on GPC result when various sampling parameters were modified. These sampling parameters were: pulse width; the electronics used; a negative, positive, arid bipolar pulse; pulse amplitude; direct current fields; carrier gas type; analyte concentration; carrier gas flow rate; and detector temperature. The results of these experiments indicated that none of the hypotheses was a complete solution to the GPC result frequency dependency. It was found that by proper adjustment of these parameters that the frequency dependency on GPC result could be minimized, but not eliminated. A hypothesis, that could account for this problem, is presented at the end of this work. It involves the possible side reaction of analyte with free radicals or some other reactive species that would be in unequal concentration between the two cells. Background air was used as an accurate standard to test for the quantitative accuracy of GPC. It was found that GPC provides accurate results when the proper pulse period is used.

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Robert Jerry Crawford, Jr.

A thesis submitted in partial fulfillment
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APPROVAL

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Robert Jerry Crawford, Jr.

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistancy, and is ready for submission to the College of Graduate Studies.

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Date July 24, 1985

DEDICATION

This thesis is dedicated to my wife Diana for her patience and understanding, and to my parents for their unfailing help and encouragement.

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I would like to thank Dr. Eric Grimsrud and Dr. W. B. Knighton for their patient, cheerful, and invaluable help with this research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

ABSTRACT

In the initial testing of the theory for absolute quantitative analysis of halogenated methanes by tandem electron capture detector (ECD) gas phase coulometry (GPC), the result was found to vary with the frequency of the pulse applied to the ECD's. Several hypotheses developed that could cause this problem were: collection of negative ions at the central anode of the ECD, field induced dissociation of the analyte, associative electron capture by the initial dissociative electron capture products, the ECD not acting as a well-mixed reaction vessel, and thermal degradation of the analyte. These hypotheses were investigated by observing the effect on GPC result when various sampling parameters were modified. These sampling parameters were: pulse width; the electronics used; a negative, positive, and bipolar pulse; pulse amplitude; direct current fields; carrier gas type; analyte concentration; carrier gas flow rate; and detector temperature. The results of these experiments indicated that none of the hypotheses was a complete solution to the GPC result frequency dependency. It was found that by proper adjustment of these parameters that the frequency dependency on GPC result could be minimized, but not eliminated. A hypothesis, that could account for this problem, is presented at the end of this work. It involves the possible side reaction of analyte with free radicals or some other reactive species that would be in unequal concentration between the two cells. Background air was used as an accurate standard to test for the quantitative accuracy of GPC. It was found that GPC provides accurate results when the proper pulse period is used.

INTRODUCTION

Background

Gas phase coulometry (GPC) is a term used to describe the quantitative analysis of certain halogenated hydrocarbons by using the signal from an electron capture detector (ECD) as an absolute indicator of the concentration of the analyte. The technique was first described by Lovelock, Maggs, and Adlard (1) in 1971. This concept caused considerable interest in the field of trace atmospheric analysis because it offered a means of quantitation in a concentration range where it is very difficult to prepare reliable calibration standards. In Lovelock's original work a nickel-63 ECD of concentric coaxial design with a volume of 2 ml (similar to the detectors used in this work) was shown to yield quantitatively accurate GPC results for sulfur hexafluoride in the parts per billion to parts per trillion (v/v) concentration range when the detector was operated with a pulse period of 400 us and a low flow rate to provide nearly 100% ionization. Sulfur hexafluoride is a strongly responding ECD compound and is thought to be a "well behaved" GPC compound. The use of two idential ECD's in series to correct for the efficiency of ionization in the first cell was also described for the first time in this paper. Other studies have been done with various

adaptations and tests of the original method. In a later paper (2) Lovelock described an ECD specifically designed for coulometry that uses a large length to diameter ratio so that it provides nearly 100% efficiency over a wide range of operating conditions (e.g., flow rate and pulse period). In yet another paper Lovelock and Watson showed that by preparing seemingly accurate standards in a huge exponential dilution chamber that coulometric analysis could be performed on fluorotrichloromethane ($CFCl_3$) consistently and accurately to within a precision of ± 5% with several different detectors (3). Lillian and Singh (4), using two identical ECD's in series that were very similar to the ones used in this research, found that the GPC result was within ± 5% of supposedly accurate standards for fluorotrichloromethane and carbon tetrachloide (CCl_4) when a pulse period of 400 us and a low flow rate was used to give nearly 100% ionization efficiencies. But at lower efficiencies the GPC result was found to drop as the efficiency was decreased. Lee and Hirsch (5) have extended the theory of tandem ECD's to provide for coulometric analysis with unidentical detectors, and proved psuedo first-order kinetics for electron capture to be a valid approximation. Grimsrud and Warden (6) have suggested the use of displaced concentric coaxial design in ECD's to be used for coulometry. This design places only the tip of the anode into the active volume of the ECD. This reduces

the number of positive ions that drift to the central anode during the period between pulses as described by the recently proposed "space-charge" model of the pulsed ECD (7,8). At present, the method is still not considered a valid means of analysis because of many reports of anomalous, inconsistant, and unexplained results (4,9). These problems are attributed to physical and chemical complexities existing in the gaseous reaction medium of the pulsed ECD. However, recent advances in ECD theory have made it possible to characterize several critical aspects of the pulsed ECD in greater detail than could be done during the early years of GPC. In this paper a model for GPC will be described which utilizes all the presently known factors thought to affect GPC. The model will be tested and be found to have a problem which the experimental work of this paper will address.

To understand the results of this paper, and how they relate to existing theory, it will be helpful to first consider a broad view of GPC. For GPC to be successful it must meet the same criteria as any chemical method (e.g., classical liquid phase coulometry). In the case of GPC the chemical reaction is between thermalized electrons (the reagent) and the analyte. The five following criteria must be met to achieve true coulometric analysis.

(1) The EC reaction must be stoichiometrically distinct.

(2) The reaction must proceed to either completion, or to a known fraction of completion.

(3) Uncompensated side reactions of the analyte must not occur.

(4) Uncompensated side reactions of the reagent must not occur.

(5) The electrometer used to observe the EC reaction must accurately measure the loss of reagent.

The current literature on GPC and ECD theory displays no stringent reason why the above criteria cannot be met for at least some compounds. Support for meeting each of these criteria is provided below as each is examined individually.

Criterion 1

From atmospheric pressure ionization mass spectroscopy (APIMS) measurements of the negative ions produced when bromotrichloromethane (CCl_3Br) is passed through the source (in this case an ECD) (10), it appears that the EC reaction of halogenated methanes (except iodo compounds) is stoichiometrically distinct, with a 1:1 ratio. The results indicated that the neutral products CCl_3 and $CBrCl_2$, of this EC reaction, do not undergo additional electron capture during their residence time within the cell. In another study it was shown that, with the possible exception of the iodo compounds, the neutral products formed from the

recombination product of Cl^- and Br^- with positive ions do not undergo further electron attachment. Although, the positive ion recombination product of I^- probably does undergo electron capture, at least at low detector temperatures (11). These results indicate that criterion one is satisfied for at least some well behaved chloro and bromo methanes.

Criterion 2

Some very strongly electron attaching molecules will react with the reagent to near completion in the typical nickel-63-ECD if the flow rate is kept low. The second order EC rate constants of these compounds is approximately 2×10^{-7} cc/sec (12). Provided that the pulsing frequency is moderately fast the electron population is approximately 10^{-8}/cc (13). Therefore, the pseudo-first order rate constant for electron attachment is approximately 20/sec, and the lifetime of the analyte in the ECD will then be about 0.05 sec. Consider a typical ECD with a volume of 1 cc operated at a flow rate of 60 cc/min. Under these conditions the residence time of the analyte within the cell would be 1 sec. This is a relatively long time compared to 0.05 sec. But, with the use of two identical ECD's in series (4), as was the case in this study, it theoretically does not matter if the reaction goes to completion or not because the efficiency is then known and the first cell response can be corrected to 100%

efficiency.

Criterion 3

Possible side reactions of the analyte are; degradation on hot cell surfaces, reactions with positive ions, and reactions with reactive species such as free radicals. By using low detector temperatures degredation on cell walls can be kept to a minimum. Analyte reactions with positive ions occur with a maximum rate constant of approximately 1×10^{-9} cc/sec (14); therefore, they should be insignificant with respect to electron capture. Even if reactions with positive ions were a problem it could be stopped by doping the carrier gas with a strong gas-phase base such as trimethylamine (15,16). These compounds form unusually stable, and unreactive positive ions that do not undergo electron capture. Relatively little is known about the possible reaction of the analyte with free radicals. It is thought that these processes should be relatively slow compared to fast electron capture provided the concentration of reactive radicals is not large with respect to the electron population. Thus, there is no obvious reason why criterion three should not be satisfied.

Criterion 4

Possible side reactions of the reagents (electrons) are; reaction with carrier gas impurities, recombination with positive ions, and neutralization on cell walls. The

reaction of electrons with impurities and positive ions can be accounted for in the model to be presented in the next chapter. Neutralization on cell walls can be completely prevented by using reasonably fast pulsing because a positive ion space charge is then maintained within the cell that "holds" the electrons within a specific "cylinder shaped" region of the cell (13).

Criterion 5

An accurate electrometer is expected to indicate the electron population within the cell; therefore, the integrated GC peak area should indicate the number of electrons lost to reaction with the analyte. Although it has recently been found that positive ions migrating to the anode in the period between pulses may account for part of the observed signal (7,8,17), a correction factor can easily be obtained (17). Therefore, the fifth and final criterion for the chemical method of GPC would seem to be satisfied.

In the next section a model will be developed that incorporates all the above considerations. This model is then tested in the fourth chapter. The effect of pulsing parameters on the GPC result will be of particular interest because it has previously been found that the model cannot predict the effect of changing pulse parameters as expected (18).

Theory

According to the present theory of the pulsed ECD (7), the significant reactions occuring inside the cell are:

$$\text{neutrals} \xrightarrow{S} P^+ + e \qquad (1)$$

$$P^+ + e \xrightarrow{R} \text{neutrals} \qquad (2)$$

$$e + \text{analyte} \xrightarrow{K} B^- + \text{neutrals} \qquad (3)$$

$$P^+ + B^- \xrightarrow{R} \text{neutrals} \qquad (4)$$

where P^+ are positive ions and B^- are the negative ions produced by irreversible electron capture. Siegel and McKeown (19) have found the recombination rate of electrons with positive ions in reaction 1 and the recombination rate of negative ions with positive ions in reaction 3 to be approximately the same.

Since the signal obtained from the pulsed ECD is related to the average electron population rather than the instantaneous population, an equation that describes the rate of change for the former is written as follows:

$$\frac{d\bar{N}e}{dt} = S - \bar{I}e - EFC_o - Rn_+\bar{N}e - Bn_b\bar{N}e \qquad (1)$$

where $\bar{N}e$ is the average electron population over several

pulse cycles, S is the electron-positive ion production rate by nickel-63, $\bar{I}e$ is the time averaged loss of electrons to the electrometer, E is the fraction of analyte molecules reacted as they pass through the cell, F is the carrier gas flow rate, C_o is the concentration of the analyte in the carrier gas as it enters the detector, R is the electron-positive ion recombination rate, n_+ is the positive ion density, B is the rate constant for electron attachment by carrier gas impurities, and n_b is the concentration of carrier gas impurities. Electron loss by ventilation through the cell, and diffusion to the cell walls have been shown to be unimportant (13,19). As stated in the introduction, electron loss to the cell walls by migration through contact potentials could only be important at relatively long pulse periods (> 2 ms) (10).

If the decrease in standing current is very small with respect to the standing current then the change in Ne with respect to time is very small and a steady state approximation can be applied to equation 1.

The average electron current ($\bar{I}e$) can be related to the instantaneous electron population existing at the last moment of each pulse period (Ne^T) by equation 2.

$$\bar{I}e = Ne^T \times f \qquad (2)$$

Where f is the frequency of pulsing. The average electron current ($\bar{N}e$) is directly proportional to Ne^T by the

following equation:

$$\bar{N}e = \Phi \times Ne \qquad (3)$$

where Φ is a constant ranging from 0.5 to 1 depending on the pulse frequency. At the pulse frequencies used here 0.5 is a good approximation. An equation will be derived later in this model from which an exact value of Φ can be calculated at a given pulse frequency. Combining equations 2 and 3, an expression for the average electron population can be derived.

$$\bar{N}e = \Phi \frac{\bar{I}e}{f} \qquad (4)$$

By setting equation one equal to zero, solving for S, and substituting equation 4 for $\bar{N}e$, equation 5 is obtained.

$$S = \bar{I}e + EFC_o + \frac{(Rn_+ + Bn_b)\Phi\bar{I}e}{f} \qquad (5)$$

Now solving for the average electron current, replacing ($Rn_+ + Bn_b$) with L (the extra electron loss rate constant), and substituting T (the pulse period) for 1/f yields equation 6.

$$\bar{I}e = \frac{S - EFC_o}{1 + \Phi LT} \qquad (6)$$

The reduction in the average electron current due to the elution of the analyte ($\Delta\bar{I}e$) is given by equation 7.

$$\Delta\bar{I}e = \frac{EFC_O}{1 + \phi LT} \qquad (7)$$

But, Ie is not equal to the current measured at the electrometer (I). Some of the current measured is due to positive ions drifting to the central anode during the field free period between pulses (7,8,16,17). The relationship between $\bar{I}e$ and I is given by equation 8.

$$\bar{I}e = \frac{I}{(1 - r)} \qquad (8)$$

Where r is the fraction of the current resulting from the collection of positive ions (8). The magnitude of r is independent of the pulse frequency, and wholly determined by the cell geometry for a nickel-63 cell because the positive ions are not affected by the field during the pulse (17). Substituting equation 8 into equation 7 yields equation 9.

$$\Delta I = \frac{EFC_O(1 - r)}{1 + \phi LT} \qquad (9)$$

The total number of analyte molecules eluted from the column (A) will be given by equation 10.

$$A = \int FC_O \, dt \qquad (10)$$

The peak area of the cell-one response (Q_1) will then be given by equation 11.

$$Q_1 = \frac{EA(1 - r)}{1 + \phi LT} \tag{11}$$

Solving for A yields equation 12.

$$A = \frac{Q_1(1 + \phi LT)}{E(1 - r)} \tag{12}$$

For two identical cells in series the efficiency (E) is given by equation 13.

$$E = 1 - \frac{Q_2}{Q_1} \tag{13}$$

Where Q_2 is the area of the peak from the second cell. Substituting equation 13 into equation 12 yields equation 14.

$$A = \frac{Q_1}{1 - Q_2/Q_1} \times \frac{1 + \phi LT}{(1 - r)} = A' \times Z \tag{14}$$

Where A' is the result obtained directly from the areas of the two peaks and Z is the correction factor for extra electron loss processes and the collection of positive ions.

Equation 14 should provide the same result regardless

of the pulse period used since this is a variable in the correction part of the equation (Z), and the changes in efficiency should be accounted for by the A^{s} part of the equation which theoretically corrects for varying efficiency.

Determination of r, L, and ϕ

Now, all that remains to complete the theory is the determination of r, L, and ϕ. r can be determined by measuring the positive standing current obtained with reverse polarity pulsing (Ir) (7,8,17). In normal pulsing the cell wall is pulsed negative to collect all the electrons at the central anode, but with reverse polarity pulsing the cell wall is pulsed positive to collect all the positive ions at the central anode. Therefore, r will be given by equation 15.

$$r = \frac{Ir}{In + Ir} \qquad (15)$$

Where In is the measured current with normal or negative pulsing.

The value of L can be obtained from the following equation;

$$Ne^{T} = \frac{IT}{1 - r} = \frac{S}{L}\,(1 - \exp(-LT)) \qquad (16)$$

by plotting Ne^{T} vs. T, and fitting the curve to the

equation (13). The shape of the curve is determined by 1 - exp(-LT), so S need not be determined.

ϕ can be determined, at each pulse period, from equation 17.

$$\phi = \frac{\bar{N}e}{Ne^T} = \frac{\frac{1}{T}\int_0^T Ne^t \, dt}{Ne^T} = \frac{1}{1 - \exp(-LT)} - \frac{1}{LT} \qquad (17)$$

Where Ne^t is the instantaneous electron population at any time.

Propagation of Errors

Before leaving the theory of GPC it may be useful to explore the propagation of errors as applied to GPC with tandem cells. The relative standard deviation of the GPC result is given by the following equation.

$$\frac{\sigma_A}{\sigma_Q} = Z\sqrt{\frac{2(1 - 2Q_2/Q_1 + 2Q_2^2/Q_1^2)}{(1 - Q_2/Q_1)^4}} \qquad (18)$$

It is obvious upon examination of equation 18 that the relative uncertainty in the GPC result increases continuously as Q_2/Q_1 approaches one. Table one illustrates this effect assuming that Z is close to one.

Table 1. Propagation of Error in the GPC result.

Q_2 / Q_1	σ_A / σ_Q
.05	1.5
.25	2.0
.50	4.0
.75	18.0
.90	128.0

STATEMENT OF PROBLEM

The model developed in the introduction claims to yield the same GPC result regardless of the pulse period used to pulse the ECD's (T is a variable in equation 14). But in the initial testing of this model (18) it was found that the GPC result showed a very significant dependency on the pulse period used to pulse the ECD's. Figures 1 and 2 show the cell-one (Q_1) and cell-two (Q_2) responses, raw GPC responses (A'), and the corrected GPC response (A) vs. pulse period for two strongly responding, well behaved halomethanes (CCl_4 and $CFCl_3$).

Figure 1. Cell-One, Cell-Two, Uncorrected GPC Response, and Corrected GPC Response for Carbon Tetrachloride.

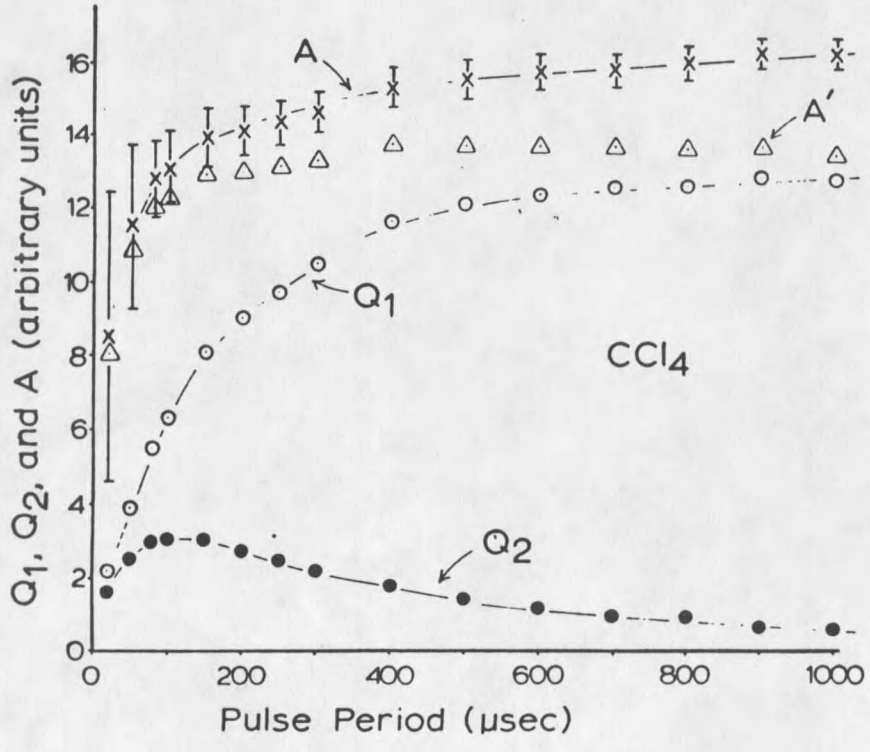
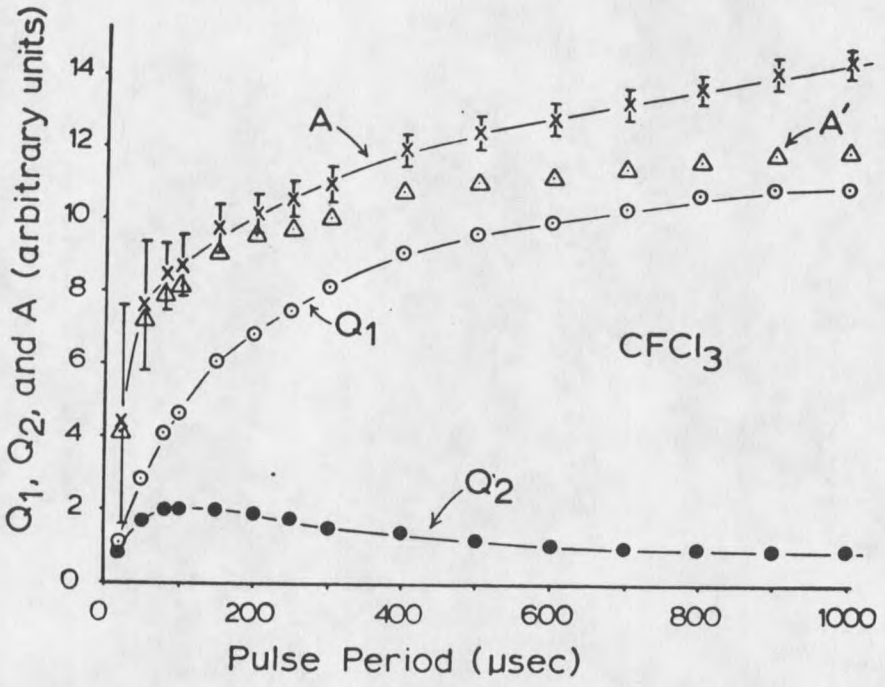


Figure 2. Cell-One, Cell-Two, Uncorrected GPC response, and Corrected GPC Response of Fluorotrichloromethane.



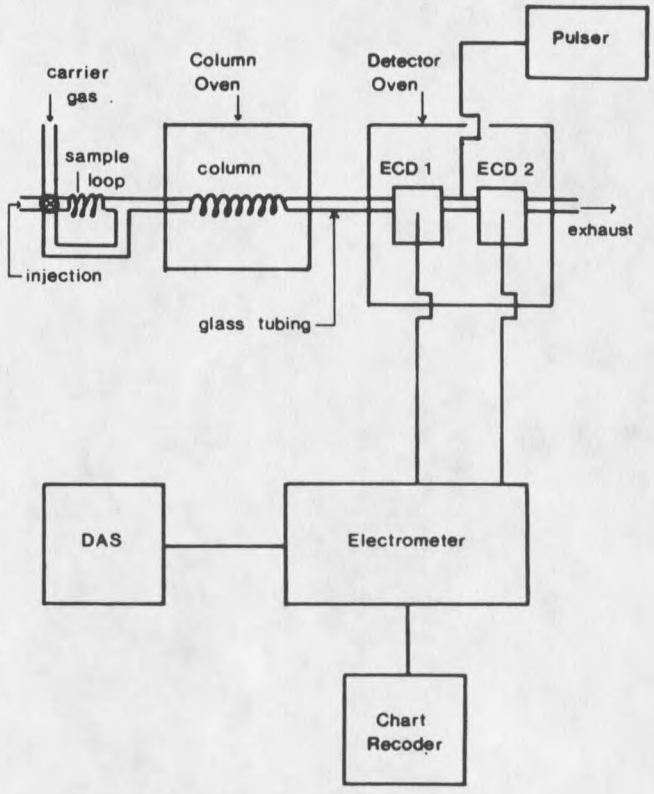
It is obvious from looking at these two figures that the GPC result vs. pulse period curves do not follow the theory which insists that the result be the same regardless of the pulse frequency used to pulse the ECD's. The A' result stays fairly constant over the frequency range from 1000 us to 300 us, but then it starts to fall off rapidly as the pulsing frequency increases. It is ironic that the corrected result (A) is even less constant than A'. This dependency of GPC result on pulse period is the problem that will be addressed in the following pages.

EXPERIMENTAL PROCEDURES

System Configuration and Component Explanation

The specialized gas chromatograph (GC) used for this research was almost entirely home built. Figure 3 is a schematic of this system.

Figure 3. Block Diagram of Specialized GC Used in this Research.

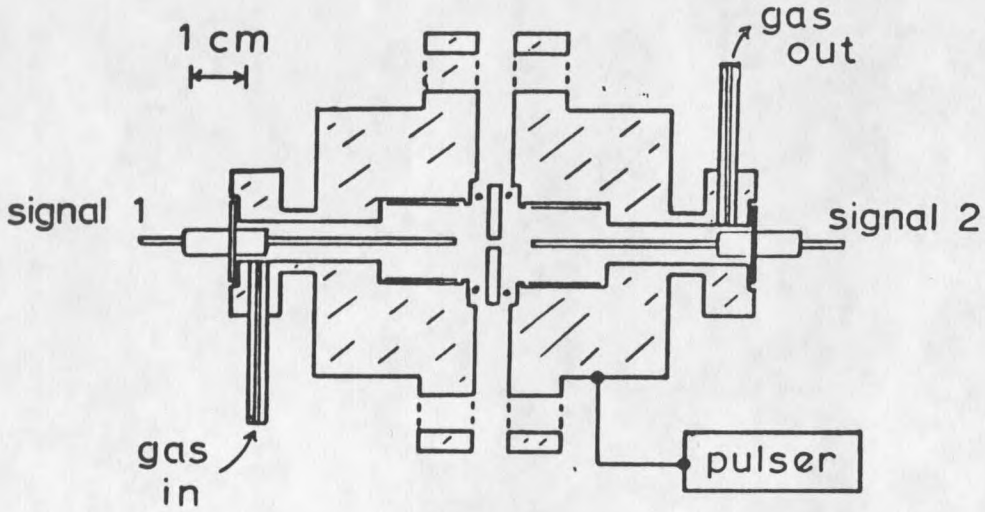


A 2 ml sample loop (Carle 8030) is used for reproducible sampling. The packed GC column (10-ft by 1/8-inch stainless steel tube packed with 10% SF-96 on

chromosorb W) was housed in a commercial thermostatically controlled oven (Gow-Mac model 750). The two ECD's were housed in a separate home built oven that is not thermostatically controlled, but the temperature was usually fairly constant in the room (at least over the time span of one chromatogram). The two ECD's were also home built from stainless steel by a master machinist. These two cells are identical with both being of concentric coaxial design. Both of the cells have equal volumes and lengths of 1.4 cm. The cylindrical walls of the cell are lined with nickel-63-on-platinum foils supplied by New England Nuclear.

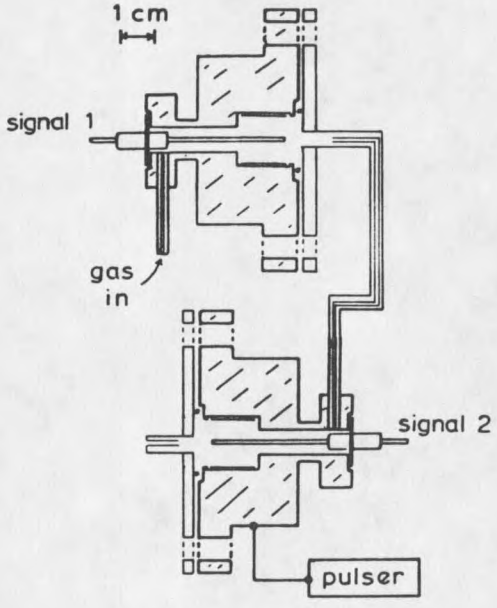
For most of the work done here the two cells were joined "back to back" as shown in figure 4. A 1/8-inch disk with a 1/16-inch hole in it allowed the gas to flow between the two cells.

Figure 4. ECD's in Back to Back Configuration.



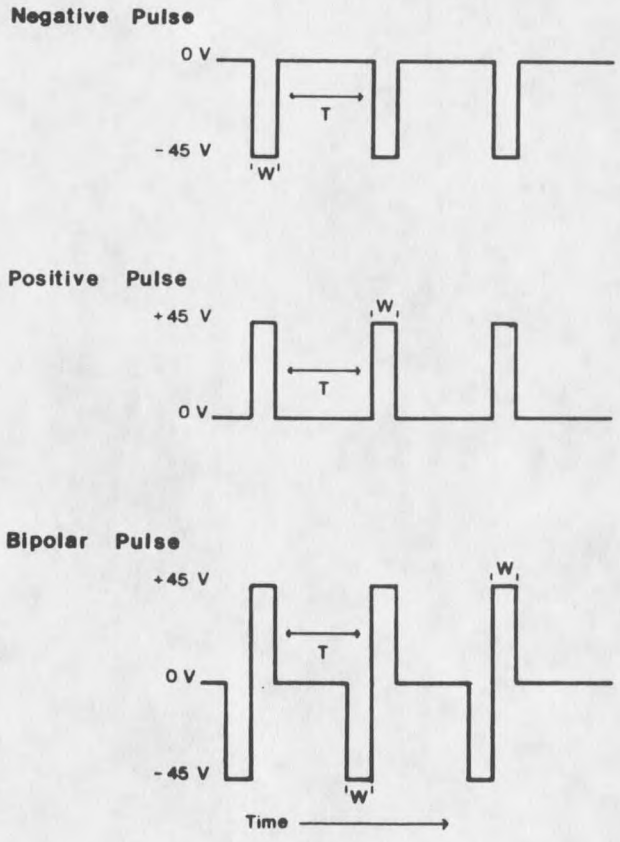
For a short time at the beginning of the research the cells were joined in a "back to front" configuration as shown in figure 5 where each cell had an endplate on it, and they were connected by a 3-inch by 1/8-inch stainless steel tube. No difference in response characteristics was noted between the two configurations.

Figure 5. ECD's in Back to Front Configuration.



The pulser, also of home built origin, is capable of delivering a negative, positive, or bipolar pulsed waveform of 0 to 50 V magnitude. Figure 6 illustrates these three waveforms where T is the pulse period and W is the pulse width.

Figure 6. Three Waveforms Used to Pulse the ECD's.



The two ECD's were electrically isolated to allow pulsing of the cell walls. This means that to collect electrons the cell walls were pulsed negative (usually -45 V), to collect positive ions the walls were pulsed positive. The bipolar pulse was used to test a possible cause of the frequency dependency on the GPC result that will be dicussed in the next chapter.

The electrometers used to measure the ECD currents were constructed from RCA CA3140S operational amplifiers with precision 10^9 ohm ($\pm$ 1%) feedback resistors as

previously described (21).

Experimental Methods

The carrier gas normally used was high purity 10% methane in argon. The gas was first passed through oxygen removing (Altech Oxy) traps then water removing $CaSO_4$ and finally 13X molecular sieve.

For some of the early experiments, results were tabulated and compared by peak height (ΔI) rather than area because no means of measuring peak area was currently available in the lab. Although peak area is certainly a superior measurement, peak height measurements are acceptable for the experiments that were done at the time where the ECD responses were compared with different sampling parameters. For later measurements peak areas were obtained from the chart recorder chromatogram with an analog planimeter. The peak areas from a few of the later experiments were obtained with an A to D converter connected to a computer, and the appropriate software to manipulate the digitalized chromatogram and integrate the peaks.

The samples used for this research were prepared by successive dilution of the pure halocarbons into clean nitrogen diluent gas. Airtight, pressurized glass and stainless steel flasks were used as the dilution and storage vessels. The nitrogen was always checked before

use to insure that it did not contain any ECD active compounds that could interfere with the analysis. The final dilution was into a 22 liter flask pressurized to 200 torr above atmospheric pressure. Individual identical 30 ml samples were then drawn from this flask with a 100 ml ground glass syringe employing a Hamilton valve between the needle and the syringe so that the tip could be closed off as the gas was transfered between the flask and the sample loop. A prodigious number of identical 30 ml samples could be drawn from this flask. Although this method of sample preparation and GC introduction allows excellent reproducibility (better than $\pm$ 1%), quantitative accuracy is neither expected or achieved. But, for the investigation of this problem it is not necessary to know the absolute concentration of the sample provided that it uses less than 5% of the standing current upon elution of each compound. Therefore, the conditions of the theory are maintained ($\Delta I << I$).

Adsorption and desorption of the compounds on the storage flask walls will generally change the initial concentration of the compounds for several days before equilibrium is reached. This difficulty in preparing quantitatativly accurate gaseous samples at the parts per trillion level illustrates the advantage of doing quantitative analysis at this concentration range coulometrically.

RESULTS AND DISCUSSION

A logical starting place in the investigation of this problem was to see if this previously reported frequency dependency on GPC response could be reproduced. Figure 7 illustrates typical chromatograms obtained with this system, from the same sample, at two different pulse periods.

Figure 7. Chromatograms Showing the Effect of Pulse Period on Unprocessed Data.

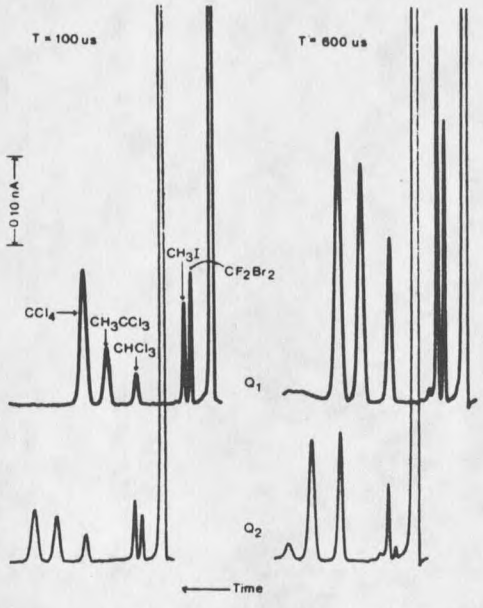
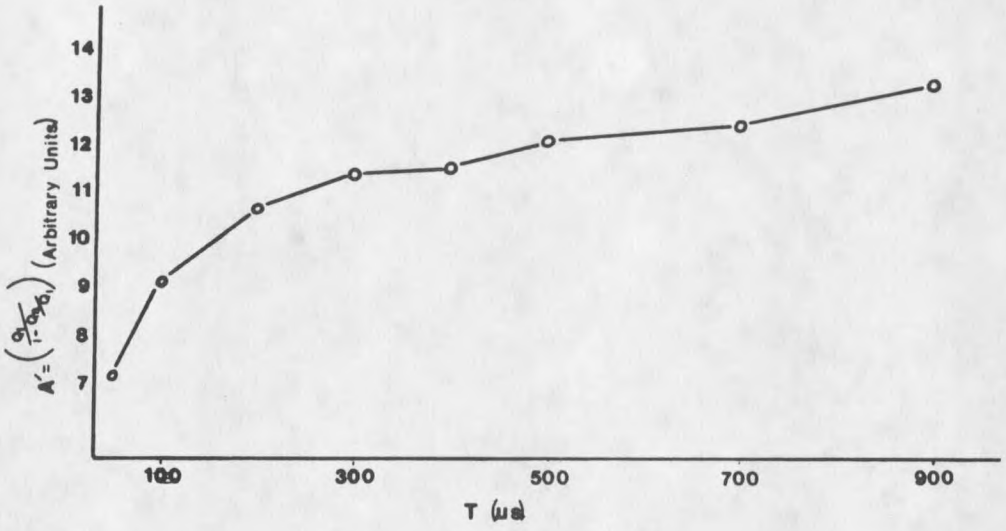


Figure 8 is a typical plot showing the raw GPC response (A') of carbon tetrachloride vs. pulse period. The same type of frequency dependency is observed that has been previously reported (18).

Figure 8. Typical GPC Response vs. Pulse Period Plot for Carbon Tetrachloride.



Lillian and Singh (4) have reported an effect similar to this in an experiment where they ploted tandem cell GPC result vs. ionization efficiency, and found the response to drop off at lower efficiencies. This is analogous to the GPC response drop with decreasing pulse period because the ionization efficiency decreases with fast pulsing due to the decrease in the average electron population within the ECD. The effects of various sampling parameters on this problem are investigated in the following paragraphs.

Pulse Width

Tables 2, 3, and 4 illustrate the effect of pulse width (W) on ΔI at different pulse periods. For all three of these compounds (fluorotrichloromethane, carbon

tetrachloride, and bromotrichloromethane) it is quite obvious that variation in W has no effect on the cell-one and cell-two responses except at very short pulse periods (50 and 100 us).

Table 2. Cell 1 and Cell 2 Responses of Fluorotrichloromethane as a Function of W and T.

		ΔI (nA)	
T (us)	W (us)	Cell 1	Cell 2
100	0.5	.0244	.0984
	1	.0244	.0984
	2	.0236	.0976
	3	.0230	.0976
	4	.0224	.0969
250	0.5	.0411	.0825
	1	.0409	.0829
	2	.0406	.0839
	3	.0404	.0848
	4	.0402	.0846
500	0.5	.0528	.0484
	1	.0531	.0484
	2	.0531	.0488
	3	.0531	.0490
	4	.0528	.0494

Table 3. Cell 1 and Cell 2 Responses of Carbon Tetrachloride as a Function of W and T.

T (us)	W (us)	ΔI (nA) Cell 1	ΔI (nA) Cell 2
50	1	.193	.0882
	2	.185	.0866
	3	.177	.0850
	4	.165	.0843
100	1	.299	.0913
	2	.291	.0921
	3	.287	.0929
	4	.280	.0937
250	1	.472	.0555
	2	.474	.0555
	3	.472	.0559
	4	.476	.0622
500	1	.575	.0232
	2	.571	.0236
	3	.575	.0236
	4	.571	.0256

Table 4. Cell 1 and Cell 2 Responses of Bromotrichloromethane as a Function of W and T.

T (us)	W (us)	ΔI (nA) Cell 1	ΔI (nA) Cell 2
50	1	.134	.035
	2	.130	.034
	3	.118	.031
	4	.114	.030
100	1	.236	.048
	2	.232	.050
	3	.228	.051
	4	.220	.050
250	1	.539	.076
	2	.539	.079
	3	.539	.079
	4	.555	.080
500	1	.809	.072
	2	.835	.076
	3	.827	.075
	4	.807	.073

With fast pulsing both cell responses decrease with increasing pulse width. Quite possibly the pulse width to pulse period ratio is becoming too large to interpret the response in the context of the pulsed mode of operation with fast pulsing and wide pulse widths. This indicates that using wide pulse widths could contribute to the frequency dependency on GPC response. But since the responses are highest at approximately 1 us pulse width, and that is the width normally used in these GPC experiments, this is not the cause of the frequency dependency illustrated in figure 7.

Electrometer Accuracy

An easily tested, but possible cause of this problem would be a failure of the electrometer to accurately measure the ECD signal. Tables 5 and 6 are comparisons of the signal from both cell-one and cell-two electrometers compared to the signal from a high quality commercial elecrtrometer (Keithly Instruments #602 solid state electrometer). The standing current measurements are made at pulse periods ranging from 50 us to 5 ms, and with both the single negative and bipolar pulse to insure accuracy under all the experimental parameters used in this research.

Table 5. Comparison of Electrometers with Bipolar Pulse.

	ΔI (nA)					
	Cell 1			Cell 2		
T	Keithly	Elec.1	Error(%)	Keithly	Elec.2	Error(%)
50	9.71	9.74	0.3	9.98	9.89	-0.9
75	9.63	9.67	0.4	9.88	9.80	-0.8
100	9.58	9.60	0.2	9.79	9.70	-0.9
200	9.28	9.31	0.3	9.39	9.32	-0.7
250	9.12	9.17	0.5	9.19	9.13	-0.7
500	8.40	8.44	0.5	8.25	8.24	-0.1
1000	7.11	7.17	0.8	6.74	6.74	0.0
2000	4.69	4.70	0.2	3.80	3.84	1.0

Table 6. Comparison of Electrometers With -45 V Pulse.

	ΔI (nA)					
	Cell 1			Cell 2		
T	Keithly	Elec.1	Error(%)	Keithly	Elec.2	Error(%)
50	9.59	9.63	0.4	9.98	9.90	-0.8
75	9.72	9.76	0.4	9.88	9.81	-0.7
100	9.67	9.70	0.3	9.79	9.72	-0.7
150	9.48	9.49	0.1	9.59	9.53	-0.6
200	9.31	9.36	0.5	9.40	9.34	-0.6
250	9.19	9.22	0.3	9.20	9.16	-0.4
300	9.03	9.08	0.6	9.00	8.96	-0.4
400	8.77	8.81	0.5	8.63	8.61	-0.2
500	8.50	8.54	0.5	8.29	8.26	-0.4
600	8.23	8.29	0.7	7.95	7.94	-0.1
700	8.00	8.04	0.5	7.62	7.63	0.1
800	7.73	7.80	0.9	7.35	7.34	0.1
900	7.50	7.46	0.8	7.05	7.06	0.1
1000	7.30	7.34	0.5	6.79	6.79	0.0
1200	6.88	6.91	0.4	6.28	6.27	-0.1
1400	6.49	6.51	0.3	5.78	5.77	-0.2
1600	6.08	6.11	0.5	5.02	5.04	0.4
1800	5.61	4.61	0.0	4.33	4.35	0.5
2000	5.02	5.04	0.4	3.80	3.82	0.5
2500	3.90	3.91	0.2	2.92	2.94	0.7
5000	1.92	1.87	2.6	1.43	1.42	-0.7

Inspecton of the data reveals that our electrometers are accurate over the entire frequency range to ± 1%, with the single exception of 5000 us using the -45 V pulse. The frequency dependency is not simply an artifact of the electronics.

Collection of Negative Ions

Bipolar Pulse

Simon and Wells (22) have suggested that collection of negative ions along with electrons at the central anode of

their constant current ECD may be occurring, and adding to the nonlinearity of the device. If negative ions were being collected in the fixed frequency ECD's used in this research, the response would be expected to fall off with increasing frequency because the field free time between pulses is reduced; thereby, causing more negative ions to be drawn to the anode. The bipolar pulse shown in figure 6 was designed to test this possibility. If the negative ions were drawn toward the pin during the application of the -45 V pulse to the cell wall, then the immediately following +45 V pulse would be expected to return the ions to their original location. Table 7 shows the results of experiments done to test this hypothesis.

Table 7. GPC Response vs. T for Carbon Tetrachloride and Dibromodifluoromethane with Negative (NP) and Bipolar Pulse (BP).

	A' (Arbitrary Units)			
	CCl_4		CF_2Br_2	
T (us)	NP	BP	NP	BP
50	798	691	281	376
80	905	828	276	291
100	913	937	301	296
150	1027	1015	318	325
200	1089	1059	351	344
300	1142	1177	375	388
400	1304	1262	358	392
500	1296	1255	426	424
700	1372	1366	443	441
900	1449	1395	466	463

This table illustrates the uncorrected GPC response

vs. pulse period for carbon tetrachloride and dibromodifluoromethane (CF_2Br_2) (both well behaved GPC compounds) with the single negative and bipolar pulse. The bipolar pulse has no effect on the response over the entire frequency range.

Pulse Amplitude

The effect of pulse amplitude on the GPC result was another experiment designed to test for the collection of negative ions along with electrons at the central anode. If the collection of negative ions occurred, more electrons should be drawn to the central anode at higher pulse amplitudes. The results of these experiments are illustrated in tables 8 and 9. The responses of bromotrichloromethane and carbon tetrachloride respectively are ploted vs. pulse period at three different pulse amplitudes (-45, -22, and -12 V).

Table 8. GPC Response of Carbon Tetrachloride vs. Pulse Period at Various Pulse Amplitudes (V).

	A' (in^2)		
T (us)	-45 V	-22 V	-12 V
50	.274	.300	.123
250	.459	.457	.193
500	.525	.515	.218

Table 9. GPC Response of Bromotrichloromethane vs. Pulse Period at Various Pulse Amplitudes (V).

	A' (in^2)		
T (us)	-45 V	-22 V	-12 V
50	.216	.227	.307
250	.899	.871	.486
500	1.30	1.33	.636

Inspection of these results shows no significant difference in the results between -45 and -22 V which is the lowest pulse amplitude that can be used before the standing current is decreased, and thus causing all the electrons to no longer be collected with each pulse. The results are much more linear at a pulse amplitude of -12 V, but they are also reduced, which is the opposite of what should be observed with a lower pulse amplitude if negative ions were being collected. Also, since the GPC theory requires that all the electrons are collected with each pulse, experiments with pulse amplitudes lower than -22 V are interesting, but they cannot be used to prove or disprove the collection of negative ions as the cause of the pulse frequency dependency on GPC result.

Since neither the bipolar pulse, or the lowering of the pulse amlplitude from -45 V to -22 V had any effect on the GPC result, the collection of negative ions is not thought to be occurring.

Field induced dissociation of the analyte, although it

is certainly unlikely to occur, was considered as an explanation for the pulse frequency dependency of the GPC response. It has been shown that He^- can be neutralized by high electric fields (> 300 Kv) in extremely low pressure systems (23). Although this is a much higher field than exists in the pulsed ECD, field induced dissociation of Cl^- and Br^- was still considered a faint possibility because it could be acting in conjunction with many other processes occurring at atmospheric pressure in the complex reaction medium of the ECD. If this occurred, the presence of the field in the cell during the pulse would strip some of the negative ions of an electron; thereby, reducing the response. Obviously, this effect would be expected to intensify as the pulsing frequency becomes faster because the field is applied a higher percentage of the time. If field induced dissociation is occurring, the response would be expected to become more linear and overall larger at lower pulse amplitudes because of the lowered field strength. This is certainly not the effect seen in these experiments; thus, as was expected, it seems that field induced dissociation is not causing the frequency dependency on GPC result.

Various DC Conditions

Pulse Amplitude

Several other experiments were designed to test the

effect of an applied field on the ECD responses of both cells. In the first of these experiments, ECD response was recorded at different pulse amplitudes (V), ranging from -40 to -7.5 V, for carbon tetrachloride and bromotrichloromethane. Tables 10 and 11 show the response of the first and second cell for CCl_4 and CCl_3Br respectively. The standing currents are also tabulated.

Table 10. ECD Responses of Carbon Tetrachloride at Varying Pulse Amplitudes.

V (volts)	Cell 1 I	Cell 1 ΔI		Cell 2 I	Cell 2 ΔI
-40	9.87	1.72		10.23	1.10
-23	9.87	1.66		10.23	1.10
-15	9.54	2.08		9.95	0.82
-10	8.81	1.80		9.23	0.26
-7.5	8.19	1.68		8.63	0.18
-10	8.87	1.70	(W=2 us)	9.28	0.28

Table 11. ECD Responses of Bromotrichloromethane vs. Pulse Amplitude.

V (volts)		Cell 1 ΔI	Cell 2 ΔI
-40		0.80	0.36
-23		0.78	0.40
-15		1.48	0.66
-10		1.82	0.56
-7.5		1.52	0.30
-10	(W=2 us)	1.50	0.54

During this experiment T was held constant at 50 us,

and W was held constant at 1 us, with the exception of -10 V amplitude where the response was recorded at W = 1 us and W = 2 us.

It is interesting to note that the standing current only decreases one nA between -23 V, where all the electrons are still collected, and -10 V. At -15 V the highest cell-one response for carbon tetrachloride, and cell-two response for bromotrichloromethane are recorded. The only response highest at -40 and -23 V, where all the electrons are still collected, is the second cell response of carbon tetrachloride. This data indicates that either the lowered field strength, and/or the presence of uncollected electrons is certainly having an effect on the responses.

DC Fields in Cell-One

In another experiment the response of the second cell was measured when -36 or +36 VDC was applied to the pin of the first cell, and both cell walls were pulsed -45 V with T = 50 us and W = 1 us. The results for carbon tetrachloride and bromotrichloromethane are shown in table 12.

Table 12. Cell-Two Responses of Carbon Tetrachloride and Bromotrichloromethane with -/+36 VDC Applied to Cell-One.

DC voltage	Peak Heights (cm)	
	CCl_4	CCl_3Br
-36v	2.6	1.6
+36v	8.1	2.2

It is expected that the response would be greater with +36 VDC applied to the pin because of the changed space charge effects in the first cell. When -36 V is applied to the pin, positive ions are drawn to the pin and set up a positive sheath around it so that the electrons do not feel the full 36 V potential. This causes the electrons to be moving slower and therefore more likely to react with a sample molecule. This effect is observed for carbon tetrachloride, and somewhat for bromotrichloromethane, but with smaller magnitude; thus, suggesting that the presence of a field (positive or negative), and/or some other mechanism besides electron capture is causing destruction of bromotrichloromethane.

With the next set of experiments the effects of various DC conditions are further explored. The pulse parameters (T and W) are unchanged. In the following experiment ΔI is measured for cell-one and cell-two with the normal mode (-45 V pulse applied to the wall of both cells, and the two ECD currents measured at the central

anodes), and the normal mode with the electrometers switched. Also, cell-two responses were measured with +36, +50, +100, and +200 VDC applied to the pin of the first cell, and both cell walls pulsed -45 V. The results are tabulated in tables 13 and 14.

Table 13. ECD Responses (nA) of Carbon Tetrachloride with Normal Mode and DC Voltages applied to the Pin of Cell One.

	Normal Mode		DC Voltage Applied to Pin Cell 1			
Cell	Electrometer Stand.	Elect. Reversed	+36	+50	+100	+200
one	.0709	.0716	---	---	---	---
two	.0449	.0464	.059	.059	.061	.059

Table 14. ECD Responses (nA) of Bromotrichloromethane with Normal Mode and DC Voltages applied to the Pin of Cell 1.

	Normal Mode		DC Voltage Applied to Pin Cell 1			
Cell	Electrometer Stand.	Elect. Reversed	+36	+50	+100	+200
one	.0315	.0346	---	---	---	---
two	.0150	.0157	.016	.016	.017	.017

With these magnitudes of DC voltages applied to the first cell all thermal electrons should be removed from the cell before they can react with the analyte. Therefore, if the only destruction of the analyte is from electron capture, the second cell response with the DC voltages applied should be equal to the cell-one response in normal

mode. But for carbon tetrachloride the cell-two response with all magnitudes of DC voltages applied to the first cell is only midway between the normal mode cell-one and cell-two response. And for the bromotrichloromethane the cell-two response is unchanged between the mormal mode and +DCV responses, indicating that some mechanism other than electron capture is primarily responsible for bromotrichloromethane destruction in the first cell. The second cell response for bromotrichloromethane is somewhat increased at +100 VDC and +200 VDC, but the reason for this phenomenon is unknown. Later in this research it is shown that both CCl_4 and CCl_3Br undergo thermal degradation to some extent. Quite possibly, this is the mechanism that is causing the extraneous analyte removal in these expeiments.

Tables 15 and 16 show the results of an experiment identical to the last experiment except that only +50 VDC is applied to the pin of cell-one, and it is done with a pulse period of 250 us as well as 50 us.

Table 15. ECD Responses (nA) of Carbon Tetrachloride with +50 VDC Applied to the Pin of Cell One at T = 50 and 250 us.

	T = 50us		T = 250us	
Cell	Normal Mode	+50VDC	Normal Mode	+50VDC
one	.0709	---	.240	---
two	.0464	.059	.0709	.193

Table 16. ECD Responses (nA) of Bromotrichloromethane with +50 VDC Applied to the Pin of Cell One at T = 50, 250 us.

	T = 50us		T = 250us	
Cell	Normal Mode	+50VDC	Normal Mode	+50VDC
one	.0345	---	.165	---
two	.0157	.0170	.0677	.0866

The same type of results and conclusions apply to this experiment as to the previous experiment. The significance of this experiment is that the same type of results are observed at 250 us as at 50 us.

The last DC experiment gives the ECD responses of cell-one and cell-two operated in the normal mode vs. the cell-two response with the cell walls grounded, +50 VDC applied to the pin of cell-one, and the pin of cell-two pulsed +50 V to collect the electrons (mode 2 in table 17). Table 17 shows the results with T = 50 us.

Table 17. ECD Responses (nA) of Carbon Tetrachloride and Bromotrichloromethane with the Cells Pulsed Normally and in Mode 2.

Compound	Cell	Normal Mode	Mode 2
CCl	one	.0709	----
	two	.0464	----
CCl Br	one	.0345	----
	two	.0157	.0157

The same results as in the two previous experiments

are observed even though the -45 V pulse to the walls is removed and the pin of cell-two is pulsed positive to collect the electrons.

This set of experiments indicates that the presence of a field in the first cell > 36 V whether positive, negative, DC, or pulsed yields the same response to bromotrichloromethane in the second cell. For carbon tetrachloride the responses in the second cell with all the DC modes tested were the same, but different from that of the normal mode.

Nitrogen Carrier Gas

The change in response at -12 V amplitude indicates that the continuous presense of free electons in the cell due to incomplete collection might affect the response. Table 18 shows that in nitrogen carrier gas all the electrons are not collected with a -45 V pulse at a pulse width of 1 us because of the reduced standing currents over the entire frequency range, but they are collected with a 2 us pulse width. Thus, this is a means to test the effects of incomplete electron collection without changing the pulse amplitude.

Table 18. Standing Currents (nA) with Nitrogen Carrier Gas at Pulse Widths of 1 and 2 us.

	W = 1us		W = 2us	
T (us)	Cell 1	Cell 2	Cell 1	Cell 2
40	7.10	7.41	7.17	7.44
50	7.08	7.40	7.17	7.43
60	7.06	7.38	7.16	7.42
80	7.02	7.34	7.15	7.41
100	6.97	7.31	7.13	7.39
120	6.93	7.27	7.11	7.37
150	6.87	7.20	7.08	7.34
175	6.81	7.15	7.05	7.32
200	6.76	7.08	7.03	7.29
250	6.64	6.95	6.98	7.24
300	7.51	6.82	6.93	7.19
350	6.38	6.68	6.88	7.14
400	6.25	6.54	6.82	7.08
450	6.11	6.40	6.77	7.03
500	5.98	6.26	6.72	6.98
600	5.74	6.00	6.61	6.88
700	5.48	5.74	6.50	6.78
800	5.25	5.49	6.38	6.67
900	5.04	5.27	6.26	6.56
1000	4.83	5.05	6.14	6.45

Tables 19 and 20 illustrate the uncorrected GPC response in nitrogen carrier gas of carbon tetrachloride and bromotrichloromethane respectively vs. pulse period. In both cases it is indicated that the response is increased with incomplete electron collection (T = 1 us), especially at long pulse periods. Since this is the opposite of the effect observed in tables 8 and 9, when the pulse amplitude was lowered, it is probable that incomplete electron collection is not the cause of the reduced frequency dependency observed there. It is quite likely that unknown problems are occurring in these situations,

and causing the increased responses with incomplete electron collection.

Table 19. GPC Responses of Carbon Tetrachloride with Nitrogen Carrier Gas.

	A' (in^2)		
T (us)	W = 1 us	W = 2 us	W = 4 us
50	.295	.276	.224
250	.551	.437	.413
500	.755	.604	.505

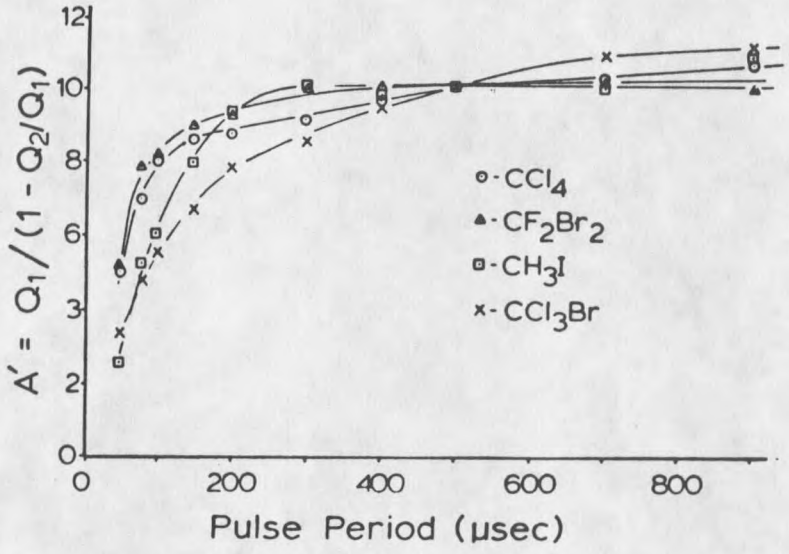
Table 20. GPC Responses of Bromotrichloromethane with Nitrogen Carrier Gas.

	A' (in^2)		
T (us)	W = 1 us	W = 2 us	W = 4 us
50	.393	.168	.166
250	1.308	.737	.680
500	1.929	1.182	1.069

Chemical Factors

It is possible that chemical factors could be responsible for the frequency dependency on GPC response. The results of the experiment depicted in figure 9 suggest that chemical factors may be involved in the response drop off. In this experiment the pulse frequency vs. the uncorrected GPC result (A') curves have been plotted for carbon tetrachloride, dibromodifluoromethane, bromotrichloromethane, and methyl iodide (CH_3I). The curves are normalized to one another at T = 500 us.

Figure 9. Uncorrected GPC Response of Carbon Tetrachloride, Dibromodifluoromethane, Bromotrichloromethane, and Methyl Iodide vs. Pulse Period. The Curves are Normalized at T = 500 us.



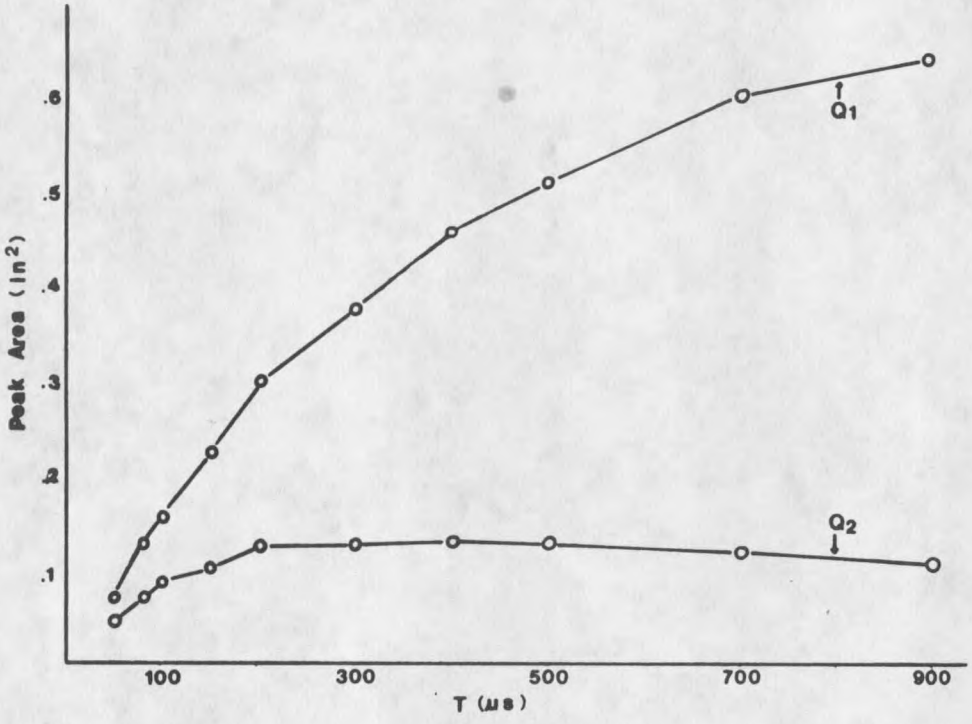
Carbon tetrachloride and dibromodifluoromethane, both well behaved compounds, show almost the same frequency dependent curves despite the fact that the former produces a Cl^- negative ion; whereas, the latter produces a Br^- ion upon electron attachment.

Bromotrichloromethane and methyl iodide exhibit similar frequency dependent response curves with both falling off farther than carbon tetrachloride and dibromodifluoromethane. For the case of methyl iodide it has been shown in a previous study (11) that it is probably not a coulometrically well behaved compound because the product of positive ion recombination (probably HI) is

thought to undergo electron capture to some extent.

Evidence in this research indicates that bromotrichloromethane is not a well behaved compound either. Figure 10 shows the cell-one and cell-two areas vs. pulse period for bromotrichloromethane from the data used to calculate the curves in figure 9.

Figure 10. Cell-One (Q_1) and Cell-Two (Q_2) Responses of Bromotrichloromethane vs. Pulse Period.



If this graph is compared to figures one and two (the corresponding graphs for carbon tetrachloride and fluorotrichloromethane) it is immediately obvious that the cell-one response drops off at least as fast, and that the cell-two response does little to nothing for correcting the

cell-one response, as compared to these supposedly well behaved compounds.

Nevertheless, it is apparent from figure 9 that chemical factors can and do play a part in the response vs. frequency curves; otherwise, these curves would be identical.

Figure 9 also lends support to the argument that negative ions are not being collected at the anode. If this were the case, the carbon tetrachloride curve should drop off faster than the other three because it produces the more mobile Cl^- negative ion upon electron attachment; whereas, the other three compounds produce the less mobile Br^- and I^- negative ions.

Another argument made previouly that figure 9 can support was that this frequency dependency is not simply an artifact of the electronics used to pulse the cells and measure the current. If this were so the curves should be identical.

Direct Measurement of Positive Ion Signal

The positive ion signal was also measured at each pulse period (by reverse polarity pulsing) during the experiment depicted in figure 9. Table 21 shows the A' and $A'/(1-Q_+/Q_1) = A''$ (Q_+ is the area of the peak from cell-one with reverse polarity pulsing) GPC responses vs. pulse period for carbon tetrachloride, methyl iodide, and

bromotrichloromethane.

Table 21. GPC Responses of Carbon Tetrachloride, Dibromodifluoromethane, and Methyl Iodide with and without Direct Positive Ion Correction.

	CCl_4		CF_2Br_2		CH_3I	
T	A'	A"	A'	A"	A'	A"
50	626	707	165	191	111	149
80	869	927	250	270	220	266
100	992	1070	259	277	253	302
150	1070	1120	286	300	333	367
200	1080	1130	296	308	392	422
300	1130	1180	303	314	419	446
400	1200	1240	321	332	410	430
500	1250	1290	321	331	420	436
700	1280	1320	324	334	421	435
900	1320	1360	317	327	452	464

It was thought that a direct mesurement of the positive ion current at each pulse period might improve the linearity of response, but inspection of these tables reveals that this added correction does little to nothing for the linearity.

An interesting observation from this reverse polarity pulsing is that there is no positive ion response from the second cell for any of these four compounds. To test if this was simply a problem with the second cell or electrometer, both cells and the electrometers were switched one at a time. Table 22 shows the results of this experiment for carbon tetrachloride, dibromodifluoromethane, and methyl iodide. Only cell-one responses are tabulated. All cell-two responses were still

zero.

Table 22. Cell 1 Responses With Cells and Electrometers Switched.

Compound	T (us)	Peak Heights (cm) Normal Config.	Cells Switched	electrometers Switched
CCl_4	50	2.9	2.0	1.8
	300	2.6	2.2	2.1
	900	2.5	2.7	2.8
CF_2Br_2	50	2.3	1.3	1.1
	300	1.8	1.5	1.6
	900	1.8	1.9	1.9
CH_3I	50	2.8	2.1	1.8
	300	2.2	1.7	1.7
	900	1.8	1.6	1.7

Neither electrometer or cell configuration seemed to have any significant effect on the positive ion current from the cell. There was a trace of chloroform in the sample probably from desorption off the carboy walls. The chloroform did show a very small response in the second cell.

GPC Measurements of Background Air

If it was known where the correct concentration was on the GPC response vs. pulse period curves it could help explain what the problem was, and would perhaps indicate if the method of GPC has any validity at all. As previously stated, it is very difficult to prepare accurate standards

in the parts per trillion concentration range, so in this research background air was used as an accurate standard.

Because of the ozone controversy (24) the tropospheric concentration of fluorotrichloromethane and carbon tetrachloride in background air is fairly well established. Extensive measurements of tropospheric carbon tetrachloride and fluorotrichloromethane in 1980 indicated that the carbon tetrachloride concentration was 118 parts per trillion and increasing at a rate of 1.8% annually (25); whereas, the concentration of fluorotrichloromethane was 168 and increasing at an annual rate of 5.7% (26). Therefore, the background air concentrations of carbon tetrachloride and fluorotrichloromethane in the northern hemisphere should be about 126 and 210 parts per trillion respectively (26).

Bozeman, Montana, being a small town hundreds of miles from any industrial center should contain relatively pristine background air especially when the proper atmospheric conditions prevail (mainly northwest winds). Figure 11 is a typical chromatogram obtained from an air sample with excellent conditions. This chromatogram is an excellent example of the exquisite sensitivity of the ECD, and the quality of the GC since even at these very low concentrations the signal to noise ratio is still very good.

Figure 11. Chromatogram of Background Air.

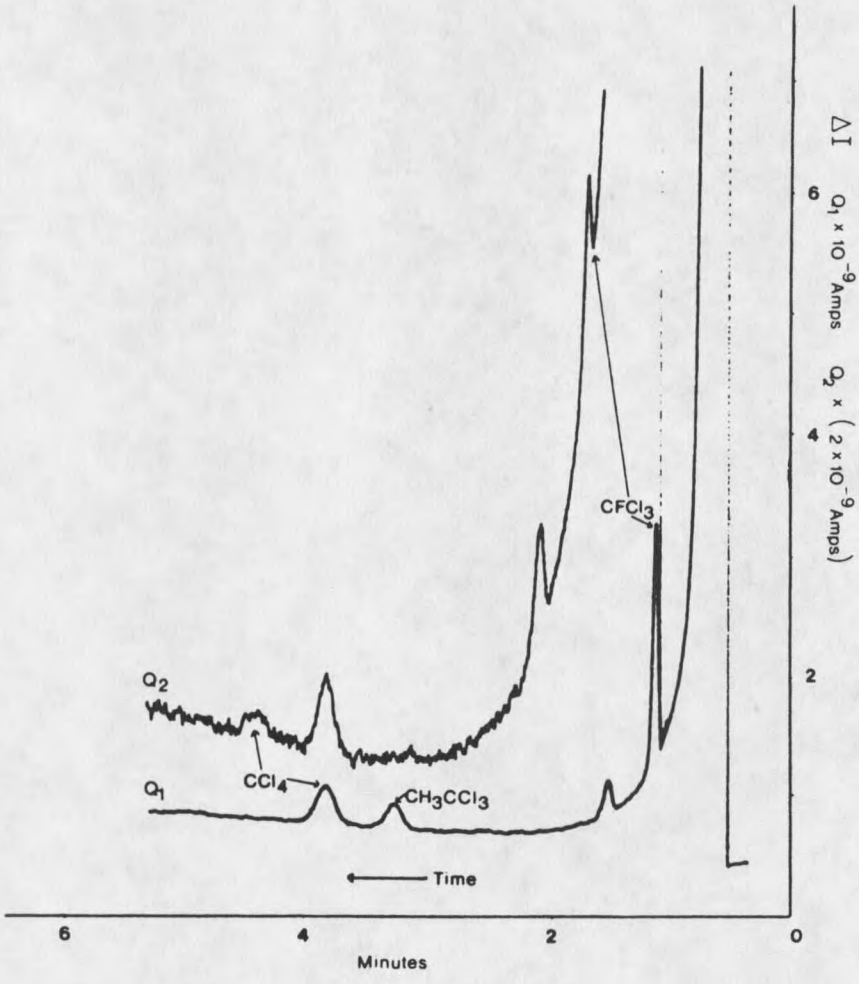


Table 23 shows the part per trillion GPC concentrations obtained from three consecutive days in September 1984 with a pulse period of 400 us. This pulse period was chosen because it had been previously used by Lovelock, Maggs, and Adlard (1) to yield quantitatively accurate GPC results for sulfur hexafluoride. These air samples were taken from the northwest corner of the roof on Gaines Hall at Montana State University with a strong

northwest breeze blowing.

Table 23. Atmospheric Concentrations of Carbon Tetrachloride and Fluorotrichloromethane Obtained from GPC.

	Parts Per Trillion (V/V)			
	$CFCl_3$		CCl_4	
Date	A'	A	A'	A
9/3/84	188	210	138	154
9/4/84	187	209	129	144
9/5/84	189	211	133	148

The data for fluorotrichloromethane is extremely encouraging, but the data for carbon tetrachloride is about 20% too high. Measurements under less than ideal atmospheric conditions have indicated that the fluorotrichloromethane measurement is fairly constant; whereas, the carbon tetrachloride measurment can vary considerably; therefore, suggesting that fluorotrichloromethane should be a more reliable standard. It is difficult to know whether the GPC method is at fault in the carbon tetrachloride measurements, or if the air had a higher than background concentration.

Nevertheless, these measurements suggest that the GPC response is most nearly correct at the slower frequency end of the response curve (> 400 us), and that the results become increasingly too low with faster pulsing.

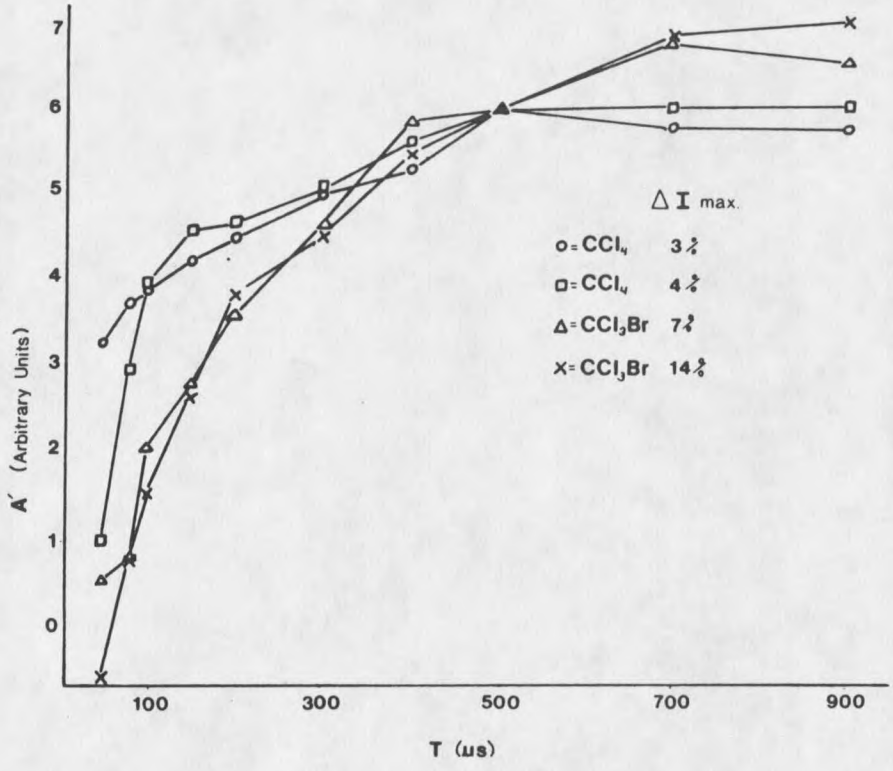
Analyte Concentration

In developing the GPC theory it was assumed that $\Delta I << I$. This has been taken to mean that the highest concentration sample measurable by GPC would utilize 10% or less of the standing current. Perhaps the frequency dependent response is caused, or contributed to, by this reduction in I being too large.

Lillian and Singh (4) have noted, in an experiment where they plotted the first cell response vs. analyte concentration for carbon tetrachloride and fluorotrichloromethane, that the curve is linear at only very low concentrations, and increasingly falls below the linear values extrapolated from low concentrations as the analyte concentration increases.

The GPC response vs. frequency curves, for carbon tetrachloride and bromotrichloromethane, from figure 9 are plotted in figure 12 along with the curves obtained after the sample was diluted to approximately 75% of its original concentration. All four curves have been normalized to one another at T = 500 us. The original maximum reductions in standing current (ΔI_{max}) were 4% for carbon tetrachloride and 14% for bromotrichloromethane; whereas, after dilution they were 3% and 7% respectively.

Figure 12. GPC Response vs. Frequency Curves for Carbon Tetrachloride and Bromotrichloromethane at Two Different Concentrations. The Less Concentrated Sample is Approximately 75% of the Other Sample.

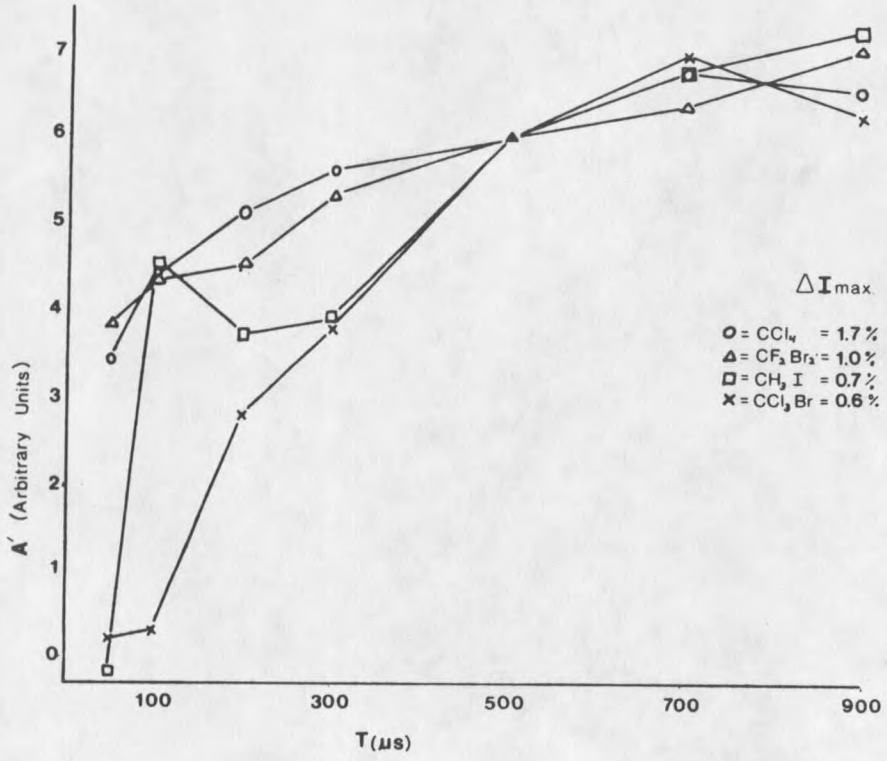


The response falls off farther for both compounds in the more concentrated sample. The response of the 4% ΔImax sample falls off 50% between T = 500 and T = 50 us; whereas, it only falls off 26% for the 3% ΔImax sample.

To further test the possibility of concentration dependence on GPC result a sample was prepared that had maximum reductions in standing current of 1.7% for carbon tetrachloride, 1% for dibromodifluoromethane, 0.7% for

methyl iodide, and 0.6% for bromotrichloromethane. The response vs. frequency curves for this sample are plotted in figure 13. The four curves have been normalized to one another at T = 400 us.

Figure 13. GPC Result vs. Frequency Curves for Carbon Tetrachloride, Dibromodifluoromethane, Methyl Iodie, and Bromotrichloromethane with ΔImax < 1.8%.

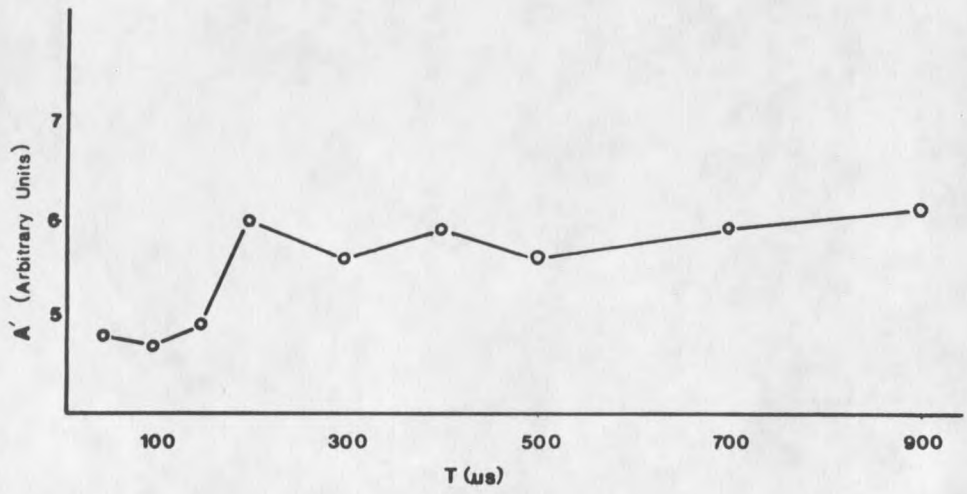


The frequency dependency is still present even in this very low concentration sample. Even though the concentration of carbon tetrachloride has been reduced to give only a 1.7 nA maximum reduction in standing current it

still shows a 26% reduction in response between T = 500 and T = 50 us. The standing current reduction over this frequency range for dibromodifluoromethane (ΔImax = 1.0%) is 22%; whereas, in figure 9, where ΔImax = 3%, the reduction in response over this same frequency range was 49%. Thus, dibromodifluoromethane is showing concentration dependent response vs. frequency curves similar to carbon tetrachloride, as would be expected since they are both supposedly well behaved compounds.

Figure 14 is the response vs. frequency curve from a dibromodifluoromethane sample that had a maximum standing current reduction of 0.4%.

Figure 14. GPC Response vs. Frequency Curve for Dibromodifluoromethane with ΔImax = 0.4%.



The response seems to be linear down to about T = 200 us, but is then reduced with faster pulsing. The drop off

in response seen here is about 15% between pulse periods of 500 and 50 us.

These experiments show that the frequency dependency on GPC response becomes markedly worse when the maximum reduction in standing current is above approximately 3%, but that little improvement is seen at lower concentrations.

Flow Rate

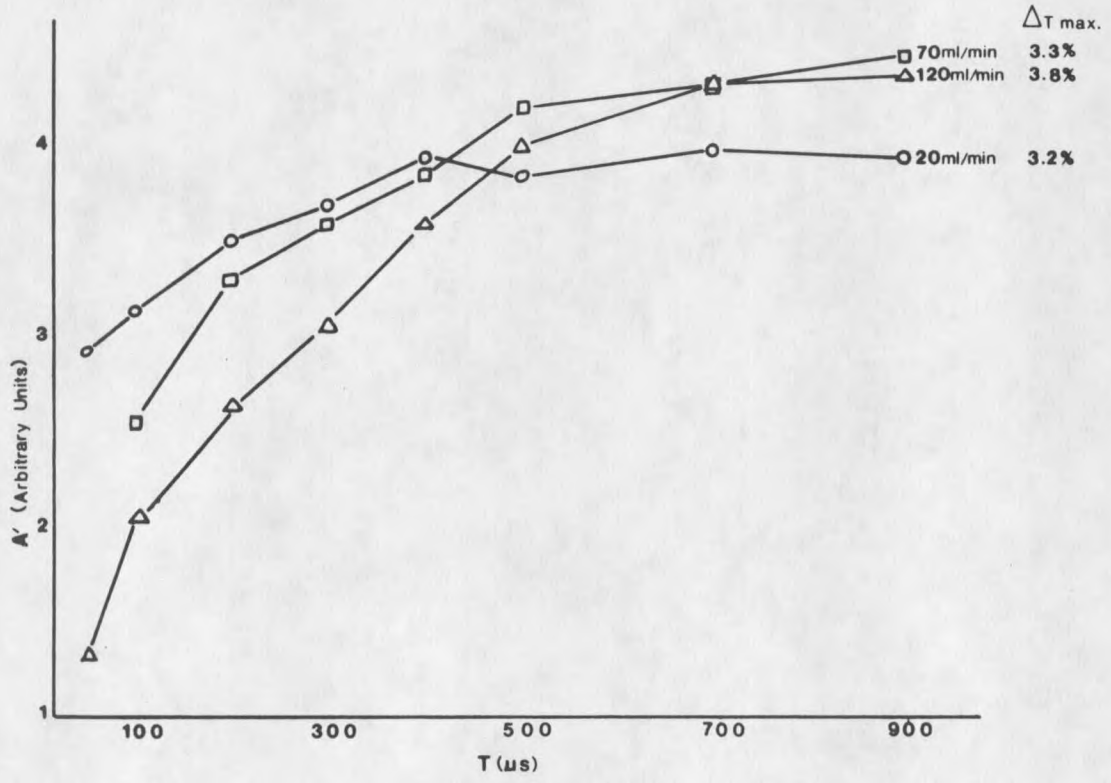
In the GPC theory it is assummed that the ECD is a well mixed reaction vessel. It has been shown that the electrons are contained in a donut shaped portion of the cell when moderately fast pulse frequencies are used, due to the positive space charge from the positive ions remaining in the cell after the application of an electron collecting pulse (13). And the area of the cell occupied by electrons becomes smaller as the period between pulses is reduced. As the flow rate is changed, so is the residence time of the analyte within the cell.

If the ECD is not behaving as a well mixed reactor, then increasing the flow rate, and thus decreasing the residence time of the analyte should not cause the frequency dependency on GPC result to be increased because this would simply lower the entire curve. But, increasing the flow rate also lowers the ionization efficiency (1) due to the decreased residence time of the analyte within the

cell; thus, this would cause the frequency dependency on GPC result to be intensified if the second cell is not properly correcting for efficiency.

Figures 15, 16, and 17 show the effect of flow rate on the result vs. frequency curves of dibromodifluoromethane, carbon tetrachloride, and fluorotrichloromethane respectively.

Figure 15. GPC Response vs. Frequency Curves for Dibromodifluoromethane at Flow Rates of 20, 70, and 120 ml/min.

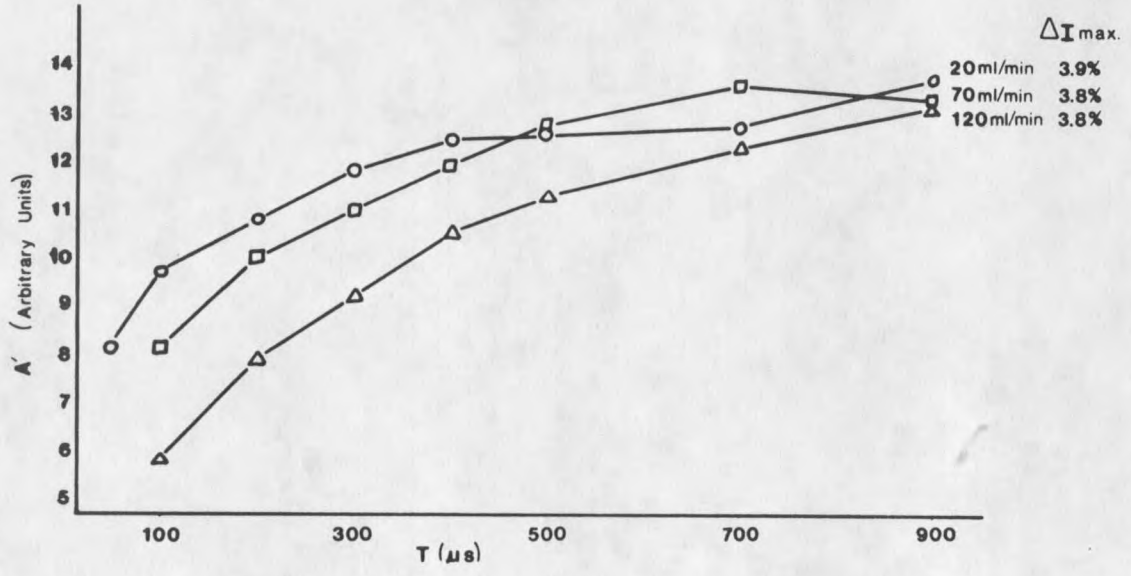


Dibromodifluoromethane shows a dramatically increased

frequency dependency with higher flow rates from a 15% response drop off (between T = 500 and T = 50 us) at 20 ml/min to 66% at 120 ml/min. ΔImax does change slightly over this range, from 3.2% at 20 ml/min to 3.8% at 120 ml/min, but earlier experiments indicate that this 0.6% change in ΔImax is not enough to cause a 41% response decrease.

Carbon tetrachloride also shows a dramatically increased frequency dependency on GPC result, but in this case ΔImax is virtually unchanged.

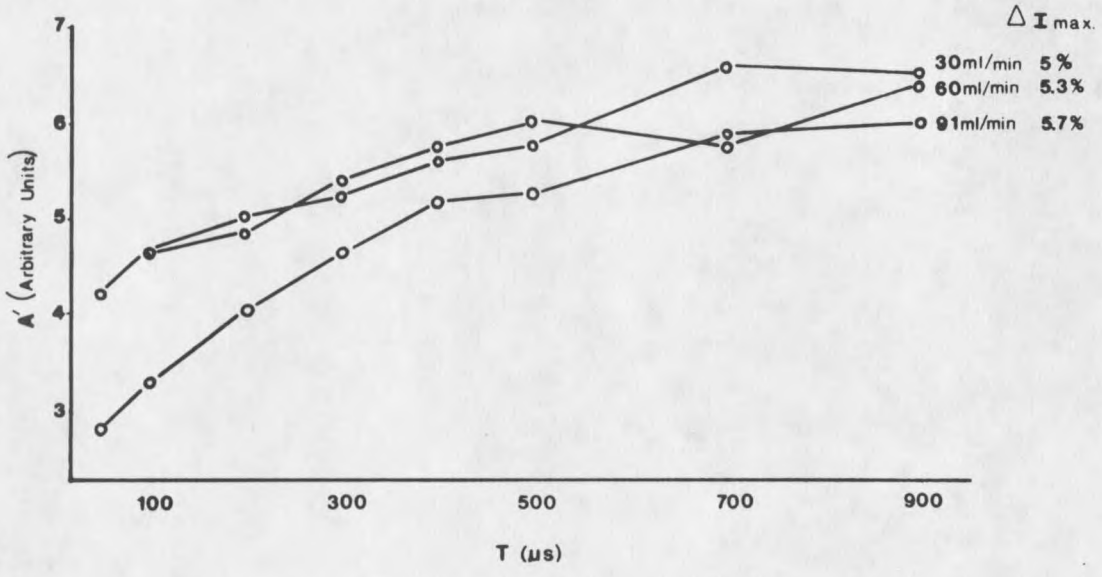
Figure 16. GPC Result vs. Frequency Curves of Carbon Tetrachloride at Flow Rates of 20, 70, and 120 ml/min.



The fluorotrichloromethane curves were taken at 30, 60, and 90 ml/min flow rates rather than the 20, 70, and

120 ml/min used for carbon tetrachloride and dibromodifluoromethane. The results at 30 and 60 ml/min are comparable, but the 90 ml/min curve shows a significantly reduced response.

Figure 17. GPC Result vs. Frequency Curves of Fluorotrichloromethane at Flow Rates of 20, 70, and 120 ml/min.



It is interesting to note that for all three of these compounds the response curves begin falling off at higher pulse periods when faster flow rates are used. Since the frequency dependency on GPC result is intensified at higher flow rates, a failure of the second cell to correct for efficiency is indicated.

Detector Temperature

The effect of temperature on GPC was characterized in the following experiment. Figures 18-22 show the GPC response (A') vs. pulse period at three detector temperatures (101, 151, and 201°C) for carbon tetrachloride, bromotrichloromethane, methyl iodide, dibromodifluoromethane, and fluorotrichloromethane respectively.

Figure 18. GPC Response vs. Frequency Curves of Carbon Tetrachloride at Detector Temperatures of 100, 150, and 200°C.

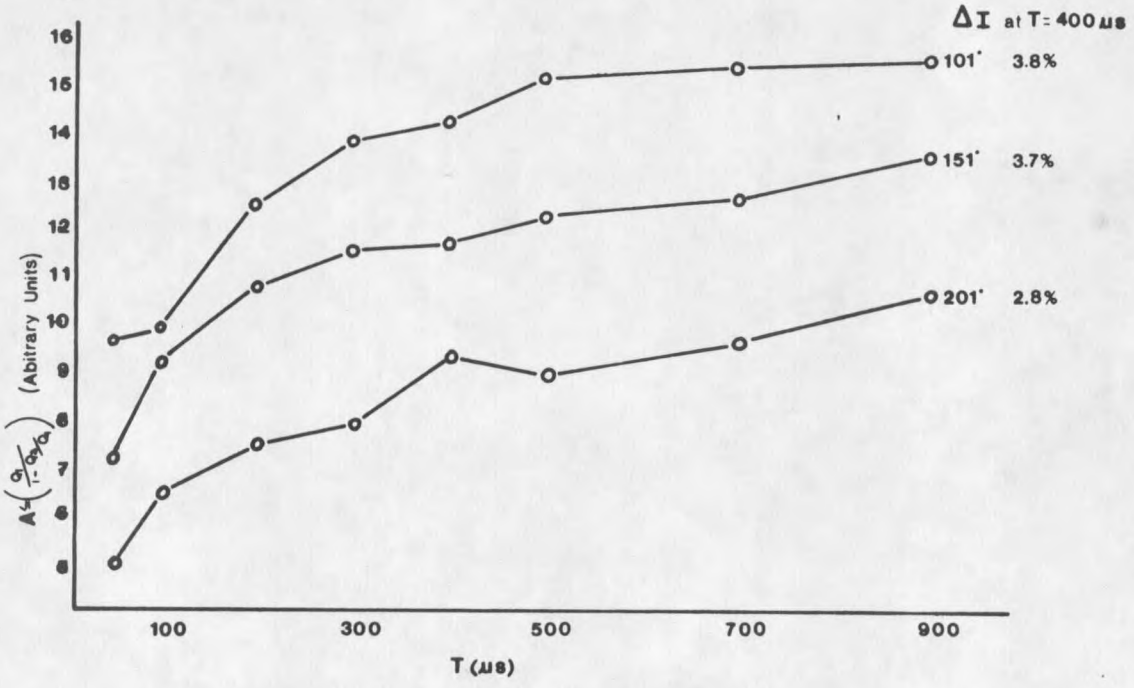


Figure 19. GPC Response vs. Frequency Curves of Bromotrichloromethane at Detector Temperatures of 100, 150, and 200°C.

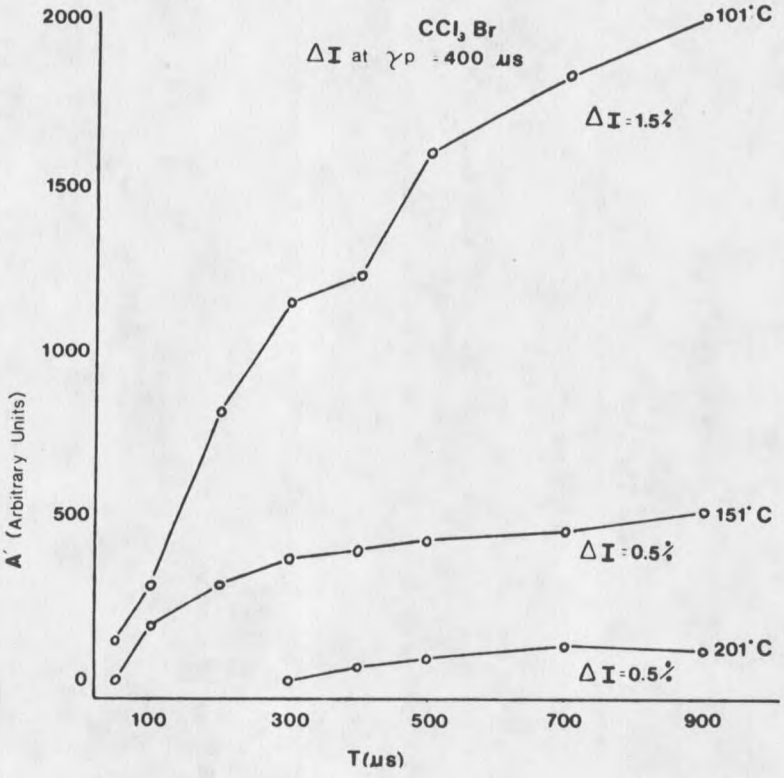


Figure 20. GPC Response vs. Frequency Curves of Methyl Iodide at Detector Temperatures of 100, 150, and 200°C.

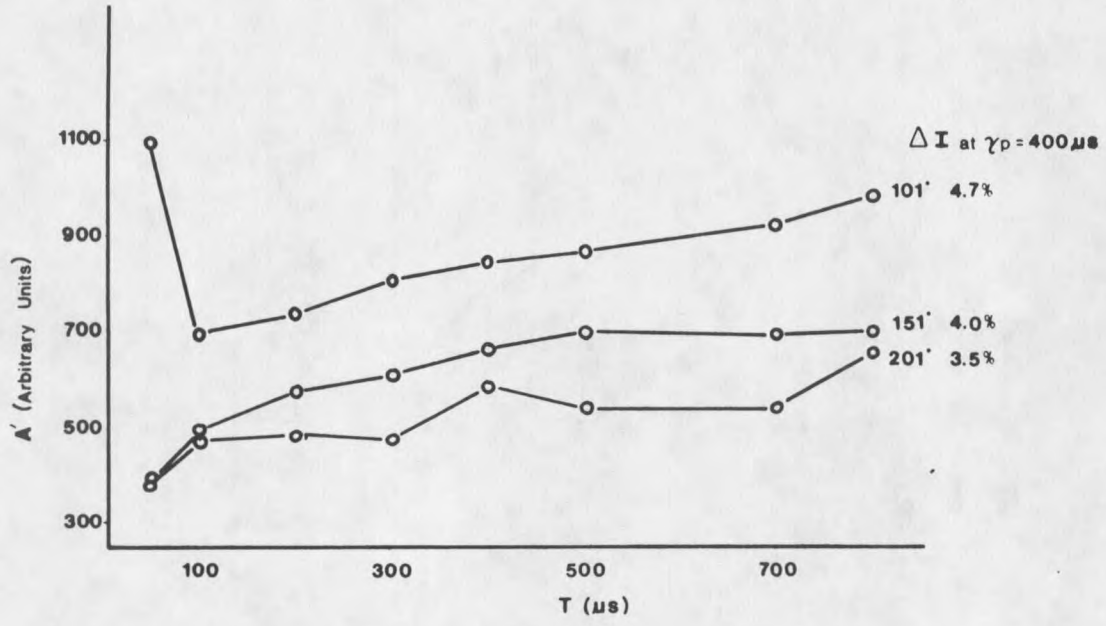


Figure 21. GPC Response vs. Frequency Curves of Dibromodifluoromethane at Detector Temperatures of 100, 150, and 200°C.

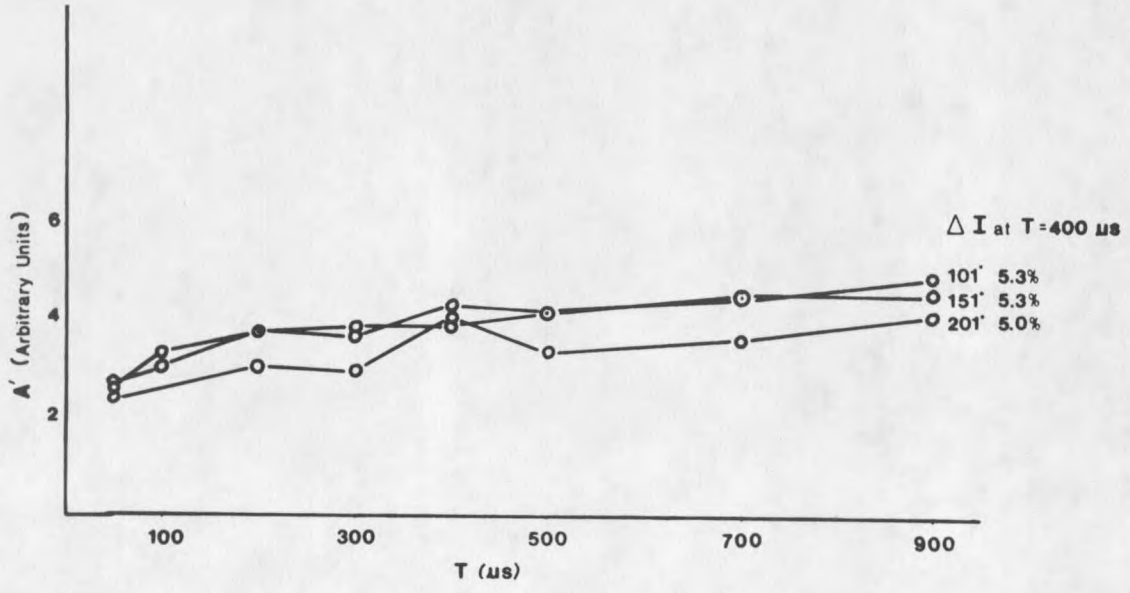
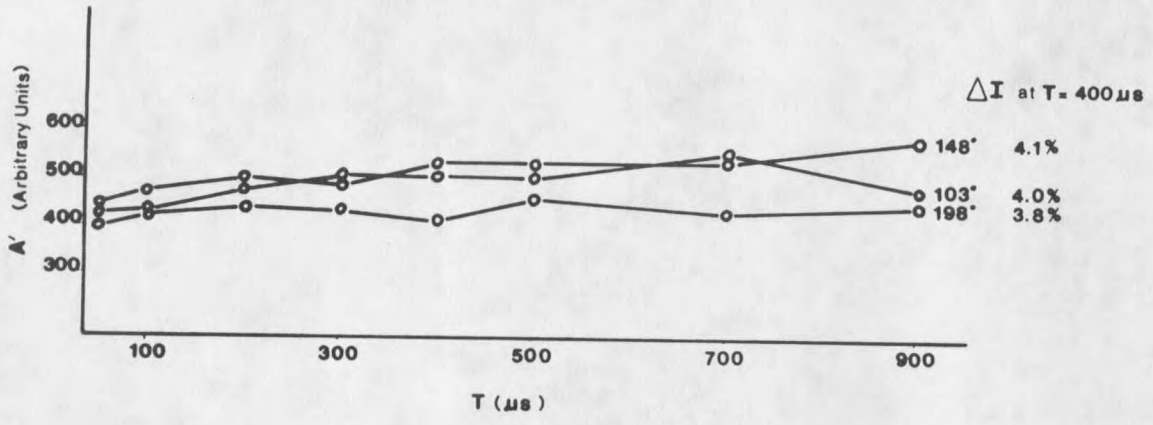


Figure 22. GPC Response vs. Frequency Curves of Fluorotrichloromethane at Detector Temperatures of 100, 150, and 200°C.



For the first three of these compounds there is a definite effect of temperature on the GPC result; although, the linearity of the curves is relatively unaffected, with the exception of bromotrichloromethane. A possible explanation for this is associative electron capture by the original dissociative electron capture products. This would cause the responses to be higher at low temperatures, as is the case in figures 18-20, because this process is disfavored at higher temperatures; thus, causing the error in GPC result to be high. But the air sample analyses indicated that the GPC result was fairly accurate at long pulse periods, and then became too low at short pulse periods. The most likely cause of the temperature dependency on GPC result for these compounds is simply

analyte destruction on the hot cell walls. This means that if true coulometry was ever done with these compounds the detector would have to be run at a low enough temperature to prevent degradation, or a correction factor for temperature would have to be included in the GPC theory.

The latter two compunds (dibromodifluoromethane and fluorotrichloromethane) both show consistant GPC results at 101 and 151^{o}C, but there is a slight decrease between 151 and 201^{o}C. These compounds would be expected to exhibit more temperature stability than the other three; thus, thermal degradation is supported as the reason for their temperature sensitivity.

SUMMARY

Initially a theory was described that should give quantitatively accurate GPC results regardless of the pulse frequency used. But when this theory was tested it was shown to give results that varied with the pulse frequency. A series of experiments were then done to try to determine the cause of this unexplained pulse frequency dependency on GPC result.

The effect of pulse width on ECD response was the first variable tested. The results showed that using wide pulse widths lowered both the cell-one and cell-two responses at fast pulse frequencies; thus, causing the frequency dependency on GPC result to become larger. This means that narrow pulse widths (1 us), as were routinely used in this research, should be used for the best consistency.

The electrometers, used to measure the ECD currents, were then tested to insure that the frequency dependency on GPC result was not simply a result of frequency dependent electronics. Both electrometers were found to yield accurate measurements over the entire frequency range.

The possibility of negative ion collection at the anode leading to erroneous GPC results was tested primarily by experiments with a bipolar pulse; and secondarily by the effects of pulse amplitude, and type of negative ion

produced upon electron capture. All three of these experiments indicated that negative ions are not being collected.

Field induced dissociation of the analyte, although it is certainly unlikley to occur, was tested as a possible cause of the frequency dependency on GPC result by varing the amplitude of the electron collecting pulse. This experiment showed the GPC result to be independent of pulse amplitude until it was lowered below the point where all the electrons are collected with each pulse (-22 V). At lower voltages the results became more linear, but they also are lower overall. Since all the electrons are not collected, as the GPC theory requires, this increased linearity is probably not significant.

Several other experiments were designed to test the effects of applied DC and pulsed fields on the analyte. In these experiments the ECD response of the second cell was recorded with positive or negative DC voltages of various magnitudes, and 50 V pulses applied to either the pin or the wall of cell-one. The cell-two response of bromotrichloromethane was found to be independent of these various DC and pulsed conditions in cell-one. The cell-two response of carbon tetrachloride with the various DC conditions was always the same magnitude which was between the cell-one and cell-two responses obtained with the cells operated in the normal pulsed mode. This set of

experiments indicated that some method other than electron capture is primarily responsible for bromotrichloromethane destruction in the first cell, and partially responsible for carbon tetrachloride destruction in the first cell.

The effect of incomplete electron collection was tested in nitrogen carrier gas by changing the pulse width rather than the pulse amplitude. The results showed that at narrow pulse widths (where incomplete electron collection occurs) the response is increased, but the linearity of response vs. pulse period is not improved.

Chemical factors were shown to affect GPC result vs. frequency curves by normalizing the curves of four compounds (carbon tetrachloride, dibromodifluoromethane, methyl iodide, and bromotrichloromethane) at T = 500 us. The bromotrichloromethane and methyl iodide curves showed a much larger frequency dependency between 500 and 50 us than either carbon tetrachloride or dibromodifluoromethane. Thus, adding support to the arguments that negative ion collection is not occuring, and that the electrometer is not frequency dependent.

Direct peak area measurements of the positive ion signal, from reverse polarity pulsing, were made at each pulse period and incorporated into the GPC result. But this produced little improvement in the linearity of the curves.

Background air was analyzed by GPC, and considered to

be an accurate standard. GPC results at a pulse period of 400 us were found to be accurate for fluorotrichloromethane, and 20% too high for carbon tetrachloride.

The effect of analyte concentration on GPC result vs. frequency curves was tested. It was found that for "well behaved" GPC compounds the frequency dependency became much worse when the maximum reduction in standing current was above approximately 3%.

Carrier gas flow rate was found to have a large effect on GPC result vs. frequency curves. As the flow rate was increased the response showed an increased frequency dependency, suggesting that the ECD is not a well mixed reaction vessel, and/or the second cell response does not correct for efficiency.

Finally, the effect of temperature on GPC was characterized to test for the possibility of associative electron capture by dissociative electron capture products. The response vs. frequency curves of fluorotrichloromethane and dibromodifluoromethane were unaffected by detector temperature; whereas, the curves of carbon tetrachloride, bromotrichloromethane, and methyl iodide were lowered as detector temperature was increased, but the curvature was unchanged. Thus, indicating that these compounds are undergoing thermal degradation at high detector temperatures.

The results from all these experiments indicate that the frequency dependency on GPC result can be minimized, but not eliminated, by using narrow pulse widths, direct measurement of positive ion signals at each pulse period, low concentration samples, and low carrier gas flow rates.

Since slowing the carrier gas flow rate to increase the efficiency of the ECD tended to minimize the frequency dependency, the most likely cause of this problem is a failure of the second cell to properly correct for efficiency. Perhaps a reaction that involves dissociative electron capture products from the first cell is occuring in the second cell. It would seem that the concentration of the various ions and molecules in the second cell would be different from that of the first cell since only neutral carrier gas and analyte enter the first cell, but all the products of reaction from the first cell enter the second cell. If any of these species from the first cell affect ECD response, then the GPC theory is violated since it requires the conditions that affect response to be identical in both cells. The fact that there was not a positive ion signal from the second cell with reverse polarity pulsing is a very good indicator that the chemistry occurring in the tandem cells is not identical. This could possibly tie into recent work by Aue and Sie (27) where they have found evidence for more than one response mechanism in the pulsed ECD. As stated in the

introduction, relatively little is known about the possible reaction of analyte with free radicals. The ratio of free radicals to analyte is probably much greater in the second cell than in the first cell; thus, this side reaction of the analyte would be greater in the second cell, and the efficiency of the first cell would not be corrected.

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