



Chemical and physical events affecting the quantitative response of the pulsed ^{63}Ni electron capture detector

by Walter Berkett Knighton

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

An extended means of processing the signal of a constant current pulsed electron capture detector (CCP-ECD) is proposed. This new response function provides a significant improvement in the quantitative analysis by the ECD because it provides linear calibration curves for strongly electron attaching molecules over the entire dynamic range of the instrument. The theoretical basis and experimental support for the proposed EC response function are presented, using CCl_4 , CFC13 and CHCl_3 as test compounds.

Calibration curves for the responses of an ECD to CFC13 , CH_3I , CCl_4 , CH_3Br and CHCl_3 are reported. The first three compounds listed are ones which attach electrons extremely rapidly and, because of this, are not expected to produce linear calibration curves over the entire dynamic range of the detector. While the calibration curves of CFC13 and CCl_4 are consistent with this expectation, that of CH_3I is not. At low detector temperatures the EC molar response of CH_3I significantly exceeds those of CFC13 and CCl_4 , yet its molar response remains nearly constant over the entire response range of the instrument. A mechanism is suggested which attempts to explain these superior response characteristics of CH_3I .

Calibration curves for the response of an ECD to ethyl chloride are shown to be non-linear. The apparent molar response is observed to be much greater for low concentration samples than high concentration samples. A mechanism is proposed for the enhanced low concentration responses.

Physical factors which might affect the quantitative response of the CCP-ECD are examined in detail. These include the effects of non-analyte electron loss by reaction with carrier gas impurities, by recombination with positive ions, by diffusion to walls, by ventilation with carrier gas flow, and by migration through small fields generated by contact potentials. Experiments indicate that so long as the frequency of pulsing is moderate to fast, the effects of non-analyte loss processes on the response of the CCP-ECD will be well-behaved and in harmony with the expectations of simple and idealized theory. With the use of slower frequencies of pulsing, however, non-analyte electron losses are more complicated and non-idealized behavior and nonlinear calibration curves are observed. An attempt is made to identify the specific causes of the non-ideal behavior which accompanies the use of slower pulse frequencies.

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APPROVAL

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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 consistency, and is ready for submission to the College of Graduate Studies.

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DEDICATION

I would like to dedicate this to my wife Maryanne, whose faith in me never faltered, to my mother who never doubted that I had the ability, and to my father who will be proud of my accomplishments.

VITA

Walter Berkett Knighton IV was born December 24, 1955 in West Chester, Pennsylvania, son of Walter B. and Charlotte D. Knighton. He graduated in 1973 from Henderson High School, West Chester, Pennsylvania. Walter entered Montana State University in 1973 and received his Bachelor of Science with Honors in Chemistry in 1978. He was accepted to graduate school at Montana State University in 1978 and received his Master of Science degree in Chemistry in 1980. In September of 1980 Walter re-entered graduate school at Montana State to pursue his Doctorate of Philosophy in Chemistry.

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ABSTRACT

An extended means of processing the signal of a constant current pulsed electron capture detector (CCP-ECD) is proposed. This new response function provides a significant improvement in the quantitative analysis by the ECD because it provides linear calibration curves for strongly electron attaching molecules over the entire dynamic range of the instrument. The theoretical basis and experimental support for the proposed EC response function are presented, using CCl_4 , CFCl_3 and CHCl_3 as test compounds.

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Calibration curves for the response of an ECD to ethyl chloride are shown to be non-linear. The apparent molar response is observed to be much greater for low concentration samples than high concentration samples. A mechanism is proposed for the enhanced low concentration responses.

Physical factors which might affect the quantitative response of the CCP-ECD are examined in detail. These include the effects of non-analyte electron loss by reaction with carrier gas impurities, by recombination with positive ions, by diffusion to walls, by ventilation with carrier gas flow, and by migration through small fields generated by contact potentials. Experiments indicate that so long as the frequency of pulsing is moderate to fast, the effects of non-analyte loss processes on the response of the CCP-ECD will be well-behaved and in harmony with the expectations of simple and idealized theory. With the use of slower frequencies of pulsing, however, non-analyte electron losses are more complicated and non-idealized behavior and non-linear calibration curves are observed. An attempt is made to identify the specific causes of the non-ideal behavior which accompanies the use of slower pulse frequencies.

INTRODUCTION

Improvements in Modes of Operation of the ECD

In the late 1950's the electron capture detector (ECD) was developed in response to the need for a sensitive detector to use with the newly discovered technique of gas chromatography (GC). The first report of using an ECD as a detector for GC was by its inventor J. E. Lovelock in 1958 (1). Even at this early date it was recognized to be extremely sensitive to certain compounds, many of which also happened to be of environmental importance. Although extremely sensitive, quantitation of the responses obtained with this device was difficult, due to non-linear and often unpredictable relationships between the measured response and sample concentration. In spite of these difficulties, the ECD was pressed into service for trace pesticide residue analysis (2). Because the ECD possessed the lowest detection limits available for pesticide residue analysis at the time, instrument manufacturers began producing gas chromatographs equipped with this detector. Commercial production of the ECD, however, did not significantly lead to its improvement.

The original ECD's were operated in the direct current (DC) mode, in which a small constant potential was

applied to the cell's two electrodes and the response was taken as the change in cell current (ΔI). The responses observed with this original device were found to be very complex and could not be explained by electron capture processes alone. Lovelock (3) addressed this point and reported that, in addition to operating as an electron capture detector, this device sometimes also functioned as an ionization cross section detector, a metastable ionization detector and an electron mobility detector. These unwanted modes of detection were found to be eliminated by addition of 10% methane to the argon carrier gas. The addition of methane to the carrier gas was found to promote the thermalization of secondary electrons and facilitated the deactivation of metastables through inelastic collisions. Electron mobility effects were also eliminated because of the fast drift velocity of electrons in the argon 10% methane carrier. Lovelock (3) also recognized that the observed ECD responses were perturbed by space charge potentials arising from the separation of oppositely charged particles in the DC-ECD. Also, contact potentials resulting from the deposition of material films on the cell surfaces could affect the response. Within this report, Lovelock (3) proposed that these additional effects could be eliminated or minimized if the ECD was operated in the pulsed mode. A brief, intermittent pulsed waveform could be used to collect the electrons, thereby

allowing the electron capture reactions to occur predominantly in the field free environment which existed between pulses. With the pulsed sampling method, the responses were believed to be free of the deleterious effects of space charge and contact potentials. Contributions to the measured current from the collection of negative ions at the anode were also eliminated because the relatively immobile negative ions could not be drawn to the anode within the short duration of the voltage pulse. In spite of the improvements obtained by operating the ECD in the fixed frequency pulsed (FFP) mode, linear responses were only observed over the initial 10% of the dynamic range of the detector.

Throughout the early 1960's the events occurring within the ECD were only poorly understood and it was generally believed that the process of electron capture was analogous to the absorption of electromagnetic radiation. In a landmark report by Wentworth *et al.* (4) in 1966, a model was proposed for the pulsed ECD in which the events occurring within this device were described as a series of competitive kinetically controlled reactions. This represented the first detailed description of the events occurring within the ECD. Although this model is now known not to describe accurately the physical-dynamic aspects of the ECD plasma, it did provide a foundation

upon which significant improvements in processing the signal of an ECD have resulted. In 1967 Wentworth and Chen (5) showed that if the analytical signal was taken as the decrease in standing current divided by the instantaneous current, $(I^0 - I)/I$, linear calibration curves could be obtained up to 90% of detector saturation. A practical limitation of this mode was its requirement for unusually clean chromatographic conditions, so that a high standing current with long pulse periods could be achieved. In 1971 Maggs *et al.* (6) proposed operating the ECD in the frequency modulated, or constant current pulsed (CCP) mode of operation. In this case, an electrical feedback network maintained the magnitude of the measured cell current constant and equal to a preselected reference current value by control of the pulsing frequency. Then, as an electron capturing compound eluted through the detector, the frequency of pulsing was modulated by an amount required to keep the current constant. The analytical response was then taken as the change in the frequency of pulsing (Δf). The CCP-ECD has been shown to yield responses to many compounds which are linear with sample concentration up to 99% of detector saturation.

Non-linear Responses

Ironically, even with all of the above improvements in the operation of the pulsed ECD with $(I^0 - I)/I$ and CCP

modes of signal processing, linear responses are still not observed for many compounds. Within this group of compounds are the polyhalogenated hydrocarbons (7-9), the monochlorinated alkanes (10) and some of the polycyclic aromatics (PAHs) (11).

The PAHs, for example anthracene, undergo resonance electron capture in which stronger responses are favored by the use of low detector temperatures (4,12); hence, most analysis schemes involve using the lowest possible detector temperatures. However, Grimsrud et al. (11) have observed that at higher and more practical detector temperatures, $>300^{\circ}\text{C}$, anthracene gave a negative ECD response, whereas at detector temperatures less than 250°C normal responses were obtained. In addressing the negative response of anthracene, they conducted experiments using an atmospheric pressure ionization mass spectrometer (APIMS), in which the ion source was an actual ECD. They observed that a 10 ng sample of anthracene, which resulted in small negative ECD response, gave a large positive ion peak at m/e 179 ($M+1$ peak of anthracene). On the basis of this result, they concluded that the slight increase in the electron density (negative response) was due to a slightly smaller positive ion electron recombination rate when the positive ion character within the cell was determined predominately by anthracene positive ions.

The ECD has been used for the atmospheric analysis of the monochlorinated alkanes because of its insensitivity to the presence of interfering hydrocarbons (13-15). The ECD was expected to be well-suited for the analysis of these types of molecules, since they possess moderate to small rates of electron capture; hence, linear calibration curves were expected over the entire dynamic range of the instrument. However, Grimsrud and Miller (10) have found that with the CCP-ECD, the alkyl monochlorides exhibit unusual and non-linear calibration curves. The cause for this unusual behavior for these compounds is unknown.

Most notable of the group of compounds which exhibit non-linear behavior to the CCP-ECD are the environmentally important polyhalogenated hydrocarbons. This behavior is unfortunate because it is to these highly halogenated molecules that the ECD exhibits its strongest responses. This lack of linear behavior for these strongly responding compounds arises from the alteration of the analyte concentration within the detector by the electron attachment process itself (7-9). Several approaches have been taken to minimize or eliminate the problem of non-linear responses observed for the strongly responding compounds. One approach has been to make the detector volume very small or make the carrier flow rate very fast. The residence time of the analyte in the cell is then very short and little destruction of the sample by the electron

capture reaction is allowed. The small detector approach has been demonstrated by Patterson (16), where the active volume of a small cell was made effectively smaller by use of a displaced coaxial anode. Alternatively, high flow rates are easily obtained through the addition of makeup gases. The compromise inherent in these approaches is that, while only partially improving the quantitative response to strongly responding compounds, the sensitivity to weakly and moderately responding compounds is proportionately reduced.

Theoretical Models

In 1966 Wentworth et al. (4) presented the first detailed description of the physical events occurring within the pulsed ECD. The following is a brief summary of the pertinent points addressed in this first model. Beta radiation, through a series of elastic and inelastic collisions with carrier gas molecules was considered to produce a steady state concentration of secondary electrons, positive ions, radicals and negative ions if sample is present. The resulting current measured was due to the collection of all the electrons within the cell by the application of a short voltage pulse. Experiments in which the effects of pulse amplitude, width and frequency on the measured standing current, such as those by Wentworth, Chen and Lovelock (5) and others (17,18),

provided evidence that the short voltage pulses do indeed clear the cell of all the electrons. Negative ions formed as the result of electron capture, and positive ions were not thought to contribute to the measured current, because of their relative immobilities compared to that of the electron. Because positive ions were not removed from the cell by the pulse, and since their free diffusion to cell boundaries during the pulse free period is much slower than that of electrons, the positive ion concentration was considered always to be in great excess of that of electrons and limited by the rate of recombination with positive ions and electrons. As a result of their great excess, the positive ion concentration was assumed to remain relatively constant within the ECD. The ECD was thought to be a well-mixed reactor, in which the concentrations of all the species was described by a simple differential equation. Because of the last two assumptions the resulting differential equation describing the change in electron density with respect to time could be solved. As a result of solving the differential equation, under a steady state condition, the relationship $(I^0 - I)/I$ was found to be linearly related to sample concentration (5).

It was later proposed that a net decrease in the ion current results because of the enhanced recombination rate

of negative ions (formed from electron capture) with positive ions. The recombination rate of negative ions with positive ions was reported to be 10^5 - 10^8 times faster than that of positive ion electron recombination (19).

Siegel and McKeown (20) presented several criticisms of the original model proposed by Wentworth et al. (4,5). On the basis of their experiments using an atmospheric pressure ionization mass spectrometer (APIMS) with a ^{63}Ni ionization source, they argued that the strong interactions between charged particles cannot be ignored and that charge neutrality was strictly maintained in the field free ion source of their APIMS. They stated that because of the high density of positive and negative particles which exists within their ^{63}Ni source, or an ECD, that these charged particles do not move independently of one another, but that their diffusion behavior is described by a single ambipolar diffusion coefficient. As a result of this diffusion behavior, in a clean field free cell the major loss mechanism of electrons and positive ions was shown to be recombination with each other, while their losses through diffusion and ventilation were insignificant. They also argued that positive ion recombination rates with electrons and negative ions should be comparable, since there was no physical justification for the positive ion negative

recombination rate to be five to eight orders of magnitude greater than that of positive ion electron recombination.

Grimsrud, Kim and Gobby (21) presented evidence obtained using an APIMS, in which the ion source was an actual pulsed ECD, that supported the view of the ECD proposed by Siegel and McKeown. They noted that the positive ion density actually increased within an ECD which was saturated with CCl_4 . This indicated that the negative ion (Cl^-) positive ion recombination rate was actually slower than that of the positive ion electron recombination rate. Within this same report, they observed that, when the ECD ion source was pulsed, the negative ion API spectrum under conditions of small sample concentration was destroyed while the positive ion spectrum was unaffected. They concluded from this result that the excess positive ions left within the cell, a result of the pulse removing all the electrons, creates a positive space charge which acts to hold the negative ions within the space charge region, thereby not allowing negative ions to diffuse to the cell boundaries. The positive ion spectrum was unaffected, since the positive space charge causes positive ions to migrate to any grounded cell surfaces in an attempt to dissipate the space charge potential they themselves created. Under conditions of detector saturation, pulsing the cell did not affect either the positive or negative ion spectrum.

This result was expected, since the few electrons within the cell, under conditions of saturation, play only a minor role in maintaining charge neutrality. Measured standing currents were also shown to be influenced by the resulting positive space charge arising from the removal of electrons by the pulse. The time averaged current measured at the anode was found to reflect both negative and positive current contributions. The negative current results from the collection of electrons by the pulse. The positive current arises for the migration of positive ions to the anode, which is at virtual ground, during the period between pulses.

Wentworth and Chen (22) later revised their original model with respect to the assessment of positive ion concentration. This revision addressed only an ECD of parallel plate design using a tritium source. They argued that because of the short penetration depths of the tritium betas, ~2 mm, positive ions could not migrate to the distant anode 1.0 cm away during the pulse free period. They interpreted the positive ion contribution to the measured current reported by Grimsrud *et al.* (21) as resulting in a net loss of positive ion concentration within the cell. In their revision, they accounted for this by assuming that a fraction of the positive ions were collected at the cathode by each negative pulse. In this

way, more positive ions were removed from the detector under conditions of fast pulsing, which resulted in a better correlation between the theoretically predicted and experimentally obtained standing current versus pulse period curves.

In 1980 Gobby, Grimsrud and Warden (23) proposed a physical model for the pulsed ^{63}Ni ECD. In this model electrostatic interactions between charged particles was considered to be the dominant force in determining the concentration and location of all charged particles within the ECD. Beta radiation was assumed to result in uniform ionization throughout the active volume of the cell. This point was later addressed by Grimsrud and Connolly (24) and was shown to be true for typical ^{63}Ni ECD's. All of the electrons were assumed to be removed by the short voltage pulse. The positive ions which are left behind after the pulse were themselves thought to create a positive space charge potential, which is dissipated by the migration of the positive ions to all grounded cell surfaces. Electrons formed after the pulse were envisioned to be concentrated in a localized region in which charge neutrality exists (plasma), which grows with time. Two distinct regions were proposed to exist: a charge neutral plasma which contains an equal number of positive and negative charge carriers, and a region which contains positive ions and is void of electrons. Thus,

positive ions were thought to form a sheath which separates the plasma from the cell boundaries and shrinks with time after the pulse. The rates of positive ion losses through positive ion space charge driven migration, and recombination with negative ions and electrons, were found to be approximately equal, so the positive ion density was considered to remain constant under all conditions of pulsing frequency and sample concentration. This last result was extremely fortunate because the differential equation describing the change in electron density with time can be explicitly solved only when the positive ion density can be assumed to remain constant. As fortuitous as it seems, in their final forms both the original Wentworth model and the space charge model predict the same relationship between analytical response and sample concentration.

In a recent study by Connolly *et al.* (25), a series of experiments were reported which examined the effect of positive ions on the measured standing current and response of a pulsed ^{63}Ni ECD. Measurements were obtained with an APIMS, in which the ion source was a pulsed ECD, showing that positive ion density measured by the mass spectrometer was dependent on the frequency of pulsing, but independent of the polarity. Because the total positive ion density remained unchanged whether positive or negative polarity

pulses were applied to the anode, it was concluded that the pulse itself does not measurably perturb the location of positive ions in space. Standing current versus pulsing frequency data was also reported which supported this conclusion. The positive ion contribution to the measured current was measured with two ECD's, which had differing length to diameter ratios. The ECD which had the smaller length to diameter ratio was also found to have a smaller positive ion contribution to its measured current. This result could not be explained by the collection of positive ions by the pulse itself, since the same fraction of positive ions should have been collected by pulse in both cells. They concluded for the ^{63}Ni pulsed ECD, that positive ions are lost to cell surfaces through space charge driven migration, which provided further evidence in support of the space charge model.

RESEARCH OBJECTIVES

Within the literature several classes of chemicals for which the ECD has been used as an analysis tool, have been found to exhibit non-linear relationships between the analytical response and sample concentration. Two of these systems, the strongly responding compounds and the alkyl monochlorides, have been selected for investigation within this study. For both of these chemical systems, two objectives are established. The first objective is to identify and characterize the chemical mechanism responsible for the observed ECD responses. The second objective is to evaluate the mechanism responsible and then define new modes of operation which will either eliminate or compensate for the effects of the anomalous behavior.

A more subtle, potential cause of non-linear behavior is also addressed. The quantitative response of the CCP-ECD is also dependent on electron loss processes other than that of electron attachment to sample. These non-analyte electron loss processes are dictated by physical rather than chemical factors occurring within the ECD. These non-analyte electron losses may include diffusion of electrons to the cell walls, ventilation out of the cell with the carrier gas flow and changes in the positive ion

density. Simple theory used to derive the relationship between the change in frequency and the sample concentration for the CCP-ECD required that the magnitude of these non-analyte electron losses remain constant and independent of pulsing frequency and sample concentration. Close inspection of the physical dynamic aspects of the ECD, predicted by the space charge model, indicates that two distinctly different physical states exist within the ECD, depending on the frequency of pulsing. Under conditions of fast pulsing the space charge field acts to hold the electrons within the plasma. Therefore, the additional electron losses such as diffusion of electrons to the cell wall and ventilation with the carrier gas flow cannot occur. However, with slow pulsing frequencies sufficient time is allowed between successive pulses for the growing electron population to fill the entire cell volume. In this case, electron loss by diffusion and ventilation becomes more probable. It seems possible that the magnitude of the non-analyte electron losses is different under conditions of fast pulsing as compared to slow pulsing. If this occurs, then non-linear calibration curves will result if the change in frequency response makes the transition from a condition of slow pulsing to that of fast pulsing. In this study, an attempt has been made to identify and characterize these physical factors which may affect the quantitative response of the CCP-ECD.

EXPERIMENTAL

Ancillary Equipment

The majority of the data reported in this study was obtained using a homebuilt gas chromatograph equipped with an ECD. The gas chromatographic unit consisted of two separate ovens, one of which housed the column, and the other the detector. Both ovens were fabricated from sheet metal, which was then lined with fiber glass insulation covered by aluminum foil. The temperature within the ovens was controlled by adjusting the voltage applied to a heating element, which was mounted in the bottom of each, using a Variac. When more precise control of the detector temperature was required, a Watlow pulsed cartridge heater was used. With the pulsed heater, the detector temperature could be maintained within $\pm 1.0^{\circ}\text{C}$. An insulated stainless steel transfer line which ran between the two ovens was used to connect the column and the detector. Gas sample introduction and carrier gas connection to the column was accomplished using a Carle 8030 gas sampling valve, which was mounted on the column oven.

Detectors

Three homemade ECD's were used to collect the majority of the data in these studies. Two of these detectors are shown in Figure 1, while the third, a highly specialized cell, will be described later. Both detectors shown in Figure 1 were designed by Dr. Eric Grimsrud and machined by Technical Services at Montana State University. The detectors were machined from stainless steel and are of concentric coaxial design. The cylindrical walls are formed by a ^{63}Ni plated on Pt foil, New England Nuclear, which serves as the beta source. The activity of the sources in both cells is 15 mCi. The internal volumes of cells 1 and 2 are 1.5 mL and 2.0 mL, respectively. The coaxial anode is a 1/16" diameter stainless steel rod, the midsection of which is encased in a ceramic insulator and is held in place by a threaded stainless steel plate and a teflon spacer. Electrical connections between the anode of the detector and the electronics package which operates the detector were made using BNC connectors and coaxial cables.

Electronic Circuits for Detector Operation

The electronic package which controlled the homebuilt ECD's was constructed by the author (26). This package allows for the ECD's to be operated in either the CCP or FFP modes of operation.

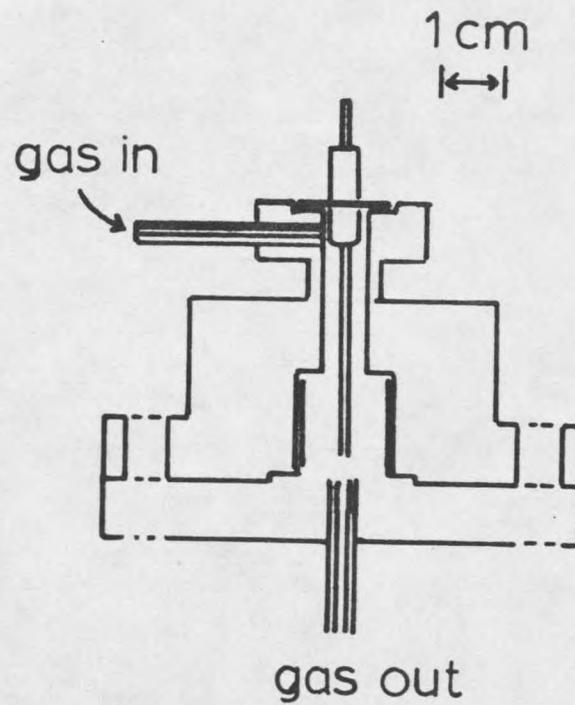
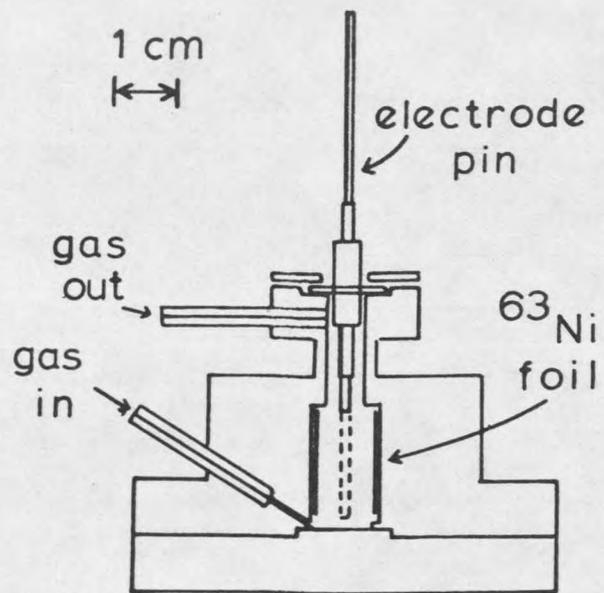


Figure 1. ECD cell designs used in this study. Both sources are 15 mCi. Dimensions of cell 1 are 1.0 cm x 1.5 cm and of cell 2 are 1.4 cm x 1.4 cm.

Figure 2 shows the complete circuit diagram for operating an ECD in the CCP mode. Circuits A and B show different configurations for pulsing an ECD. Circuit A involves pulsing the anode positively, while the cell body is grounded, whereas in Circuit B the cell wall is pulsed negatively. In both cases, the current is measured at the concentric anode. Operational amplifier one (OA 1), CA 3140, is operated as an integrator, in which the output voltage reflects the time averaged difference between the reference and cell currents. OA 2, CA 3140, inverts the output signal from OA 1, making it compatible with the voltage-to-frequency convertor (V-to-F), Burr Brown VFC52, which only operates with positive going signals. A non-inverting buffer, CD 4050, is used after the V-to-F, as a pulse shaper where the buffer improves the rise time of the pulses. The output pulses from the V-to-F are typically about 2.5 μ s in duration. This pulse width is modified to any desired width by the RC coupled Nand gates. The RC couple, shown in Figure 2, yields a pulse width of 1 μ s duration. The Nand gates are contained within a quad, two-input Nand gate IC, CD 4011B. If it is desired to pulse the wall, as in Circuit B, then a third Nand gate on the IC is used to invert the pulse. The pulse train is then amplified to 50 V by use of a transistor. For positive pulses a 2N4402 PNP transistor

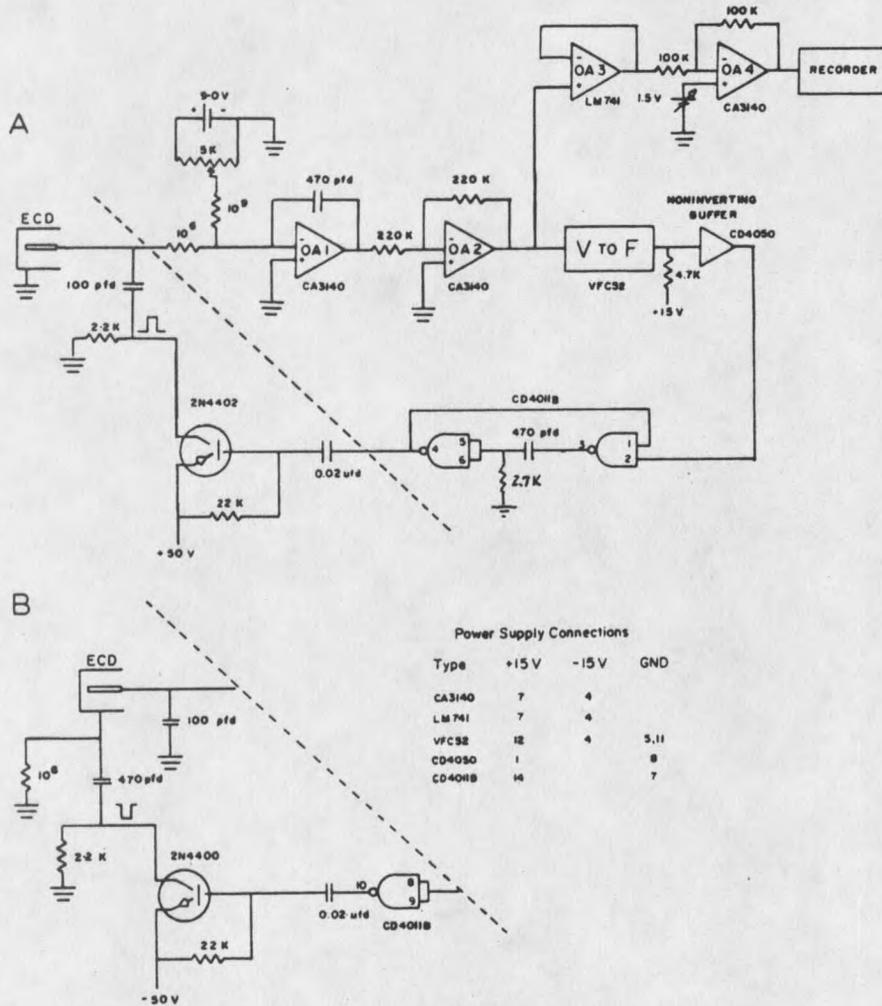


Figure 2. Circuit for constant current operation of ECD (A) where positive pulses are applied to the anode and (B) where negative pulses are applied to the cathode.

is used and a 2N4400 NPN transistor for the negative going pulse.

The base frequency of pulsing is determined by the current demanded from the reference current source and the cleanliness of the cell. The reference current desired is selected by a 10 turn $5k\Omega$ potentiometer and is variable from 0-9 nanoamps. The output signal from OA 2 is sent to a multi-range recorder by way of OA 3, LM 741, a voltage follower and OA 4, CA 3140, which is used to zero the signal. When the output signal is monitored by the computer, a low pass filter, shown in Figure 3, is inserted between OA 4 and the computer interface. This filter was used to smooth the output signal from the CCP-ECD, so that data acquired by the computer reflected the time averaged output signal. The voltage profile from the output of the integrator, OA 1, is time dependent, due to the RC network, which allows for it to operate as an integrator. Only in the case where the RC time constant is zero would the output signal from the integrator be truly constant over the period of the pulse. The low pass filter removed the time dependency of the output signal from the integrator and allowed the computer to sample the time averaged signal.

The circuit diagram for a FFP-ECD is shown in Figure 4. Nand gates 1 and 2 control the period of the pulses, while Nand gates 3 and 4 control the pulse width, as in

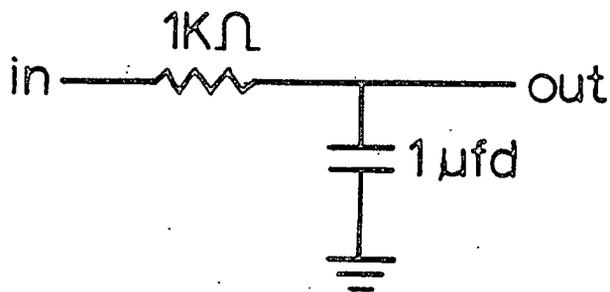


Figure 3. Low pass filter used to smooth the signal from the CCP-ECD for computer controlled experiments.

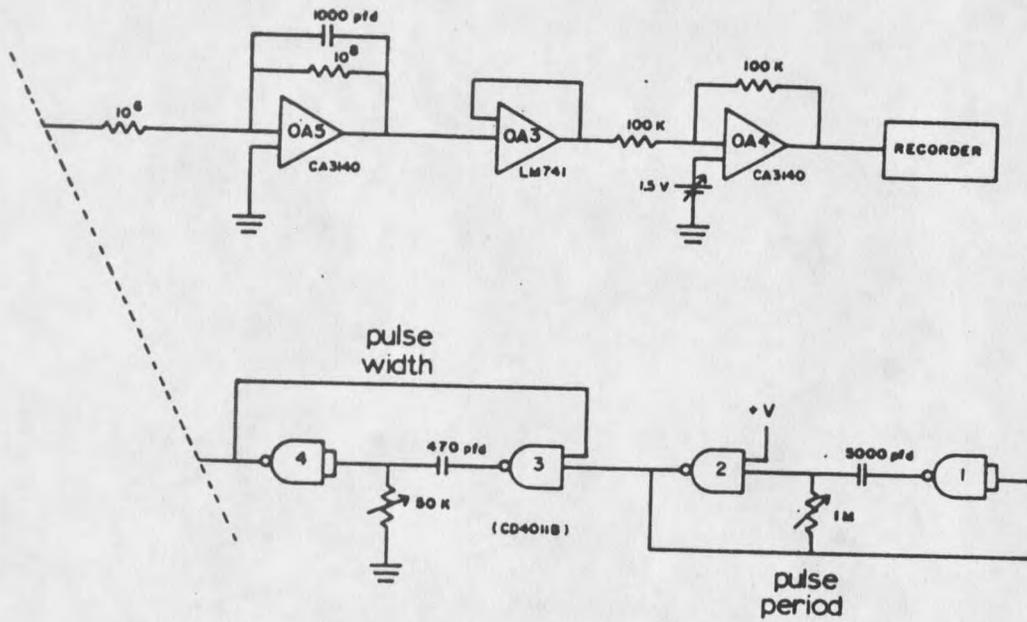


Figure 4. Circuit for fixed frequency operation of an ECD.

the constant current circuit. All four Nand gates are contained on a CD 4011B IC. The pulse period can be varied from 10 μ s to 2.5 ms, using the values of the capacitor and variable resistor shown. Longer pulse periods can be achieved by simply increasing the size of either the capacitor or resistor. The pulse widths can be varied from 0.5-15 μ s with the components shown. The pulse amplification circuitry is the same as that shown in Figure 2. The current resulting from the collection of electrons at the anode, due to the application of the pulse, is measured using a current to voltage follower, OA 5, CA 3140. With the precision resistor in the feedback network shown, the output voltage reflects the time averaged cell current times 10^8 . The signal output circuitry is the same as is shown in Figure 2.

In all the experiments reported here, the ECD was operated in the pulsed mode. Electrons were collected at the anode either by applying negative polarity pulses to the wall or by pulsing the anode positively while maintaining the cell wall at ground potential. In both cases the cell current is measured at the anode. Typically, positive pulsing is used, so that the ECD does not have to remain electrically isolated from the rest of the instrumentation. The pulsing parameters used were dependent on the application and are specified as needed in the Results and Discussion section.

Chromatograms were obtained from the homemade GC-ECD by continuously monitoring the output signal from either the FF or CC circuits, using a Houston Instruments Omniscribe strip chart recorder. For experiments in which the exponential diluter was used, the output from the CCP-ECD was monitored simultaneously with a strip chart recorder and by an Apple II plus computer equipped with a Cyborg Isaac's model 91A interface. The computer enabled the total 0-10 volt signal of the CCP-ECD to be monitored without further alteration of the signal over the entire course of each experiment. The computer retains one data point and real time clock measurement every 10 seconds. This one data point, however, represents the average of 100 individual measurements taken at 10 ms intervals over a 1 second period. Each experiment was allowed to run for 10,000 seconds and, at the conclusion, the raw data was transferred to disk.

Standard Preparation

The halocarbons utilized in this study were all purchased from commercial sources as follows: CH_3Br and $\text{C}_2\text{H}_5\text{Cl}$ were purchased as gases from Matheson Gas Products, Lyndhurst, New Jersey. Liquid CFCl_3 and gaseous CF_2Cl_2 were obtained from PCR Incorporated, Gainesville, Florida. Liquid samples of CH_3I and CHCl_3 were purchased from J. T. Baker Chemical Company, Phillipsburg, New

Jersey. Liquid CCl_4 was obtained from Matheson, Coleman and Bell Manufacturing Chemists, Norwood, Ohio.

Standards of all the aforementioned halocarbons were prepared for analysis as gases using airtight glass carboys, which were maintained at above ambient pressures. Nitrogen was used as the diluent gas and was checked for the presence of electron capturing impurities prior to sample preparation. The initial dilution was performed by injecting a small aliquot of either the neat liquid (0.5-100 μL) or gas (0.5-5 mL) into a 1.0 L gastight glass flask pressurized to 1.0 psi above atmospheric pressure. Standards prepared from compounds which are liquids at room temperature required that the airtight flask sit for a short period of time, so that the sample could evaporate and equilibrate in the gas phase. Because of the high volatility of the halocarbons used here, this was usually accomplished in 10-15 minutes. Depending on the concentration (V/V) of the standard desired, subsequent dilutions would be performed using a 30 mL gastight syringe for sample transfer, and other 1.0 L airtight flasks, before the final dilution into either a 4.5 L or 22 L glass carboy, pressurized to 5 psi above atmospheric pressure. Both large carboys allowed for multiple sampling and sample storage for up to three weeks, without noticeable sample deterioration or atmospheric infusion.

Final dilutions and sample transfer were accomplished using a 100 mL gastight syringe equipped with a Hamilton G.T.S. syringe valve.

Chromatographic Conditions

Samples were introduced into the detector by either a chromatographic column or an exponential dilution sphere. For halocarbon mixtures a 10'x 1/8" stainless steel column packed with 10% SF-96 on Chromosorb W was used. Adequate separation of the light halocarbon mixtures was obtained when the column was operated at ambient temperature. When wide range calibration curves for only a single component was desired, an exponential diluter was used, a general schematic of which is shown in Figure 5. The exponential diluter, a simple glass sphere, was manufactured from a 1 L round bottomed Pyrex flask and was connected to the sampling valve and the detector by 1/4" glass tubing with Swagelok fittings. The volume of the diluter was determined by weighing the amount of water contained within the sphere and was found to be 1093 ± 5 mL. The diluter was housed in the column oven, which was maintained at 38°C.

Carrier gases, either Ar with 10% methane or high purity nitrogen, were first passed through molecular sieve and oxygen traps. The molecular sieve trap was used to remove trace impurities of water present in the carrier

