Selective detection of iodinated hydrocarbons by the electron capture detector with negative ion hydration and photodetachment
by Rodney Edward Arbon

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

An electron capture detector is described which is capable of detecting trace levels of iodinated hydrocarbons, but does not respond to chlorinated hydrocarbons. These desirable response characteristics have been achieved by using four gas-phase processes. These are: (1) dissociative electron capture by the halogenated hydrocarbons, (2) regeneration of an electron capture-active species (thought to be HI) by the ion-ion recombination reaction of I⁻, (3) photodetachment of I⁻ and the hydrates of I⁻, (4) and prevention of Cl⁻ photodetachment by hydration. This photodetachment modulated electron capture detector is instrumentally simpler than an earlier version. Its light source consisted of a low-power Hg arc lamp and requires no monochromator or light filter. This transducer, will be shown to be capable of specific detection of methyl and ethyl iodide in an air sample which contains an excess of chlorinated hydrocarbons. This device will also be shown to hold considerable promise for the selective detection of brominated hydrocarbons in the presence of chlorinated hydrocarbons.

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For believing in me when at times it seemed hopeless, for always caring, and for doing the work of ten, this thesis is dedicated with my love and appreciation to my wife, Helen.

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ABSTRACT

An electron capture detector is described which is capable of detecting trace levels of iodinated hydrocarbons, but does not respond to chlorinated hydrocarbons. These desirable response characteristics have been achieved by using four gas-phase processes. These are: (1) dissociative electron capture by the halogenated hydrocarbons, (2) regeneration of an electron capture-active species (thought to be HI) by the ion-ion recombination reaction of I^- , (3) photodetachment of I^- and the hydrates of I^- , (4) and prevention of Cl^- photodetachment by hydration. This photodetachment modulated electron capture detector is instrumentally simpler than an earlier version. Its light source consisted of a low-power Hg arc lamp and requires no monochromator or light filter. This transducer will be shown to be capable of specific detection of methyl and ethyl iodide in an air sample which contains an excess of chlorinated hydrocarbons. This device will also be shown to hold considerable promise for the selective detection of brominated hydrocarbons in the presence of chlorinated hydrocarbons.

INTRODUCTION

Since its conception in 1952, gas chromatography has been established as the pre-eminent method of separating volatile components of complex mixtures. Of the many detectors available for monitoring gas chromatographic effluents, the electron capture detector (ECD) has proven itself to be one of the most valuable in trace environmental analysis. This results from the fact that gas-phase electron attachment reaction rates of compounds containing electronegative functionalities such as the halogenated and nitroaromatic hydrocarbons, both of environmental interest, can be extremely fast. On the other hand, the electron attachment rates of many hydrocarbons, which can constitute a majority of the sample, are slow. Therefore the ECD is blind to these substances (1). This provides the ECD with excellent sensitivity and selectivity for electron-attaching compounds in the presence of high levels of extraneous materials.

To more fully appreciate the sensitivity and selectivity provided by the ECD it is helpful to obtain a "feel" for the speed at which electron capture (EC) occurs.

This can be illustrated by examining the reaction rate coefficient for several exothermic two-body reactions given in the units that will be used in this report (reproduced from Detectors for Capillary Chromatography(2)).

Ion-molecule reactions, shown in reaction 1, have important applications in mass spectrometry, and exhibit approximately the same rate constant regardless of the ion or molecule involved. The rate of electron capture (EC), reaction 2, can be approximately two orders of magnitude faster than the rate of ion-molecule reactions. Since EC does not result from coulombic attraction, it is surprising that its reaction rate can be almost as fast as electron-positive ion recombination, shown in reaction 3.

The general utility of the ECD for a wide variety of analyses has been improved by doping the carrier gas with a number of different chemical dopants. It was found that by the intentional addition of oxygen (3,4) or nitrous oxide (5) to the carrier gas, the ECD could be made to respond to compounds which do not normally capture electrons. Compounds with low electron affinity such as anthracene (6) were made to respond with the assistance of ethyl chloride. Doping of the carrier gas has improved the sensitivity to some classes of compounds but it is not

yet known if it will help in analyzing complex samples (7).

The level of selectivity inherent in the ECD is sufficient in many cases to allow whole air samples to be analyzed with no sample clean-up (8-10). In fact, the ECD has been used extensively for the detection and quantification of chlorinated hydrocarbons (ClHC's) in the atmosphere (11). Because the sensitivity of the ECD to ClHC's is so high, and the wide use of ClHC's in the last several decades, there will typically be several peaks attributable to ClHC's in real environmental samples. The ECD's response to many brominated and iodinated hydrocarbons can be as strong as its response to ClHC's. Therefore the ECD can be used equally well as a probe for these compounds.

There is a need for a transducer capable of detecting trace amounts of brominated and iodinated compounds. There are a number of brominated compounds on the Environmental Protection Agency's list of priority pollutants (12). Examples of these amenable to electron capture are bromoform and dibromodichloromethane. Furthermore, the trace detection of iodinated compounds, in particular, methyl iodide is of considerable interest to the nuclear power industry because methyl iodide is the suspected organic carrier of the radioactive isotopes of iodide (13). Releases of radioiodides into the environment occur during enrichment of spent uranium fuels

in fuel reprocessing plants (14). Environmentally, radioiodides have been shown to deposit on foliage, which is ingested and concentrated by animals and excreted as iodine in their milk. Thus, fresh milk is the major source of ^{131}I intake for man. In fact, there is an excellent correlation between ^{131}I in milk and in human thyroids (15). The nuclide can also be taken up by ingestion through water and leafy vegetables, and possibly even absorbed through the skin. Releases of these nuclides from reprocessing plants are small (14) because of the ability to remove radioiodines by gaseous treatment systems such as silver zeolite or charcoal filtration or caustic scrubbing effective for iodine.

In many industrial settings, the extensive use of a wide variety of ClHC's has resulted in high and varied background levels of ClHC's. This can cause interference problems if one is interested in the less prevalent brominated or iodinated compounds. Often there are several ClHC's masking the ECD's response to the sought for iodinated and brominated compounds. In cases like this the ECD's inherent selectivity is insufficient to allow direct analysis for iodinated or brominated hydrocarbons. What is required is an additional element of response specificity. Recent research (7, 16-18) has provided a transducer with the required response specificity needed for the analysis of iodinated or brominated hydrocarbons

in the presence of chlorinated hydrocarbons. This specificity is provided by electron photodetachment.

Electron photodetachment from atomic and polyatomic anions has been used extensively in studying thermochemical and spectroscopic properties of negative ions and their photoproducts (19-23). The photodetachment (PD) process is a transition from a bound electron in an anion to a neutral plus a free electron (7). The PD process is shown in reaction 4.

Photodetachment from numerous atomic (24-29) and polyatomic (30-37) negative ions has been reported. Photodetachment has been used extensively for the measurement of gas phase electron affinities (38). The minimum energy required of a photon to induce PD is equal to the electron affinity of the neutral. Electron affinities rarely exceed 4eV. Therefore light in the visible and near-UV region is sufficient to induce PD. Photodetachment spectra can also provide information concerning the excited states of the negative ions and the neutral products. Photodetachment measurements of this kind were typically made by one of two approaches. For studies involving atomic anions (24,25) measurements were made utilizing shock tubes. Cesium halides were subjected to shock heating which caused them to ablate and dissociate. A light source was introduced into the tube and the absorption of the light measured.

The amount of light absorbed was proportional to the PD cross section of the halide anion. For polyatomic anions, the most typical approach involved the ion cyclotron resonance mass spectrometer and an associated light source.

Research (7,16-18) conducted at Montana State University has resulted in a new version of the ECD, the Photodetachment-Modulated Electron Capture Detector (PDM-ECD), in which light-induced photodetachment of electrons from negative ions produced within an ECD provides the needed additional element of response specificity. With this detector, the photodetachment (PD) of electrons is measured in addition to a normal ECD response. This results in the simultaneous generation of two responses: a normal ECD response due to dissociative EC, reaction 5, and a PD-modulated response due to reaction 4.

When an electron capturing compound enters the detector the electron population in the ECD decreases and there is a corresponding decrease in the measured current. This decrease in current is the basis upon which the ECD responds. That is, the change in current can be related to the amount of analyte present.

The measurement of the photodetachment-modulated (PDM) signal is accomplished in the following way. The ECD is modified so as to allow light in the uv-visible region to pass through the cavity of the ECD. This is accomplished

by installing quartz windows on opposite sides of the ECD. When a chopped light beam of the appropriate wavelength is passed through the detector, PD of the negative ion will occur to give the corresponding neutral and a free electron (7). Photodetachment of the anion results in a slightly increased electron density within the ECD. The small perturbation caused by PD can be amplified by passing the ECD signal through a lock-in amplifier which can then extract the modulated signal. The ECD is run in the pulsed mode of operation which has several advantages for PD experiments. The negative ions generated within the pulsed ECD are known to be long-lived (7) and will be concentrated by a positive ion space-charge field within specific regions of the ionization volume (39,40). Mock and Grimsrud (7) used this knowledge to contain the negative ions in a region where photon-negative ion interactions would be maximized.

Halogen-containing compounds generally undergo dissociative EC to give halide ions. It can be seen by examining Figure 1 that for atomic negative ions, such as the halides, the increase in cross section with photon energy is quite abrupt in the region of the electron affinity of the ion. The onsets of PD for Br^- , Cl^- , and I^- reflect the different electron affinity of each halide ion.

By proper selection of the wavelengths of light used, Mock and Grimsrud (7) demonstrated that the PDM-ECD could

Figure 1. Photodetachment cross sections of iodide, bromide, and chloride ions (reproduced from references 24 and 25). The relative emission intensity of the Hg arc lamp over this spectral range is shown as the dotted line.

be used to sensitively detect organic iodides and bromides in the presence of ClHC's. This was accomplished by the use of an intense source of monochromatic light which caused PD of I^- and Br^- , but not Cl^- . An application of this work to a complicated chromatographic analyses is shown in Figure 2. Within this figure are the two responses that are provided simultaneously when the ECD is run in the PDM mode. A normal ECD response is sent to pen one of a two pen chart recorder and the PDM-ECD response is sent to pen two. It is noted that only compounds that produce I^- and Br^- respond at the chosen wavelength, thereby greatly simplifying the chromatographic interpretation. The light source for the above study consisted of a 1,000-Watt Hg/Xe arc lamp and a high throughput monochromator. The detection limit for CH_3I using this instrument was demonstrated to be 70 parts per billion (ppb) in a gaseous mixture including ClHC's.

The PD instrument built by Mock was designed for general studies of PD. As was mentioned a high power arc lamp and monochromator were required in the above study. While impressive results were obtained, the extremely intense light source required for the above study constituted the most expensive and maintenance-intensive part of that instrument. In addition to this, the lamp and monochromator are also quite large and require signi-

Figure 2. Chromatographic analyses of a complex mixture of halogenated hydrocarbons with simultaneous detection by the PDM-ECD (reproduced from reference 7). Chromatogram A, normal ECD function, provides responses to all compounds present, while chromatogram B, PD-modulated response, provides responses only to the bromides and iodides. 365 nm light from a Hg/Xe arc lamp is used. The concentrations of the halocarbons, in the order shown in chromatogram A, are: 1.3, 2.0, 0.6, 25, 8.5, 10, 19, 2.4, 900, 3.3, and 15 ppb in nitrogen.

ficant lab space.

Additional studies of the electron capture and photodetachment chemistry of halogenated hydrocarbons are reported hereinafter. These studies are specifically tailored for the detection of organic iodides, especially methyl iodide, in the presence of ClHC's. To accomplish this task, the current study had the following objectives: 1) optimize PDM-ECD sensitivity to organic iodides, 2) optimize response specificity for organic iodides in the presence of ClHC's and 3) simplify instrumentation for application to routine field analysis.

This work has resulted in an instrumentally simpler version of the PDM-ECD without sacrificing response specificity and sensitivity. To do this, this instrument utilizes four gas phase processes to maximize its response to CH_3I and eliminate its response to ClHC's. These processes are: 1) EC by the original analyte molecules, 2) regeneration of an EC-active species (probably HI) through ion-ion recombination reaction of I^- with positive ions, 3) PD of I^- or hydrates of I^- , and 4) prevention of PD from Cl^- through clustering of Cl^- by water. In the instrument to be described, the 1,000-Watt arc lamp and the associated high throughput monochromator have been replaced by a simple 100-Watt arc lamp. No associated monochromator or light filter of any kind are used. One application of this instrument would be for the trace measurement of

methyl iodide above process streams and in ambient air in the presence of ClHC's. A detector which is capable of doing this is of interest to the nuclear power industry. This detector will also be shown to hold considerable promise for the selective detection of organic bromides in the presence of excess ClHC's.

THEORY

A thorough understanding of the physical processes occurring within the ECD is critical in understanding the response observed when an electron capturing compound enters the reaction volume. To adequately describe the reaction occurring in an ECD, the following parameters should be taken into account: the chemical reactions themselves, various negative ion loss modes, and the reaction constants for each of these processes. The following reactions are known to occur within the ECD.

Ionization of the carrier by beta radiation, reaction 6, produces positive ions and secondary electrons. The energy of these secondary electrons is reduced by collisions with the carrier gas. These collisions will occur until the secondary electron is in thermal equilibrium with the carrier gas. The report of Warman and Sauer (41), for example, indicates that the time required

for high energy electrons to be reduced to within 10% of thermal energy in argon/10% methane buffer gas at atmospheric pressure is 2.5 nanoseconds. This is a very short time relative to other ECD events.

The most common beta producer in use is nickel 63. This is because it has a high upper temperature limit of 400°C with no loss of activity and a long half life of 93 years. The original PDM study by Mock and Grimsrud (7) used ^{63}Ni as its beta electron producer. However, in this study beta electrons were produced by a titanium tritide ionizing foil (Safety Light Corporation, Bloomsberg, PA). The usual drawback of ^3H based ECD's is an upper temperature limit of 200°C. This is not a problem here, however, because relatively volatile compounds are studied.

Switching to tritium has several advantages when one is interested in detecting trace levels of methyl iodide. The ^3H foil has a high total activity, 0.80 curies, which provides greater sensitivity for CH_3I . The reasons for this will be discussed in detail later in the results and discussion section. Also, the penetrating power of the ^3H beta particle is less than that of ^{63}Ni . This allows the use of a smaller ECD with higher ion density. This, in turn, allows the use of a smaller arc lamp and still maintain a strong PDM-ECD response to organic iodides. In this study, a 100-Watt arc lamp replaced the 1,000-Watt arc lamp used by Mock and Grimsrud (7) with no loss of

sensitivity.

An experiment which demonstrates that the tendency for PD of iodides is not lost by switching to a 100-Watt arc lamp and the ^3H based detector is shown in Figure 3.

Figure 3. Repeated GC-ECD analysis of a halocarbon mixture by the ^3H -based detector under normal dark conditions (A) and with the full light intensity of the 100-Watt Hg arc lamp passing through the detector (B).

Examination of Figure 3 shows that a 100-Watt arc lamp has not sacrificed cross sectional light intensity. In chromatogram 3A, the arc lamp is off and in chromatogram 3B, it is on. It is noticed that the normal ECD response to CH_3I is approximately halved when the full emission of the arc lamp is passed through the ECD cavity. The

response to the chlorinated and brominated hydrocarbons are decreased by smaller amounts. Inspection of the PD spectra of the halides (24,25) and the emission spectrum of the Hg arc lamp, given in Figure 1, indicates that the overlap integral of the available light and each PD spectrum (7) is much greater for I^- than for Br^- and Cl^- , thereby accounting for the larger effects of light on the CH_3I response in Figure 3. These observations for the normal ECD response indicate (7) that the photon flux (photons $s^{-1} cm^{-2}$) through the detector is sufficient to enable reaction 4 to strongly influence the electron density within the cell. In the light mode, the lowered ECD response observed in Figure 4B occurs as a result of the electron that was captured being ejected from the anion prior to recording the EC event by the electrometer. The experiment just described demonstrates that the low power arc lamp causes a significant fraction of the I^- ions to undergo PD. Similar results were obtained by Mock (7) utilizing the 1,000 Watt arc lamp.

The reaction rate coefficient for beta production is determined by measuring the maximum standing current during very fast pulsing of the ECD (39). The rate coefficient, β , can then be calculated and was found to be 2.54×10^{11} e/sec. With the application of a positive voltage at the anode, electrons will be collected. A measure of the average electron density is continuously provided by the

fixed frequency, pulsed mode of ECD operation (42) in which all of the electrons are periodically collected at the anode. This provides the baseline current of the ECD.

Positive ion-electron recombination is shown in reaction 7. An estimate of this value, R_e , can be obtained from the measurement of the standing current as a function of pulse frequency (39). For this detector, a pulse width of 10 μ s and pulse period of 300 μ s at 35°C resulted in positive ion-electron recombination of 1030 sec^{-1} .

When gas chromatographic effluent containing an electron-capturing compound is introduced into an ECD, electrons will be captured, as is shown in reaction 8. All of the compounds used in this study undergo dissociative electron capture and produce either I^- , Br^- , or Cl^- . The first order rate constant, k_e , for this event is dependent on several factors such as the number and location of electronegative groups or atoms (43). For the molecule of primary interest in this study, CH_3I , additional reactions are known to occur which lead to enhanced response in the normal ECD. This was characterized by Knighton and Grimsrud (44) who were the first to notice the anomalous behavior of CH_3I at low detector temperatures. A description of their discussion is provided below.

For compounds that capture electrons extremely rapidly, a nonlinear calibration curve will result for small sample sizes. This is because the electron

attachment process destroys a significant fraction or even a majority of the molecules entering the cell (45). Methyl iodide attaches electrons extremely rapidly and a nonlinear response was expected. However at low detector temperatures two results were obtained that were inconsistent. First, the EC molar response of CH_3I (peak area/concentration) exceeded that of CFCl_3 and CCl_4 , even though both of these compounds capture electrons more rapidly than CH_3I . Second, even though its molar response exceeded the above compounds its molar response remained nearly constant over the entire range of the instrument. That is, a linear calibration curve was obtained.

An alternate mechanism was then advanced that took into account these superior response characteristics of CH_3I . The following reactions were proposed:

Reaction 12 is extremely fast (1.2×10^{-7}) (46) and results in the destruction of most of the CH_3I molecules. The negative ion produced, I^- , will be destroyed by ion-ion recombination, reaction 13 (44). The product of ion-ion recombination is thought to be HI. This is reasonable because the positive ion, p^+ , is expected to be proton rich (47). The anion can then be regenerated by reaction 14. The product of this reaction, I^- , can then recombine with

positive ions and recycle. It has been estimated that, with a typical ^{63}Ni cell volume and flow rate, up to eight cycles of electron attachment recombination for a single CH_3I are possible (44). This reaction mechanism accounts for the anomalous observations. To summarize, at low detector temperatures the response of CH_3I is hypercoulometric, more than one electron per CH_3I is consumed, explaining the large EC molar response. Also, through regeneration of HI by ion-ion recombination a linear calibration curve is obtained.

One might also expect that recombination reactions involving Cl^- and Br^- would form HCl and HBr and capture electrons. However, HCl and HBr will not undergo fast electron capture. The EC rate constants of the hydrogen halides at 30°C are (46): HI, 3×10^{-7} ; HBr, $< 3 \times 10^{-12}$; and HCl, too slow to be observed.

Recombination with positive ions, reaction 9, is important because it is thought to compete with PD, reaction 10, for the available negative ions. If recombination occurs, neutrals are formed and loss of an electron will be recorded by the electrometer. If, however, X^- is destroyed by reaction 10, an electron is regenerated and the electron capture event is not recorded.

The pseudo-first order rate coefficient, R_x , cannot be measured directly by an ECD. However, a reasonable estimate of this value can be obtained. This estimate is

based on the measurement of reaction 7. It was found that at atmospheric pressure, ionization in a ^{63}Ni source leads to an increase in total positive ions whenever a high concentration of electron capturing compound is introduced (4,42). This observed increase in positive ions has consistently been between 50 and 100%. This effect was found to be independent of the electron capturing compound used. In the absence of an imposed electrostatic field the density of positive ions is thought to be solely determined by recombination reactions. These observations should give an indication of the relative magnitudes of reactions 7 and 9.

It was found that the total positive ion density is inversely proportional to the square root of the recombination coefficients involved (42,47). At atmospheric pressure, ion-ion recombination coefficients tend to a constant value of about 1×10^{-6} (48). If the positive ions are cluster ions, positive ion-electron recombination coefficients can exceed this value. The electron recombination coefficients of the cluster ions $\text{H}^+(\text{H}_2\text{O})_2$ and $\text{H}^+(\text{H}_2\text{O})_3$ are 2×10^{-6} and 4×10^{-6} (49,50). These are the proton hydrates typically observed at atmospheric pressures and relatively dry carrier gas. This led Mock and Grimsrud (7) to make the following estimate: reaction 10 was expected to be one-half to one-fourth as large as reaction 7. Therefore a reasonable estimate of the rate

coefficient of reaction nine would be $340 \pm 100 \text{ s}^{-1}$. To summarize, when a small amount of MX is introduced into an ECD, an electron will be captured and will produce a small amount of X^- . This anion will then recombine with positive ions at a rate approximately 1/3 that of reaction 7.

The rate coefficient for PD, reaction 10, will be given by $k_{\text{hv}} = \sigma\Phi$, where σ is the PD cross section and Φ is the light flux. It has been estimated (7) that for a negative ion such as I^- , (with a PD cross section of $2 \times 10^{-17} \text{ cm}^2$) and on irradiation of 1.0 Watt cm^{-2} of 380 nm light (equal to $2 \times 10^{18} \text{ photons cm}^{-2} \text{ s}^{-1}$), that $k_{\text{hv}} = 40 \text{ s}^{-1}$. This was shown to effectively compete with recombination (7). It was shown in Figure 4 that a 100-Watt arc lamp could cause PD of a major portion of the negative ions. Since similar results were obtained (7) using a 1,000-Watt arc lamp the switch to a 100-Watt arc lamp has not sacrificed PD response. A 100-Watt arc lamp does indeed compete effectively with recombination when used in conjunction with a small volume high ion density ECD.

Gas phase hydration is represented in reaction 11. In relation to selective photodetachment, gas phase hydration plays an integral part. The clustering of water with the halide ions was first reported in 1970 and hydration thermochemical data were reported (51). Equilibria involving halide ion-solvent clustering can be

measured in the gas phase in the following way. First, halide anions were typically generated by dissociative electron capture of NF_3 , CH_3I , CH_2Br_2 , and CCl_4 . Measurements were obtained by mass spectrometric sampling of the ions $\text{X}^-(\text{H}_2\text{O})_n$ appearing from an ion source containing water vapor. It was found that the halides were preferentially solvated in the following order: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. This can be understood by simple electrostatic considerations. Increased ionic radius leads to a successively weaker interaction with water. It was estimated that under their conditions the time required for clustering to reach equilibrium was achieved in less than 100 μsec (51). This was based on the measured rate constants for the hydration of the proton and the assumption that the rate constants for the halides were of a similar order of magnitude.

EXPERIMENTAL

A schematic diagram of the PDM-ECD used in this study is shown in Figure 4. The ionization chamber is cylindrical and contains a titanium tritide ionizing foil of 0.80 curies activity. The foil forms the cylindrical wall of the ECD which has a diameter of 6mm and a length of 15mm, with a total volume of 0.424 cm³. Quartz windows form the ends of the active volume and allow the passage of light through the cell. A stainless-steel pin of 1/16

Figure 4. Schematic diagram of the photodetachment-modulated electron capture detector used.

inch diameter serves as the anode of the ECD. It enters from one side, as illustrated by Figure 4, through a Teflon plug and protrudes about 1/16 inch into the active volume. The ECD can be heated by two 25-Watt cartridge heaters with thermocouple-feedback control. To prevent accidental overheating, a maximum ECD temperature of 75°C is ensured by a direct-contact thermal switch placed in series with the cartridge heaters.

Samples are introduced into the ECD by gas chromatography using a 10-ft x 1/8-in stainless steel column packed with 10% SF-96 on Chromosorb W. The carrier gas used was Argon/10% methane, which was typically first passed through water and oxygen-removing traps (purchased from Alltech). The flow rate was 60 ml/min. The water trap contains anhydrous CaSO₄ and size 5A molecular sieve. To prevent oxygen from entering the detector, a positive pressure of about 150 Torr above atmospheric was maintained by placement of a flow restrictor at the detector outlet. A 1.0-cm³ gas sampling loop (Carle Model 8030) was used to inject gaseous samples onto the column.

The optical components consisted of a 100-Watt Hg arc lamp (Photon Technology International, Model A1010) and a mechanical light beam chopper. The arc lamp has an elliptical reflector of F/4.5 which focuses its light on a spot of 3 mm diameter, 11 inches from the face of the lamp. A Hg lamp was chosen because of its concentration

of spectral irradiance in the ultraviolet region. Its emission spectrum over the range of 240 to 440 nm is shown in Figure 1. The frequency of the light chopper was set at 83 Hz.

The signal processing components consisted of an ECD pulser and electrometer (homebuilt), a lock-in amplifier, and a two pen recorder. The homebuilt ECD pulser and electrometer provide the normal ECD response to a sample at pen 1 of the strip chart recorder. The electrometer and pulser were designed by Grimsrud and Knighton (52). Minor modifications were necessary in the gain of the circuit in order to make it more fully compatible with the lock-in amplifier. The circuit is shown in Figure 5. The frequency of the ECD pulser was typically set to 3.0 kHz where an ECD standing current of 35 nA was observed.

A lock-in amplifier (Stanford Research Systems, model SR510) extracts the light beam-modulated component of the ECD signal at the 83 Hz chopping frequency and provides this signal to pen 2 of the recorder. The lock-in can accomplish this by using two signals, a reference signal and a modulated signal. Modulation is accomplished by chopping the light at a frequency which is typically removed from sources of environmental noise (i.e. 60 Hz). The chopping frequency provides the lock-in with a reference frequency. This allows the signal to be amplified in a region relatively free of noise. By

Figure 5. Circuit diagram for the pulser and electrometer used in this study.

synchronous demodulation the lock-in can then discriminate between signal and noise by optimal choice of chopping frequency and phase angle offset. That is, only signals that have both the correct frequency and phase, when compared to the reference, will be detected. (53,54).

The halocarbons used in this study were obtained in pure form from commercial suppliers. Mixtures of these in nitrogen gas were made by successive dilution into gas-tight glass vessels with final storage in a 4.5-L glass carboy. This carboy was pressurized 4-6 psi above ambient with nitrogen gas. This allowed numerous aliquots to be transferred by a 50-ml syringe to the 1ml sampling loop (Carle sample valve model) of the GC.

In some of the experiments, water was intentionally added to the carrier gas by passing a second supply of 10% methane-in-argon through a glass bubbler containing liquid water at 23°C. This gas stream was then assumed to contain 21 Torr water. The addition of small flow rates (< 10 atm-cc/min) of this humidified stream to the main carrier gas stream (60 atm-cc/min) just prior to the detector created water vapor partial pressures of up to 3 Torr in the detector gas.

RESULTS AND DISCUSSION

The following account of how ECD responses have been biased in this study for organic iodides and against organic chlorides is conveniently broken into two main divisions. One deals with gas phase electron-molecule and ion-ion interactions (EC and post-EC reactions) and the other with the photodetachment chemistry of the halides and their hydrates.

Electron Capture and Post-Electron Capture Reactions

Characterization and Optimization of ³H Based ECD Towards CH₃I

As was mentioned, CH₃I undergoes additional reactions which were taken into account in the construction of the detector used in this study. The traditional ⁶³Ni beta producer was replaced by tritium which provides an order of magnitude greater beta radiation intensity and a higher steady-state electron density within the ECD. With this high electron density recycling was hoped to be enhanced relative to ⁶³Ni ECD's.

The initial aspect of this study involved characterizing the tritium ECD and determining optimum

operating conditions for CH_3I detection. This was accomplished by evaluating the effect of ECD temperature and pulsing parameters have, if any, on augmenting CH_3I recycling.

Effect of ECD Temperature on
 CH_3I Response

Knighton and Grimsrud (44) have demonstrated that decreasing the ECD temperature from 275° to 75°C led to increased CH_3I response due to recycling. In fact at 75°C the molar response of CH_3I exceeded the molar response of CFCl_3 (43). In the above study, 75°C was the lowest temperature evaluated. The effect of decreasing ECD temperature from 70°C to 35°C on the molar response of CH_3I in a ^3H based ECD is summarized in Table 1. Carbon tetrachloride which is known to capture electrons extremely rapidly and is inert to further recycling, is included for comparative purposes.

Table 1. ^3H ECD's molar response for CCl_4 and CH_3I as a function of ECD temperature.

Compound	35°C	50°C	70°C
CCl_4	14.6	9.8	7.1
CH_3I	37.5	20.1	14.6

It is seen that the molar response for CH_3I at 70°C is approximately 2 times greater than that of CCl_4 . By

decreasing the temperature to 35°C the molar response has increased to approximately 2 1/2 times greater than that of CCl₄. Decreasing the ECD temperature does indeed benefit recycling of CH₃I. Therefore, for optimum CH₃I sensitivity, the ECD should be operated at the lowest possible temperature. Also, the molar response of CCl₄ was increased at lower detector temperatures. When CCl₄ undergoes EC CCl₃ is formed. It was found (17) that at low detector temperatures CCl₃ captures electrons extremely rapidly. At higher ECD temperatures this same species was thought to be destroyed on the walls of the ECD (17). Thus decreasing detector temperature accentuates the response of CCl₄. For the study conducted here, 35°C was the lowest stable ECD temperature achievable when the ECD was operated in the PD-modulated mode. This is because the arc lamp itself would heat the ECD to approximately 33°C. Therefore to maintain the ECD at a constant temperature it was necessary to set the ECD, at 35°C.

Effect of Pulsing Parameters on CH₃I Response

Electron capture detector pulse width and pulse period were evaluated and the optimum values were found to be a 10 μs and 300 μs respectively. These conditions were found by systematic variation of the pulsing parameters and

evaluating the resulting signal-to-noise ratio. It is interesting to note that at the optimum pulsing parameters, up to 80 recyclings of EC active species of iodide is possible. This conclusion was based on the following estimates. At the pulsing parameters mentioned above, the electron loss rate was calculated to be 1030 s^{-1} . If one then assumes that the ion-ion recombination rate is $1/3$ of 1030 (as was put forward in theory) or 343 s^{-1} , the ion density within the cell would be given by $343 \text{ s}^{-1} / 1 \times 10^{-6} \text{ cc/s}$ or $3.4 \times 10^8 \text{ ions/cc}$. If one then assumes that k_1 and k_2 for the electron attachment of CH_3I and HI are fast and equal, $k_1 = k_2 = 2 \times 10^{-7} \text{ cc/s}$, then the pseudo first-order constants will be given by $2 \times 10^{-7} \text{ cc/s} \times 3.4 \times 10^8 \text{ ions/cc}$ or 68 s^{-1} . The half-life of CH_3I and HI , against electron capture, will then be about 10 ms . With a flow of 0.5 cc/s and a ECD volume of 0.42 cc the residence time within the ECD is about 0.84 s . Therefore, up to 84 cycles of electron attachment could conceivably occur within the ^3H based ECD. This is a factor of ten larger than what was estimated for a typical ^{63}Ni ECD. This is believable because the electron production in a ^3H -based ECD is $2.54 \times 10^{11} \text{ e/sec}$, a factor of ten larger than for a ^{63}Ni ECD. The recycling of CH_3I is also calculated to be enhanced by a factor of ten.

Comparative ECD Study

After optimizing the ECD's response for CH_3I , a comparative study was made between two commercial ^{63}Ni -based GC-ECD instruments and our home-built ^3H -based instrument. A five-component mixture of halocarbons was analyzed and the results are shown in Figures 6A-C. In comparing these chromatograms, it is clear that the ^3H -based ECD in Figure 6C provides a significant enhancement in the relative response to the one organic iodide, CH_3I , included in the mixture. Also, the relative response to CHCl_3 is increased in Figure 6C. These changes in the relative responses are explained in the following five paragraphs.

As was mentioned, all of the compounds shown in Figure 6 are known to attach electrons by the dissociative EC mechanism (7) in which a halide ion, X^- , is formed as shown in reaction 4. For CF_2Br_2 , Br_2^- is also formed with about 0.2 abundance relative to the major product, Br^- (55). The rate constants for the attachment of thermal electrons by the five compounds at 30°C are: CF_2Br_2 : 2.7×10^{-7} (56), CH_3I : 1.2×10^{-7} (46), CHCl_3 : 3.2×10^{-9} (57), CCl_4 : 3.8×10^{-7} (57,58), and CH_2Br_2 : 9.3×10^{-8} (46). It can be seen that four of the five compounds have very large EC rate coefficients, in the $1 - 4 \times 10^{-7}$ range, which is near the collision limit for EC processes. Only CHCl_3 attaches electrons at a significantly lower rate and this

Figure 6. Comparative GC-ECD study of two commercial, ^{63}Ni -based detectors (A and B) and the homebuilt, ^3H -based detector (C). The sample contained approximately 2 ppb CF_2Br_2 , 1 ppb CH_3I , 300 ppb CHCl_3 , 5 ppb CCl_4 , and 100 ppb CH_2Br_2 . For all three instruments, the detector temperature was 35°C and the carrier gas was argon/10% methane.

fact, along with the differing physical designs of the three ECD's used in Figure 6, accounts for increased responses to CHCl_3 in Figures 6B and 6C relative to 6A.

Varian ECD

The Varian ECD used in Figure 6A has a relatively small ^{63}Ni reaction volume (2,59) through which the analyte molecules pass relatively quickly. This explains why the relative responses observed in Figure 6A are determined largely by the relative EC rate coefficients of each molecule, along with the amount of each chemical present in the sample. Therefore, the response to CHCl_3 is low in Figure 6A, even though its concentration is relatively high.

Hewlett-Packard

The Hewlett-Packard ^{63}Ni ECD used in Figure 6B has a significantly larger internal volume than that used in 6A. In this device, the number of EC events by CHCl_3 is increased roughly in proportion to the increased residence time the molecule experiences in passing through this larger detector.

Homebuilt ^3H ECD

The home-built instrument, used in Figure 6C, was a ^3H -

based ECD, having a much higher beta flux than either of the instruments used in Figures 6A or 6B. This increased electron density causes a proportionally larger number of EC events for CHCl_3 . The responses to CF_2Br_2 , CCl_4 , and CH_2Br_2 are not increased as strongly by the increased residence time of the larger detector in Figure 6B or by the increased electron density in Figure 6C. This is entirely due to their extremely large EC rate coefficients which cause a major portion of these molecules to be consumed by the EC process itself. Thus, for molecules with very large EC rate coefficients, the maximum magnitude of response is limited by the total number of molecules introduced to the detectors, rather than by their EC rate constants. An example that further illustrates this point is carbon tetrachloride, which is known to undergo sequential reactions 15 and 16 rapidly (17,59).

The rate of reaction 16 at 30°C is 2.4×10^{-7} (60). The further reaction of CCl_2 with electrons is endothermic and does not occur (60). Under conditions present in Figures 3B and 3C, most of the EC-active species, CCl_4 and CCl_3 are consumed by the above reactions and no EC-active species remain in the cell.

The increased response to CH_3I in Figure 6C is of central interest here. As has already been indicated, CH_3I

is one of the four compounds which attach electrons very rapidly and, therefore, the basis of its increased response in Figures 6B and 6C cannot be the same as described for the slow-reacting CHCl_3 . It was pointed out in the theory section that CH_3I is capable of generating a recyclable EC-active species by ion-ion recombination. This was thought to be HI. The molecules HBr and HCl could not undergo a similar recycling process. Therefore, it is thought that as CH_3I is consumed in an ECD, this loss is at least partially compensated for by the production of the EC-active molecule, HI, whose presence is continuously maintained by reaction 14. Therefore, in the large volume or high electron-density ECD, where the role of post-EC processes are accentuated, responses to iodinated hydrocarbons will be increased relative to those strongly responding chlorinated or brominated hydrocarbons present.

Photodetachment Chemistry of the Halides and their Hydrates

Optimization of the ^3H -based PDM-ECD Response

The initial phase of the photodetachment portion of this study involved characterizing and optimizing the tritium PDM-ECD response to the halogenated hydrocarbons used in this study. In Figure 7 a typical chromatographic

Figure 7. Typical PDM-ECD chromatogram provided after optimization. Chromatogram A is provided by the normal ECD function of the PDM-ECD at 35°C detector temperature. Chromatogram B is the PDM-ECD response simultaneously obtained using very dry carrier gas. The sample contained approximately 1.4 ppb CF_2Br_2 , 0.70 ppb CH_3I , 210 ppb CHCl_3 , 3.5 ppb CCl_4 , and 70 ppb CH_2Br_2 .

analyses is shown which was obtained using the PDM mode of the ECD. In this mode, two responses are simultaneously obtained; Figure 7A is the normal ECD response and Figure 7B is the PD-modulated ECD response using dry carrier gas. Under this condition, strong PDM-modulated responses are observed for all five of the halocarbons in the mixture. As expected (24,25), the ratios of the PD-modulated responses shown are greatest for the compound that produces I^- upon EC, less for those which generate Br^- , and smallest for those which generate Cl^- . This trend is again consistent with the overlap integral of the PD spectra and the Hg lamp emission shown in Figure 1. Responses like the one shown in Figure 7 are possible by optimizing the following operating parameters: phase angle offset, ECD pulsing parameters, electrometer electronics, and chopping frequency. Each of these parameters are important in obtaining the maximum response possible. The experimental operating conditions found to be necessary for each of the parameters will be discussed briefly in the following four paragraphs.

Phase Angle

The lock-in technique requires the frequency of the modulated signal to be removed from environmental noise. The lock-in mixes the reference and experimental signals and detects the response from the experiment by frequency

and phase causing full-wave rectification at the phase-sensitive detector output. The phase sensitive output is then applied to a low-pass filter which averages the waveform and gives a dc output proportional to mean signal amplitude. The key in obtaining optimum signal is that the experimental signal must be offset in phase, as determined experimentally, with respect to the reference signal. A sensitive way of placing the reference and experimental signal in the appropriate phase lag, and the method used in this study, is first nulling the PDM signal and then shifting the reference oscillator 90° . This operation puts the reference and experimental signal exactly in the phase angle needed for maximum signal.

ECD Pulsing Parameters and Photodetachment

No discernable change was noted in the modulated signal when pulsing parameters were varied using dry carrier gas. The optimum pulsing parameters for the normal ECD signal also resulted in optimum PDM-ECD signal.

Electrometer Electronics

When the initial PDM-ECD experiments were carried out using the optimum pulsing parameters determined for CH_3I , there was a resulting signal overload on the lock-in. The maximum signal input for the Stanford Research lock-in used

is 1 V. The ac component of the ECD signal entering the lock-in was evaluated and found to be slightly over 1 V, resulting in the observed signal overload. By adjusting the electronics within the electrometer, S/N was improved as shown in Table 2 (the circuit is shown in Figure 5).

Table 2. Photodetachment modulated S/N at various chopping frequencies before and after adjusting electrometer electronics.

Frequency Hz	S/N Before	S/N After
13	21.8	32.0
23	24.6	34.2
83	27.6	38.5
93	25.6	37.9

This was done by decreasing the gain of the electrometer by a factor of ten. The lock-in could then be operated without signal overload. Also, a higher lock-in sensitivity setting could be used. When the lock-in was operated in a high sensitivity mode, there was the expected increase in baseline noise. However, by placing a 47pf capacitor in parallel with the feedback resistor, baseline noise was smoothed.

Chopping Frequency

It was found in the study done by Mock and Grimsrud (7) that the magnitude of the modulated response was dependent

upon the chopping frequency. The effect chopping frequency has on modulated signal for the ^3H ECD was also evaluated. The results shown in Table 2 indicate the most favorable PD-modulated signal-to-noise was found to be 83 Hz. This is in contrast to that found for the ^{63}Ni PDM-ECD (7), optimum sensitivity was achieved with chopping frequencies of 13-20 Hz. Apparently, the high ion density provided by the ^3H foil allows the chemistry to occur at a faster rate. This allows chopping at faster frequencies, which results in the slightly more favorable PD-modulated S/N ratio.

Hg Line Interference Filter

To enhance the selectivity of the PDM-ECD, Grimsrud and Mock used an intense light source and monochromator (6) to select the appropriate wavelength needed for PD of a given anion. The problem with this approach, besides being expensive, labor intensive and bulky, is that by using a monochromator there is significant loss of light available for PD. This loss of light intensity is due to the aperture limitation in the monochromator and the need to focus onto a small slit. Since light intensity is directly related to modulated signal (7), response sensitivity was lost. However, by switching to a filter, the arc lamp may be focused directly on the ECD. Increases in percent transmittance of light to the ECD should occur which in

turn should result in a better signal-to-noise ratio. In addition to this, since only a few wavelengths are of interest, filters are a much more economical means of light isolation when compared to a monochromator.

The filter chosen was the Oriel Mercury Line Interference Filter. A mercury arc lamp has a spike of spectral irradiance at 365 nm (shown in Figure 1). Matching this peak with a bandpass filter of the same wavelength should result in favorable PDM-modulated signal-to-noise. This was done and the result can be seen in Figure 8. Specificity was achieved, as the only response observed was for CH_3I . However, the PD-modulated signal for CH_3I was reduced 94% when compared to the CH_3I PD-modulated signal measured the same day but with the Hg interference filter removed. This was an unacceptable loss of sensitivity. The reason for this loss can be seen by examining Figure 9. Although the filter used was specifically designed for mercury arc lines with high throughput there is only 22.2% transmittance for the filter used. This greatly reduces the overlap integral of the arc lamp emission and the I^- PD cross section. Ideally there should be strong and selective PDM-ECD responses to organic iodides in the presence of ClHC's using only a 100-Watt arc lamp and no associated light filters. By allowing full light intensity, overlap integral would be maximized resulting in maximum PD signal. However, with

Figure 8. PDM-ECD chromatogram obtained using a mercury line interference filter. Chromatogram A is the normal ECD function of the PDM-ECD and chromatogram B is the PD-modulated ECD response. The sample contained approximately 2 ppb CF_2Br_2 , 1.0 ppb CH_3I , 210 ppb CHCl_3 , 5 ppb CCl_4 , and 100 ppb CH_2Br_2 .

Figure 9. Transmission curve provided by Oriel 365 nm narrow band mercury line interference filter.

full light intensity one should expect responses to all compounds present including ClHC's. What was needed was a method that allowed full light of the entire spectrum to be used while eliminating the response to ClHC's.

Photodetachment of Hydrates

In Figure 10 a series of repeated chromatographic analyses are shown which were obtained using the PDM mode of the ECD. For all of the analyses shown in Figure 10, the normal ECD response, shown in Figure 10A, was essentially identical and, therefore, this response is shown only once. The PD-modulated response using dry carrier gas is shown in Figure 10B. Under these conditions, strong PDM-modulated responses are observed for all of the compounds. The relative amount of PD response is again consistent with the overlap integrals of the PD spectra and the Hg arc lamp emission. An important and advantageous change in the PD-modulated response to this same sample has been caused in Figure 10C simply by removing the CaSO_4 water trap from the carrier gas supply line. It can be seen in this figure that the PD-modulated response to the chloride producing compounds, CHCl_3 and CCl_4 , have almost disappeared. At the same time, the response to bromine producing compounds, CF_2Br_2 and CH_2Br_2 , have not disappeared and remain about 65% as strong as in 10B. Most importantly, the response to the CH_3I has been

Figure 10. Chromatogram A is that provided by the normal ECD function of the PDM-ECD for the halocarbon mixture described in Figure 6 at 35°C detector temperature. Chromatogram B is the PDM-ECD obtained with use of very dry carrier gas. Chromatogram C is the PDM-ECD response obtained after removal of the water-removing trap in the carrier gas supply line. Chromatogram D and E are the PDM-ECD responses obtained with about 1 and 3 Torr water vapor, respectively, present in the detector gas.

essentially unaffected by the removal of the water trap. Since the normal ECD response obtained simultaneously with chromatogram 10C was nearly identical to that shown in Figure 10A, the EC reactions of CH_3Cl and CCl_4 were not affected by the removal of the water trap. Therefore, it appears that the PD of Cl^- has been prevented in Figure 10C by the presence of a small amount of water.

The changes in the PD-modulated response are thought to be due to clustering of the halide ions by water as shown in reaction 17. To confirm that this was occurring,

atmospheric pressure ionization mass spectrometric (APIMS) measurements were taken. The results are shown in Figure 11A. The same carrier gas was used for Figure 10 and 11. The temperature of the source was also identical to the ECD temperature, 35°C . The APIMS measurements indicate that Cl^- is indeed clustered by water under these conditions to the extent that $\text{Cl}^-(\text{H}_2\text{O})_2$ appears to be the dominant ion. Due to uncertainties associated with apparatus sampling in APIMS (61), the measurements shown in Figure 11A should be considered to provide rough estimates of the actual ion abundances in the ion source. Under these same conditions, it is seen in Figure 11A that Br^- , and I^- are less heavily clustered by water, and that most of the I^- is not clustered at all. The APIMS measurements in Figure 11A were then repeated at an ion source temperature of

Figure 11. Measurements of relative intensities of halide ion water clusters by APIMS in argon-methane buffer gas without use of a water removing trap at 35° (A) and 100°C (B).

100°C and these results are shown in Figure 11B. As expected, the equilibrium position of reaction 14 is shifted to the left by increased temperature so that at 100°C the unsolvated halide ions are the prominent ions in all three cases.

In Figure 12 the effect of increasing the ECD temperature on the PD-modulated response shown previously in Figure 10C is shown. It can be seen that increasing the temperature tends to restore the PD-modulated ECD response to CHCl_3 and CCl_4 , which had been lost at 35°C. Thus, the effects of temperature demonstrate in Figures 11 and 12 that water clustering of the halides is responsible for the observed changes in the PD-modulated response noted in Figure 10.

The equilibrium water clustering reactions of Cl^- , Br^- , and I^- have been previously characterized by Arshadi, Yamdagni, and Kebarle (62) and by Hiraoka, Mizuse and Yamabe (63). The measurements of Hiraoka *et. al.* included relatively large cluster ions of $n = 7$ for Cl^- and Br^- , to $n = 5$ for I^- .

From these measurements the relative abundances of the clustered halide ions at a temperature of 35°C and as a function of the partial pressure of water were calculated (see appendix) and plotted in Figure 13.

Again, it is clearly seen in these predictions that the tendency for water clustering increases in the order I^- , Br^- , and Cl^- . If the APIMS measurements in Figure 11

Figure 12. Chromatogram A is the normal ECD response of the PDM-ECD to the halocarbon mixture described in Figure 6 at 35°C detector temperature without use of a water-removing trap in the carrier gas supply. Chromatograms B, C, and D are the PDM-ECD responses simultaneously obtained at 35°, 50°, and 70°C, respectively.

Figure 13. Predictions of relative abundances of the halide ions water clusters as a function of the partial pressure of water at 35°C. Predictions are based on thermochemical determinations reported in reference 63.

provide a valid approximation of the relative cluster abundances at 35°, a comparison of these with the predictions in Figure 13 suggest that the partial pressure of water in the carrier gas supply (without the water trap) is somewhat less than 0.1 Torr. In Figure 10D, about 1 Torr water vapor has been intentionally added to the carrier gas supply. Again, the PD-modulated response to CH₃I remains strong (about 90% of that in 10B), while the responses to the two chlorinated hydrocarbons have been completely eliminated. From the predictions shown in Figure 13, it is seen that Cl⁻ should be highly clustered in 1 Torr water at 35°C, with n = 2, 3, and 4 species dominant. While the PD spectra of the halide hydrates are not known, these results suggest that this degree of clustering has shifted the onset of PD for the chloride ion to wavelengths shorter than 269 nm where there is very little light provided by the Hg arc lamp.

Hiraoka et. al. (63) report enthalpies of 14.7, 13.0, and 11.8 Kcal/mol for the addition of the first, second, and third water molecule to Cl⁻ in reaction 14. If one assumes that the PD for the hydrated chloride species are blue-shifted by magnitudes equal to these enthalpy values, the onset of PD for the n = 0, 1, 2, and 3 clusters of Cl⁻ would be about 345 nm, 295 nm, and 235 nm, respectively. This is represented graphically in Figure 14 where the estimated PD cross-section for the hydrates is shown.

Figure 14. Photodetachment cross sections of iodide and chloride ions (reproduced from references 19 and 20). Estimated PD onsets and cross sections for the $n = 1$ to 2 hydrates of chloride are shown as dashed lines. The relative emission intensity of Hg arc lamp is shown as the dotted line.

From these estimates it is seen that the $n = 2, 3$, and 4 cluster would not undergo PD by the available light in the detector and this appears to provide a reasonable explanation for the lack of PDM-ECD responses to the chlorinated hydrocarbons in Figure 10C. It also explains why there was no bromide signal observed in the mercury interference filter experiment.

A quantitative assessment of the brominated and iodinated hydrocarbons in Figure 10D is more difficult. The onsets of PD for the Br^- and I^- hydrates are likely to occur at wavelengths longer than 260 nm and, therefore, detailed knowledge of the PD spectra of these hydrates is required. Hiraoka *et.al.* (63) report enthalpies of hydration of 11.7, 11.6, and 11.4 Kcal/mol for the addition of the first, second, and third water molecule to Br^- and 10.3, 9.5, and 9.2 Kcal/mol for the water addition to I^- . If the onsets of PD are again assumed to be shifted by amounts equal to these enthalpy values, the PD onsets for the $n = 0$ to 4 hydrates of Br^- would be about 370 nm, 320 nm, 285 nm, and 255 nm, respectively. Correspondingly, the onset of PD for the $n = 0$ to 4 hydrates of I^- would be about 405 nm, 353 nm, 316 nm, and 287 nm, respectively. Inspection of Figure 13 indicates that with 1 Torr water vapor at 35°C, the $n = 2$ and 3 cluster for Br^- and the $n = 1$ and 2 clusters for I^- should be prominent. In view of these predictions, the persistence of a strong PDM-ECD

response to CH_3I in Figure 10D might be rationalized through PD of the $n = 1$ and 2 clusters of I^- by the abundant light available with wavelengths shorter than 320 nm. The persistence of relatively strong PDM-ECD response to the two bromides in Figure 10D might be attributed to PD of the $\text{Br}^-(\text{H}_2\text{O})_2$ ion by light of wavelengths shorter than 285 nm. This suggests that the PD cross sections of $\text{Br}^-(\text{H}_2\text{O})_2$ are quite large in this spectral region.

In Figure 10E the PD-modulated response to the same five-component mixture has been measured with about 3 Torr water vapor in the detector gas. Under these conditions, only a small fraction of the bromide species will have $n = 2$ while most will be clustered by three or more water molecules. Since the onset of PD for bromide species with $n = 3$ or greater will be below 220 nm, the residual response to the bromides in Figure 10E might be attributable to the small amount of $\text{Br}^-(\text{H}_2\text{O})_2$ ion remaining under these conditions. It is noted that there is a strong modulated PD-Modulated response to CH_3I in Figure 10E. In the presence of 3 Torr water vapor, the dominant cluster ion of I^- should be the $n = 2$ species with significant amounts of the $n = 1$ and 3 species also present. The fact that the response to CH_3I in Figure 10E is about 60% as great as that with no water present in Figure 10B indicated that the PD cross section of at least the $n = 2$ iodide water clusters is quite large in the

spectral region below 320 nm where an abundance of light is available.

Inverted Modulated Response

Surprisingly, an inverse PD-modulated response to CCl_4 is observed in Figure 10E. The fact that this response to CCl_4 is inverted relative to those which are known to be due to PD indicates that there is a decrease in electron density in the ECD when the light is on. This is the opposite effect of the increase in electron density due to PD. In characterizing inverted peaks further there have been a number of interesting discoveries and the causes of inverted peaks continue to be an active area of research.

We presently believe that the inverted PD responses are caused by an impurity introduced with water. If this contaminant in the buffer gas captures an electron to form a negative ion which undergoes PD, inverted peaks can then be explained as follows. The negative ion formed would be continuously undergoing PD providing an artificially high and constant PD baseline response at pen two of the chart recorder. When an electron capturing compound is introduced, such as CCl_4 , it will compete with the contaminant for electrons. This will decrease the amount of contaminant negative ions when CCl_4 passes through the detector and an inverted PD response will be obtained.

Complex Air Analysis

A demonstration of the use of this detector for the analysis of a mixture of iodinated and chlorinated hydrocarbons in a air sample is shown in Figure 15. The PDM-ECD simultaneously provides the normal ECD response to the sample shown in Figure 15A and the PD-modulated response shown in Figure 15B. While the responses to all of the halogenated hydrocarbons are provided by the normal ECD response in 15A, responses to only the two iodinated compounds are provided by the PD-modulated response in Figure 15B. It is significant to note that ethyl iodide emerges from the GC along with a hundred-fold excess of chloroform. Nevertheless, the response to ethyl iodide in 15B is unaffected by the simultaneous presence of chloroform in the detector and, therefore, provides an unambiguous means of determining the concentration of ethyl iodide in this sample. With the apparatus described here, the detection limits of the PDM-ECD for CH_3I in air is about 0.01 ppb. This is a slight improvement in the detection limits achieved by Mock and Grimsrud (7). Anticipated improvements in the electronic components of this detector should lead to additional reductions in detection limits.

Figure 15. PDM-ECD chromatographic analyses of an air sample containing approximately 4 ppb CFCl_3 , 1 ppb CH_3I , 100 ppb $\text{C}_2\text{F}_3\text{Cl}_3$, 3 ppb $\text{C}_2\text{H}_5\text{I}$, 700 ppb CHCl_3 , 300 ppb CH_3CCl_3 , and 5 ppb CCl_4 . Chromatogram A is that provided by the normal ECD function of the detector and B is that simultaneously provided by the PDM function with 0.6 Torr water vapor in the detector gas at 35°C .

Industrial Air Sample - Real
World Application

The performance of this instrument has been evaluated by test mixtures prepared in the lab and has proven itself to be of use in the chromatographic analysis of iodide in the presence of interfering organic chlorides. It was shown that the PDM-ECD could be used to quantify organic iodides in the presence of high levels of coeluting chlorides. A further evaluation of this instrument has been made by examination of real industrial air samples. These air samples were provided by Westinghouse Idaho Nuclear company located on the Idaho National Engineering Laboratory Site, Idaho Falls, ID. Fifteen stainless-steel cylinders containing air samples taken from various locations within the nuclear waste processing facilities were sent for analyses using the PDM-ECD.

The PDM-ECD proved to be extremely useful in the qualitative analysis of the samples provided. This was demonstrated by first examining a test mixture, taken with the water trap removed from the carrier gas line. This test mixture was analyzed the same day as the industrial air samples. The results of the test mixture which contained compounds yielding iodide, bromide, and chloride upon electron capture is shown in Figures 16A-B. Again, the modulated response observed in 16B is dependent upon the degree of hydration and the PD overlap integral for a

Figure 16. PDM-ECD chromatographic analysis of an test sample, chromatograms A and B, and industrial air sample, chromatograms C and D. Chromatogram A and C provided by the normal ECD function and B and D is provided by the PDM-ECD function with the water removing trap removed from the carrier gas supply line. The concentrations of the halocarbon mixture in A have been reported in Figure 6. The concentrations in the industrial sample C and D were found to contain approximately 0.400 ppb CFCl_3 , (twice its normal background level), 320 ppb $\text{CF}_2\text{ClCCl}_2\text{F}$, and 1 ppb CH_3CCl_3 .

given anion. It is seen that the largest response observed is for the organic iodide then the bromides and very little PDM response for the organic chlorides (apparently there was insufficient water in the carrier gas tank used to cluster the chlorides sufficiently enough to totally eliminate chloride response). A industrial air sample was then analyzed and a typical response is shown in Figure 16C-D. The obvious point to note in Figure 16C is the lack of PDM response which indicates the presence of organic chlorides. Referring back to the test mixture shows that similar results were obtained for the compounds that produced Cl^- upon electron capture. This is further conclusive support that the air sample contained only organic chlorides. The qualitative usefulness of the information gained from the PDM-ECD is obvious. The product of dissociative electron capture is indicated in these chromatograms. One can immediately eliminate numerous compounds based on the products of dissociative electron capture that are observed. Retention times of compounds known to produce the observed halogen can then be used for definite identification. One might consider using a more intelligent system such as mass spectrometry for definitive identification. However, the amount of material present in these samples, low picograms, is insufficient for conventional full scan EI or CI modes of mass spectrometry. High pressure electron capture mass

spectrometry (HPEC-MS) operated in single-ion monitoring mode is sensitive enough but, as with the PDM-ECD, it can only determine the negative ion products of dissociative electron capture. The PDM-ECD is easier to operate and maintain and is two orders of magnitude less expensive than a mass spectrometer.

No organic iodides were found in the industrial samples provided. However, the time duration between sample collection and analysis was quite long, approximately 6 months. There may have been trace levels of iodides which were destroyed on the walls of the sample container during that time interval.

SUMMARY

A simple detector has been described which is capable of detecting trace amounts of iodinated hydrocarbons in the presence of excess ClHC's. This was accomplished by using four gas phase processes which maximized the response to methyl iodide while eliminating the response to ClHC's. These processes are: 1) EC by the analyte molecules, 2) regeneration of an EC-active species (probably HI) through ion-ion recombination reaction of I^- , 3) prevention of PD from Cl^- through clustering of Cl^- by the intentional addition of about 0.1 to 1 Torr of water to the detector gas at $35^{\circ}C$. This convenient result is thought to be due to the formation on $n = 2$ and larger water clusters of Cl^- for which the onset of PD is shifted to wavelengths shorter than that available from the Hg arc lamp, and 4) photodetachment of I^- negative ion or its water clusters.

The full emission of a low power Hg arc lamp has been shown to efficiently induce PD of the $n = 0$ to 2 water clusters for I^- . This work has resulted in a instrumentally simpler and less expensive transducer as compared to the original work. The 1,000-Watt arc lamp has been replaced by a 100-Watt arc lamp and the monochromator has been eliminated with no loss of selectivity or

sensitivity. No other light filters of any kind were used. The performance of this instrument was evaluated by examination of test mixtures and real air samples and was found to be useful in the quantitative and qualitative analyses of complex chromatographic mixtures. This instrument was also shown to have good potential for the selective detection of brominated hydrocarbons in the presence of ClHC's.

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APPENDIX

A program was written which was designed to allow one to calculate fractional composition values for any complexation reactions as long as the enthalpy and entropy values are known. The usefulness of this program is apparent when calculating clustering reactions at various temperatures and clustering agent partial pressures. The program was written in basic and is run on an Apple IIe personal computer. The values reported in Figure 13 were calculated using the following program.

Figure 17. Computer program designed to calculate halide cluster abundances.

```

25 PRINT "THIS PROGRAM IS DESIGNED TO CALCULATE ALPHA
    (FRACTIONAL COMPOSITION) FOR COMPLEXATION REACTIONS.
    THUS IT IS USEFUL FOR CLUSTERING REACTIONS. THIS PRO-
    GRAM IS NOT DIMENSIONED SO ONE CAN ONLY DETERMINE UP
    TO NINE DIFFERENT FORMS."
30 PRINT "THERMODYNAMIC PARAMETERS WILL BE INPUTED NEXT."
40 PRINT "H=ENTHALPY;S=ENTROPY;T=TEMP
    (KELVINS);P=PRESSURE (TORR- THE PROGRAM WILL CONVERT TO
    ATMOSPHERES.)
41 INPUT "THE TOTAL NUMBER OF ENTHALPY VALUES NEEDED =";N
42 PRINT N
45 FOR I = 1 TO N
46 PRINT "ENTER H";I
47 INPUT H(I)
48 LET H(I) = H(I) * -1000
50 NEXT I
55 PRINT "THE ENTROPY VALUES WILL BE ENTERED NEXT."
60 FOR I = 1 TO N
70 PRINT "ENTER S";I
80 INPUT S(I)
90 LET S(I) = S(I) * -1
100 NEXT I
110 D$ = CH$ (4)
120 PRINT D$; "PR#1"
130 INPUT "THE PARTIAL PRESSURE OF CLUSTERING AGENT IN
    TORR IS =";P
140 PRINT P
150 INPUT "THE TEMPERATURE IN CELSIUS IS =";T
160 PRINT T
170 LET B = 273.15 + T
180 LET A = P/760

```

```
190 LET R = 1.987
200 LET E = 2.7182889
210 FOR I = 1 TO N
220 G(I) = H(I) - (B * S(I))
230 K(I) = (E ^ - (G(I) / (R * B)))
240 NEXT I
250 K = 1
260 R = 0
270 FOR I = 1 TO N
280 K = K * K(I) * A
290 R(I) = K
300 R = R + K
310 NEXT I
320 R = 1 + R
330 PRINT "FREE ANION ="; 1 / R
340 FOR I = 1 TO N
350 II(I) = R(I) / R
360 PRINT "CLUSTER NUMBER"; I = II(I)
370 NEXT I
380 PRINT " "
390 PRINT " "
400 PRINT D$; "PR#0"
410 PRINT "IF YOU NEED TO CHANGE THE PARTIAL PRESSURE OR
    TEMPERATURE TYPE IN A 2. IF YOU WANT TO STOP TYPE IN
    A 3."
420 INPUT Q
430 IF Q = 2 THEN 110
440 END
```

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