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## BIPOLAR PULSED MICROVOLUME ELECTRON-CAPTURE DETECTOR FOR CAPILLARY GAS CHROMATOGRAPHY

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### SUMMARY

A physical kinetic-electrostatic model of a bipolar pulsed electron-capture detector is described for a capillary microvolume cell. The Wentworth model has successfully been used to explain electron-capture detection (ECD) response in many practical and fundamental applications. However, the model fails to predict the non-linear response of constant current (unipolar pulsed) ECD at high pulser frequencies (*i.e.* frequencies approaching d.c. operation). Here, a kinetic-electrostatic model is discussed which describes the extension of the linear dynamic range of ECD by means of simple bipolar pulsed constant-current ECD. The bipolar pulse consists of an initial extraction pulse, followed immediately by a reversed biased pulse. Examples are shown which demonstrate the enhanced linearity as a function of the bipolar pulsed parameters.

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### INTRODUCTION

Electron-capture detection (ECD) has been used as a sensitive detection method for gas chromatography (GC) since 1960, and has been shown to be one of the most sensitive detection methods for qualitative or semi-quantitative trace analysis. One of the major limitations of ECD has been the non-linearity of the response to concentration. Historically, ECD has evolved with improvements in ease of useage for GC. The present electron-capture detector remains a simple chamber containing a radioactive source (typically  $^{63}\text{Ni}$ ) and two electrodes. The radioactive source emits beta particles which inelastically collide with and ionize background molecules to form multiple electron-positive ion pairs, constituting the active region of the electron-capture detector. The interactions of these ion pairs with compounds which capture electrons provide the ECD response.

The application of a d.c. voltage to the electrodes of an electron-capture detector often proved to be very limited in dynamic range. Anomalous responses were often experienced, resulting primarily from space charge regions being formed within the electron-capture detector. Additional non-linear behavior was also attributed to contact potentials being present within the electron-capture detector. This led to pulsed techniques being used to prevent space charge formation. The constant-frequency mode of operation consisted of pulsing a fixed amplitude and duration pulse,

and monitoring the resulting decrease in electron current by means of a suitable electrometer. Although Lovelock and co-workers<sup>1-3</sup> originally suggested the response of ECD to be analogous to Beer's law of light absorption, Wentworth *et al.*<sup>4</sup> developed a kinetic model which has become a useful starting point for many of the models presented in the literature.

The research of Wentworth and co-workers<sup>4,5</sup> has evolved a physical model of the pulsed electron-capture detector, which is often referred to due to its success in explaining ECD response for many practical applications as well as many gas-phase electron-attachment reactions. The basic Wentworth model assumes: (1) only electrons are collected by the extraction pulse; (2) cations and anions are immobile; (3) all free electrons are collected during each pulse; (4) and the electron-capture detector is a well-mixed reactor, one concentration exists for each species uniformly throughout the electron-capture detector. The Wentworth model contends that ECD current is a direct measurement of the electron concentration existing in the electron-capture detector immediately prior to the extraction pulse. This model is primarily used for those cases where sufficient time between extraction pulses exist for the kinetics of the cell to describe again a field-free equilibrium.

A different model has been advanced by Siegel and McKeown<sup>6</sup>, based on their studies with atmospheric-pressure ionization for mass spectrometry (API-MS). They propose that the electrostatic forces arising from the high ion densities within the electron-capture detector need to be taken into consideration. They argue that the density of these species essentially couples the electron, anion, and positive ion diffusion rates. This results in a single diffusion coefficient, characterizing the diffusion of all charged species in the electron-capture detector.

Grimsrud and co-workers<sup>7-9</sup> examined the effect of positive ions via API-MS, where, in contrast to Siegel and McKeown's work, the ion source (an electron-capture detector) was pulsed. This model acknowledges the importance of electrostatic forces between the positive and negative species, yet insists that all free electrons are collected with the application of an extraction pulse. Also between the extraction pulses, the space-charge interactions of the ions within the cell serve to effect migration of positive ions to the cell boundaries, while the electrons and negative ions will tend to migrate in the opposite direction, the electrons tending to be highly localized in the regions of highest potential.

In this article, a new mode of operating the electron-capture detector is proposed, which extends the linear dynamic range of the detector to higher concentrations. The proposed mode calls for an examination of why the cell response becomes non-linear at high pulse frequencies for a unipolar constant-current pulse-modulated electron-capture detector. The proposed model also suggests that the presence of contact potentials, as well as the mobility of both positive and negative ions be taken into consideration.

## EXPERIMENTAL

A Varian 6000 gas chromatograph with a 1075 split-splitless injector was used in this study. A Varian 402 chromatography data system was used to store and process data. The electronics for the electron-capture detector was a modification of the Varian constant-current type. A block diagram of the pulser circuit is shown in

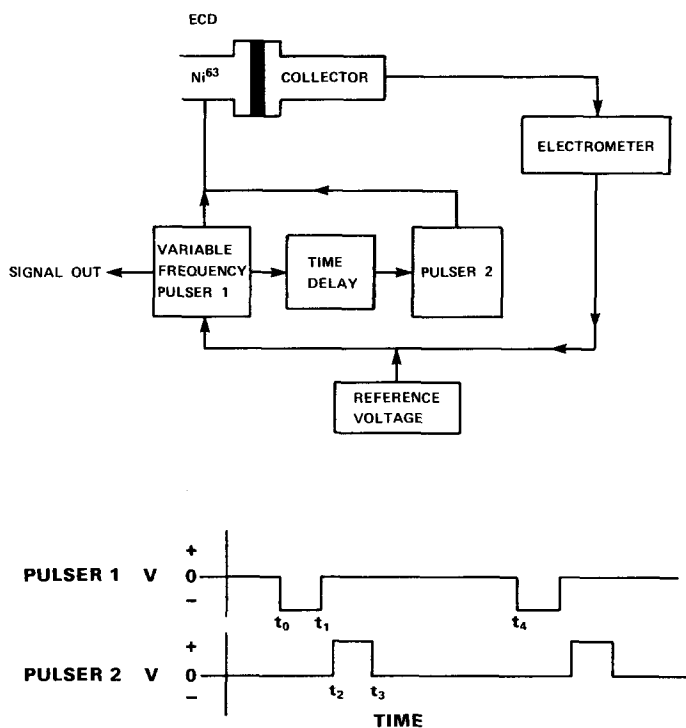


Fig. 1. Block diagram of bipolar pulsing circuit and timing diagram of pulse generators. Time markers indicate the following events:  $t_0$ , start of pulse sequence;  $t_1$ , end of first pulser waveform, start of time delay;  $t_4$ , end of time delay, start of pulser 2 waveform;  $t_2$ , end of pulser 2 waveform; and  $t_3$ , beginning of new bipolar pulse.

Fig. 1. The electrometer was not modified. The  $-60$  V supply was replaced by a HP 6116A power supply. An HP-214B pulse generator was used in an external trigger mode to enable gated positive voltage pulses with both fixed delays, duration, and amplitudes. The ECD cell was of the conventional  $350\text{-}\mu\text{l}$  displaced coaxial design. The detector temperature was maintained at  $300^\circ\text{C}$ . A SGE  $12.5\text{ m} \times 200\ \mu\text{m}$  SE-30 column was used. The 1075 split-splitless injector was maintained at  $250^\circ\text{C}$ . The column was operated isothermally at  $225^\circ\text{C}$ . The carrier gas was helium which had been passed through traps, containing activated charcoal,  $5\ \text{\AA}$  Molecular Sieve, and finally a Dow oxygen trap. Nitrogen was used as make-up gas (after being passed through a Dow oxygen trap) at a flow-rate of  $30\text{ ml/min}$ . The delay pulser utilized was a Systron Donner 100C pulse generator.

All samples were obtained from PolyScience (Niles, IL, U.S.A.) and were used without any additional purification. The solvent used was 2,2,4-trimethylpentane, and was obtained from Matheson Coleman and Bell. A stock solution was prepared by weighing the analyte, dissolving, and diluting it to  $25\text{ ml}$ . The various sample concentrations were prepared by the method of sequential dilution.

A conventional  $350\text{-}\mu\text{l}$  displaced coaxial cell was used for the bipolar pulse studies. A  $1/16$  in. outside diameter pin was inserted into the electron collector to allow comparison of the displaced coaxial cell with a concentric cylinder design.

Comparisons of these cells were made by using the constant frequency mode, provided by a Hewlett-Packard 214B pulse generator, and a Keithley 616 electrometer.

## DISCUSSION

The electron-capture detector cell geometries normally reported in the literature are primarily either concentric cylinders, or parallel plate configurations. These geometries are used in nuclear physics research to observe the arrival of single charged particles, and to determine their energy, frequency of arrival, or other phenomena. The concentric cylinder is generally configured so that the radioactive foil is part of the outer cylinder, which has a negative bias relative to the center cylinder. The electric field generated by the applied extraction pulse has the property of an increasing electric field gradient (but negative in sign) as the distance from the center pin decreases. This geometry is historically important for ionization detectors, because relatively low voltages are required to obtain gas application of ionizing events, either as a proportional counter or as the more popularly known Geiger counter. The electric field generated by a parallel plate geometry has a uniform electric field gradient across the cell. The parallel plate has been similarly used to study ionizing events and is often preferred because of its ability to quantitate higher densities of ionizing events.

The addition of a radioactive source of sufficient activity to provide enough low-energy beta particles (generating by secondary collisions a high density of electron-ion pairs) complicates the electrostatics of these designs. The effect of a constant supply of electrons and positive ions causes a long-time averaged space charge field to contribute to the electrostatics. Since the classical detectors generally analyze single ionization events, they are designed to extract rapidly electrons and ions from the active volume of the detector. The presence of contact potentials in classical ionization detectors causes no problem, because high d.c. fields are normally utilized.

In sharp contrast, the displaced coaxial design has sharp electric field gradients close to the center collector. These field gradients sharply decrease along the axis of symmetry towards the exit port. This strongly indicates that a substantial fraction of the electron-capture detector volume may not have an adequate field intensity during an extraction pulse to collect efficiently all of the electrons in the electron-capture detector. In order to probe the Wentworth premise that all free electrons are collected within a single extraction pulse, a series of experiments were conducted to evaluate different cell geometries for the same foil activity.

### *Concentric cylinder*

A 1/16-in. pin was inserted into the collector, to form a concentric cylinder of known dimensions (Fig. 2). The cell was then pulsed with an extraction pulse, and the current was monitored for all cell configurations: (1) outer cylinder pulsed positive, pin being connected to the electrometer; (2) inner pin pulsed negative, outer cylinder being connected to the electrometer; (3) outer pin pulsed negative, inner pin being connected to the electrometer; and (4) inner pin pulsed positive, outer cylinder being connected to the electrometer. The data which resulted from pulsing the above cell configurations are shown in Figs. 3-6. One notes that the electric field direction is towards the inner pin for configuration 1 and 2, while it is reversed for configu-

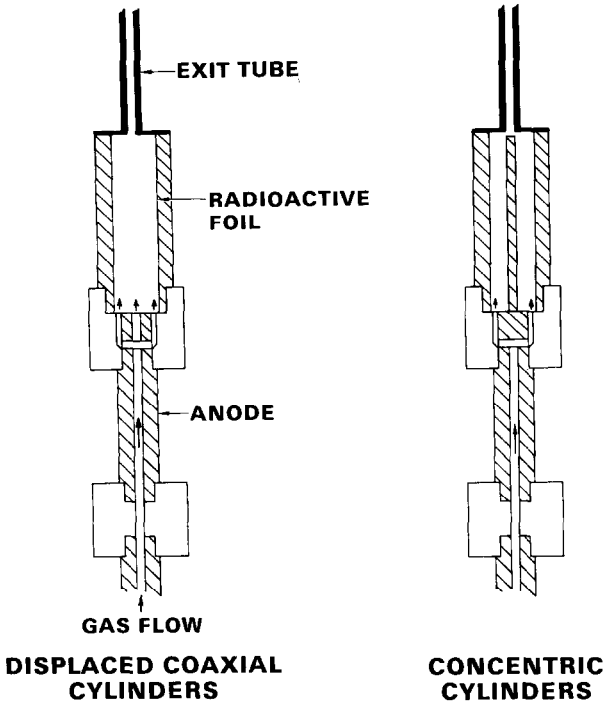


Fig. 2. Design of displaced coaxial cylinders and concentric cylinders electron capture detectors.

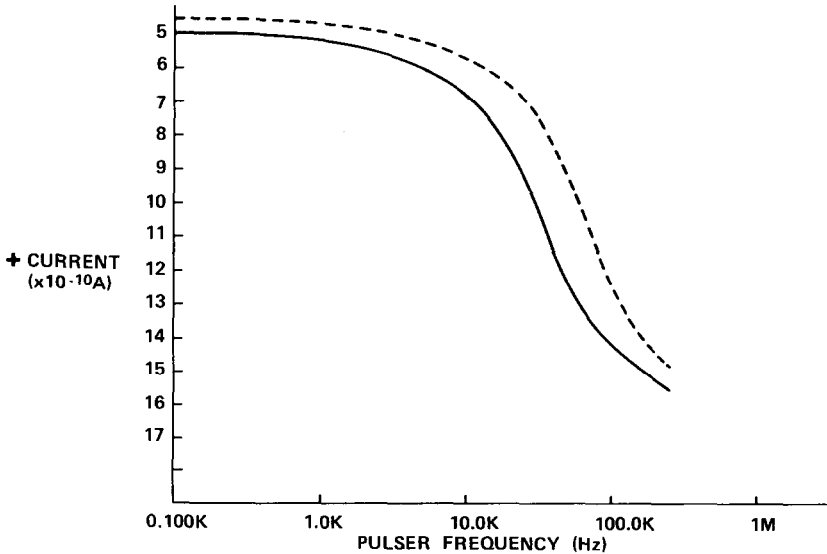


Fig. 3. Current versus pulser frequency for concentric cylinders electron-capture detector. Foil being pulsed +60 V for 600 nsec. Center pin connected to electrometer.

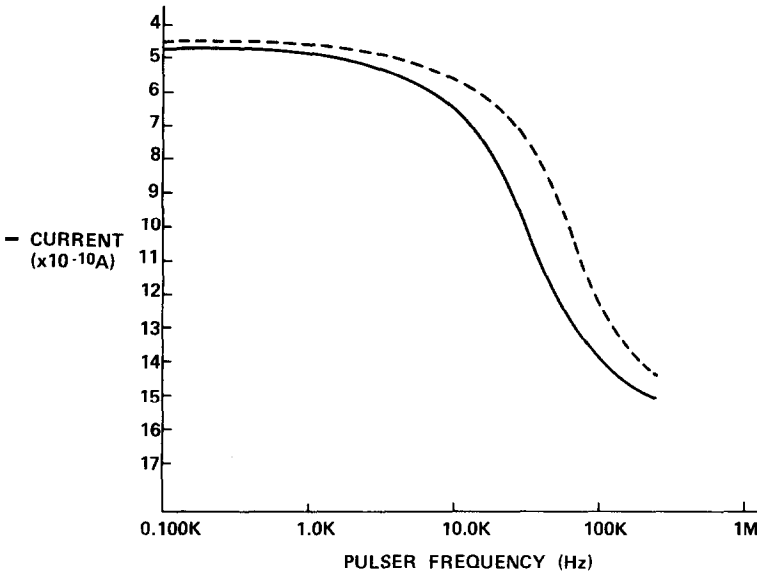


Fig. 4. Current *versus* pulser frequency for concentric cylinders electron-capture detector. Center pin being pulsed  $-60$  V for 600 nsec. Foil connected to electrometer.

rations 3 and 4. Examination of these current *versus* frequency plots, indicates that there is a considerable difference between the observed current magnitude and shape *versus* the electric field direction. However, application of a d.c. voltage across any of the cell configurations resulted in the same (absolute) current being measured. An interesting effect was also observed, which must be taken into consideration when modeling the response of the electron-capture detector, namely the presence of contact potentials within the active region of the electron-capture detector.

The effect of contact potentials is manifested by the presence of a positive current at low frequencies for configuration 3 (Fig. 5), and a negative current at low frequencies for configuration 4 (Fig. 6). However, its effect is felt at all frequencies, since it is not frequency dependent. The effect of contact potentials can also be observed at high frequencies due to an inversion of current with increasing frequency. For configuration 3, consider the effect of a contact potential located so as to generate an electric field in opposition to that generated by the pulse generator. At low frequencies, the contact potential serves to force positive ions during the pulse-free (an otherwise field-free) portion of the pulse to the center pin. During the application of an extraction pulse, the electric field generated by the pulse generator far exceeds the field generated by either the contact potential or the space charge, and therefore it simultaneously forces electrons to migrate to the wall. As a result, at the end of an extraction pulse, all the electrons are removed from the cell. Simultaneously, the positive space charge field generated by the excess positive ions forces migration of positive ions to both the wall as well as the center collector. As the electron density increases, the space charge field is overcome by the electric field generated by the contact potential, and the net effect is to force migration of the positive charge to the center pin (*i.e.* electrometer), which results in an apparently decreased current. This effect continues until the pulse generator is operating at a voltage, frequency,

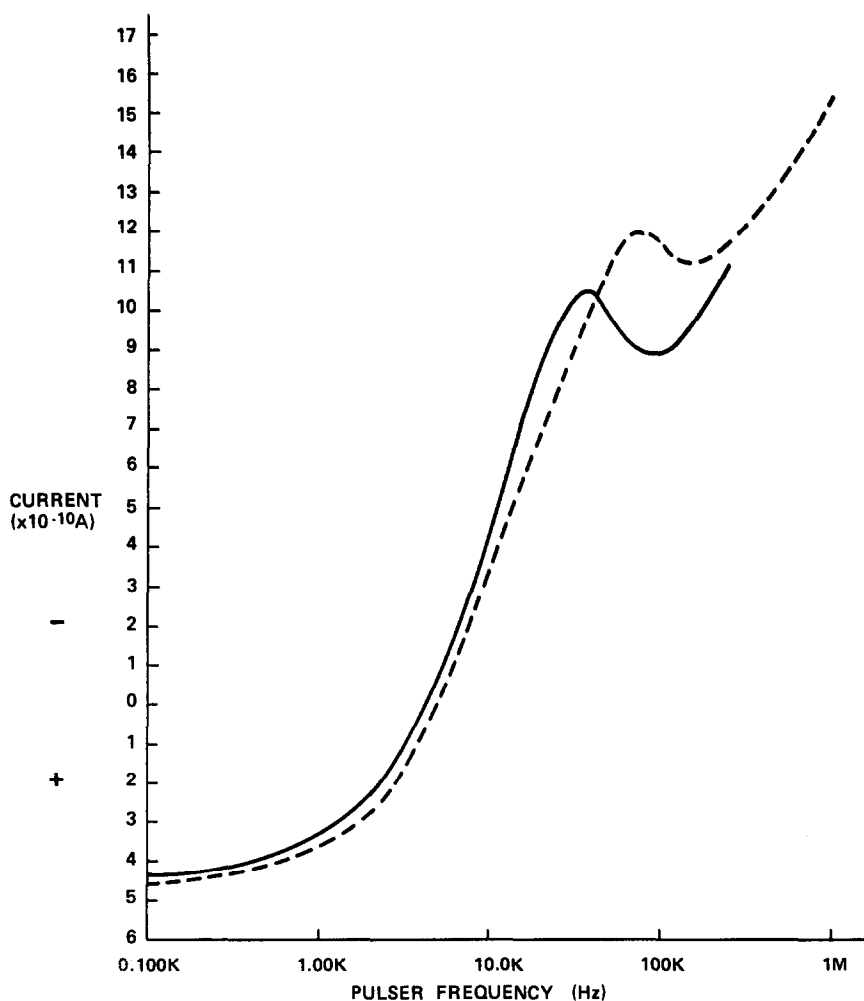


Fig. 5. Current versus pulsar frequency for concentric cylinders electron-capture detector. Foil being pulsed  $-60$  V for 600 nsec. Center pin connected to electrometer.

and pulse length sufficient to match or to overcome the contact potential. At this point, a local minimum in the current vs. frequency plot is observed. This minimum may be attributed to the averaging of the electric fields generated by the space charge (excess positive ions) and the electric fields generated by the contact potential. Increasing the base frequency results in space charge migration of positive ions to the center pin, serving to decrease the measured electron current. As the frequency is further increased, the electron-capture detector begins to operate as in the d.c. mode when an increasing d.c. voltage is applied.

Now consider configuration 4, when the center pin is pulsed positive, and the outer wall is connected to an electrometer (Fig. 6). Again, the direction of the pulsed field is towards the wall (*i.e.* positive ions are being collected by the electrometer on the outer wall). Again, the presence of a negative current at low frequencies requires

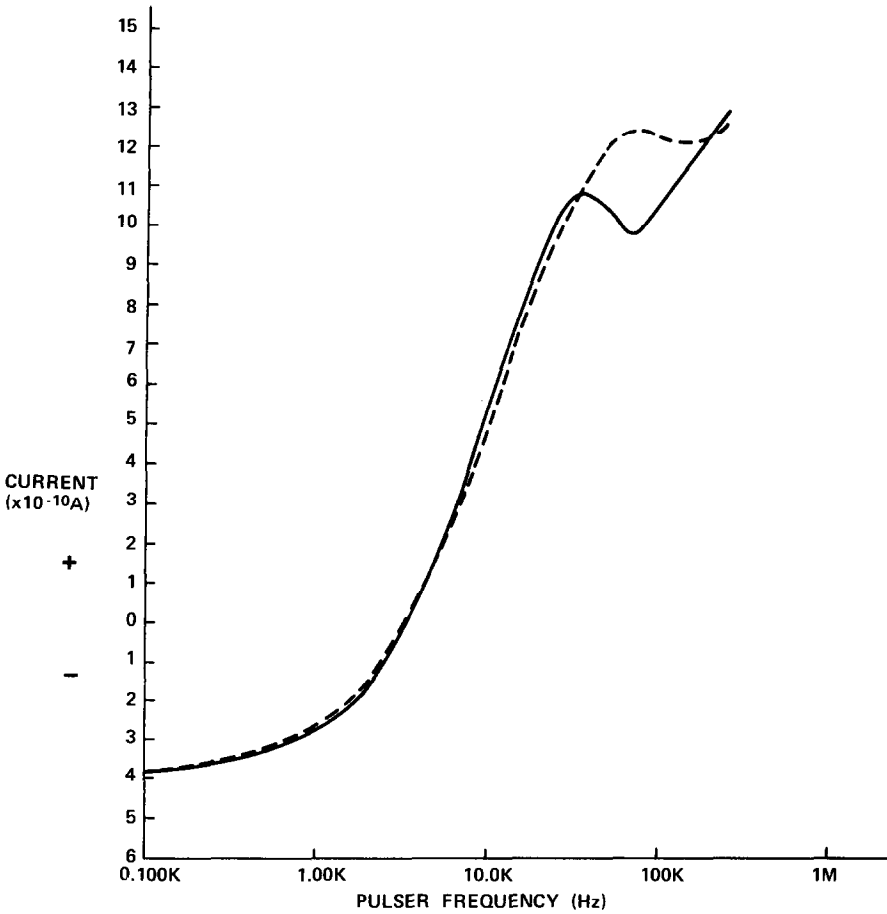


Fig. 6. Current versus pulsar frequency for concentric cylinders electron-capture detector. Center pin being pulsed +60 V for 600 nsec. Foil connected to electrometer.

the presence of a contact potential having an electric field in opposition to the pulsed electric field. The same scenario as before applies, but with the complementary charge being measured by the electrometer. At low frequencies, at the end of the extraction pulse, all electrons are extracted from the detector, and again a space charge field is generated by the excess positive ions that remain. This space charge field overpowers the electric field generated by the contact potential until enough electrons are introduced into the cell (via the radioactive source) to allow the contact potential field to exceed the diminishing space charge field. At low frequencies, the contact potential field dominates (on the average) and, indeed, even exceeds the charge extraction capabilities of the applied voltage pulse on a time averaged basis. The net effect is that a negative current is observed. Increasing the frequency results eventually in a local minimum where again the space charge field overcomes the electric field generated by the contact potential. Space charge migration of the positive ions to the center pin serves to decrease the measured positive ion current at the outer wall. With



a further increase in frequency, the electron-capture detector approaches d.c. operation.

Consider now configurations 1 and 2 (shown in Figs. 3 and 4). The electric field generated by both the contact potential and the pulser are aligned. The result of these fields being aligned is to minimize the effect of the space charge fields ordinarily present at the end of an extraction pulse. Here, the electron-capture detector is operating as a d.c. cell. The effect of an extraction pulse is to increase the time-averaged d.c. potential as a function of increasing frequency. Indeed, if a d.c. potential is applied to the electron-capture detector, the absolute current measured is the same for this concentric cylinder in any of the above configurations. At low frequencies, both configurations 1 and 2, show the same response expected of a d.c. cell. Additionally, the fact that both current *versus* frequency curves have the same shape strongly indicates that the extraction voltage is equally facile at removing positive or negative charges from the cell.

#### *Displaced coaxial cylinder*

Removal of the 1/16-in. pin from the collector returns the standard Varian 350- $\mu$ l electron-capture detector to a non-conventional design, a displaced coaxial cylinder (sometimes referred to as asymmetric cylinder geometry). This design departs from the conventional concentric cylinder design in order to minimize the collection of long range beta particles at the anode, while at the same time keeping the cell volume small relative to the size required for the concentric cylinder or parallel plate geometries. An additional benefit resulting from this design is that the extra column variance is minimized, because the flow through the detector is nearly laminar<sup>10,11</sup>. This allows the use of lower make-up flow-rates than predicted by considering the cell to be a poorly swept, turbulent volume.

According to Wentworth's model, free electrons have a high enough mobility to be readily extracted from the detector volume. To test this, the displaced coaxial cylinder electron-capture detector was pulsed with an extraction pulse, and the current was again monitored as a function of frequency for all cell configurations: (1) outer cylinder pulsed negative, displaced pin being connected to the electrometer; (2) displaced pin pulsed positive, outer cylinder connected to the electrometer; (3) outer cylinder pulsed positive, displaced pin connected to the electrometer; (4) displaced pin pulsed negative, and outer cylinder connected to the electrometer. The data obtained are shown in Figs. 7-10. The direction of the electric field is away from the displaced pin in configurations 1 and 2, while it is towards the displaced pin in configurations 3 and 4. Examination of these plots reveals that there are considerable differences between the individual pulse profiles for all the different configurations. This is primarily due to the differences in the equipotential surfaces (or field gradients) when the displaced coaxial cell is compared with the concentric cylinder cell, as shown in Figs. 11 and 12. A striking difference is immediately obvious, *i.e.* a large region of low electric field gradient in the displaced coaxial cylinder.

The effect of this region of low electric field gradient for the displaced coaxial cylinder electron-capture detector is observed by closely examining configurations 1 and 2, as shown in Figs. 7 and 8. Although the general shape of the collected current *versus* frequency curves are the same, configuration 1 results in electrons being collected, while configuration 2 results in positive ions being measured by the electrom-

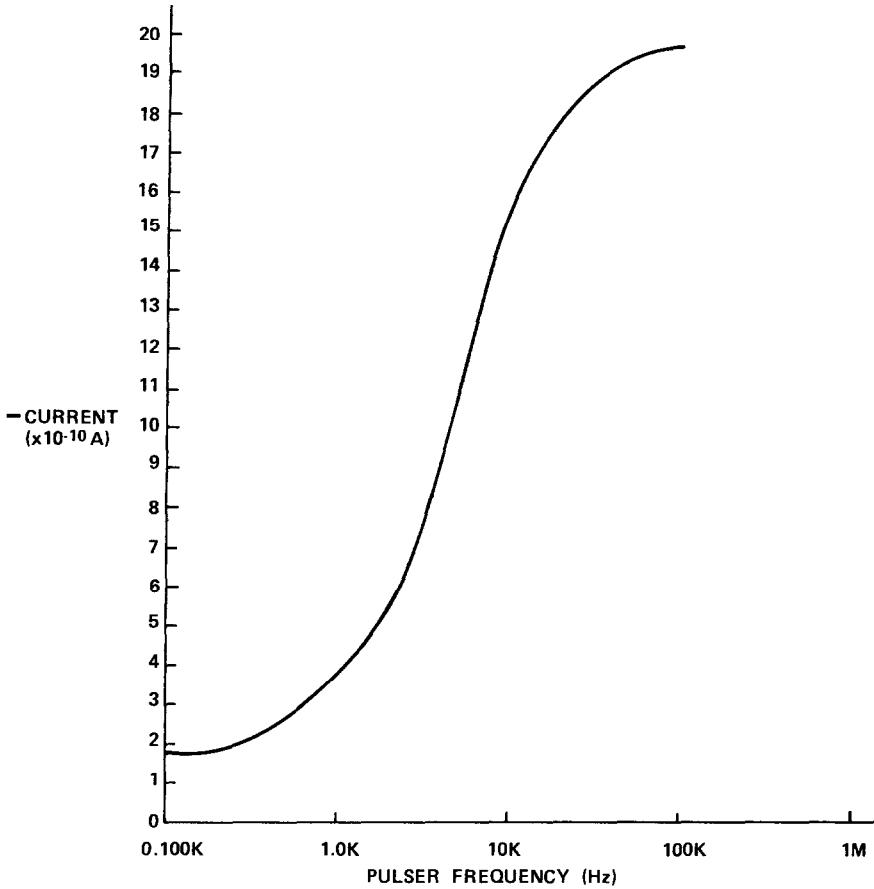


Fig. 7. Current *versus* pulser frequency for displaced coaxial cylinders electron-capture detector. Foil being pulsed  $-60$  V for 600 nsec. Displaced pin connected to electrometer.

eter. In either configuration 1 or 2, the electrons are rapidly extracted in an increasing electric field gradient, whereas the ions are being extracted, but at a substantially decreased rate. Since no major inflections are observed in these curves, any contact potentials are either aligned with the extraction field, or they are located in the region of low electric field generated by the pulsed extraction voltage.

Reversing the direction of the electric field, as per configurations 3 and 4, strongly reveals the importance of choosing the proper configuration for ECD (Figs. 9 and 10). Configuration 3 reveals that a contact potential must be present that provides a strong influence on the collection of positive ions within the electron-capture detector. Indeed, the field generated by the contact potential must be in close proximity to the displaced pin, because of the extremely high collection efficiency of electrons. This is demonstrated by the large negative current measured at low pulser frequencies for configuration 3. Configuration 4 reveals that either the field generated by the contact potential has only a modest effect on the collection of electrons at the outer cylinder, or that the mobility of the electron is significantly larger than the

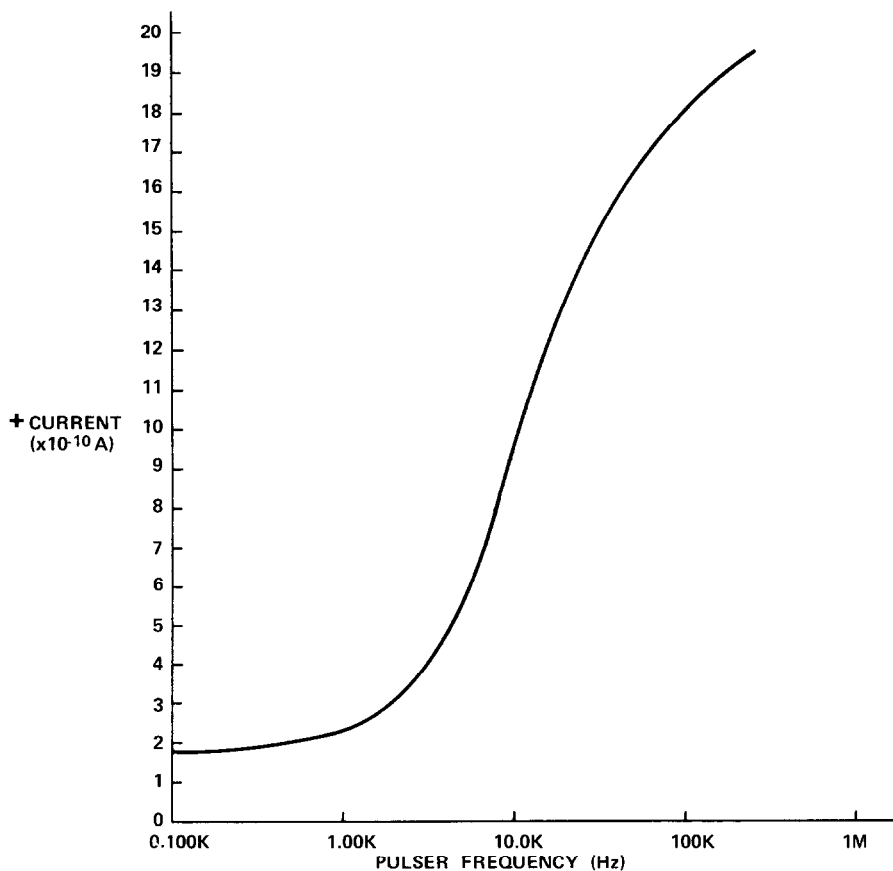


Fig. 8. Current *versus* pulsar frequency for displaced coaxial cylinders electron-capture detector. Displaced pin being pulsed +60 V for 600 nsec. Foil connected to electrometer.

positive ion mobility and space charge migration of positive ions is minimized for collection at the center displaced pin, being significant for collection at the wall.

Configuration 3 reveals the presence of an inflection in the current *versus* frequency curve, as shown in Fig. 9. On a time-averaged basis at low frequencies, the contact potential field pulls to the displaced pin more electrons than the pulsed field can pull positive ions. At the inflection point, the positive charge driven by the excess positive space charge to the displaced pin is very small, primarily because the excess positive space charge is not as large (due to the minor extraction of electrons from the low field region of the cell). A secondary factor is a geometric consideration; the surface area of the displaced pin is small in comparison to the total surface area of the electron-capture detector. Thus, one would expect the transition to occur at near equal currents of positive (pulsar field driven) ions, and electrons (contact potential-generated electric field). This is what is observed. At higher frequencies, the low mobility of the positive ions is reflected by the lack of a limiting current plateau.

Several conclusions can now be drawn: (1) contact potentials exist within an

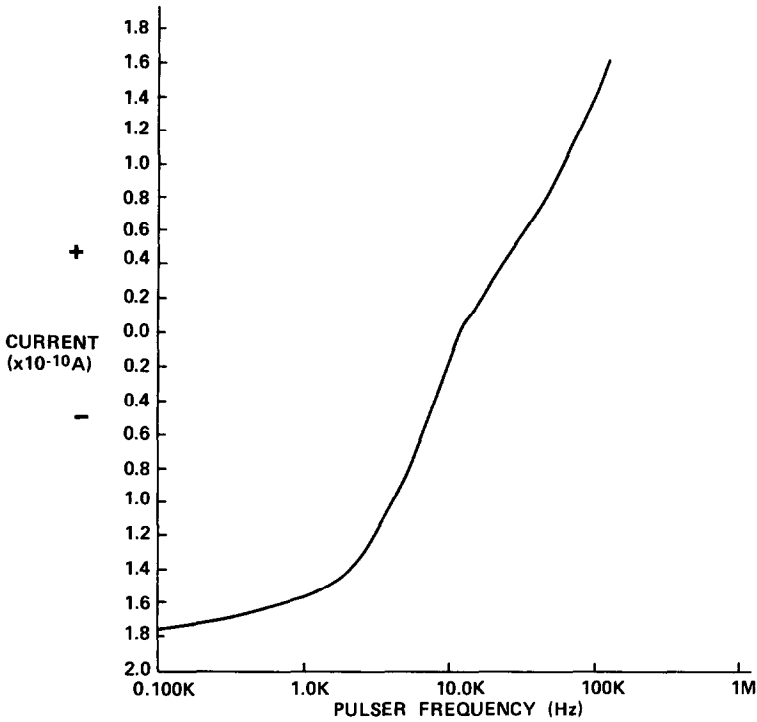


Fig. 9. Current *versus* pulsar frequency for displaced coaxial cylinders electron-capture detector. Foil being pulsed +60 V for 600 nsec. Displaced pin connected to electrometer.

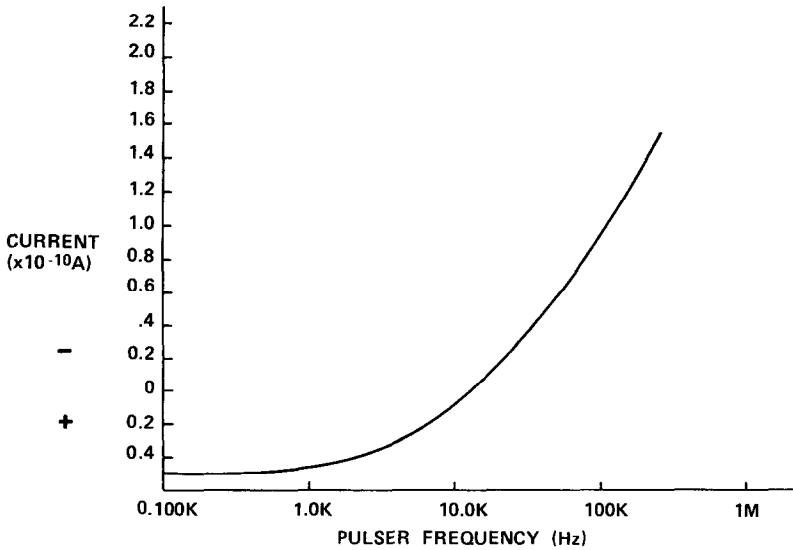


Fig. 10. Current *versus* pulsar frequency for displaced coaxial cylinders electron-capture detector. Displaced pin being pulsed -60 V for 600 nsec. Foil connected to electrometer.

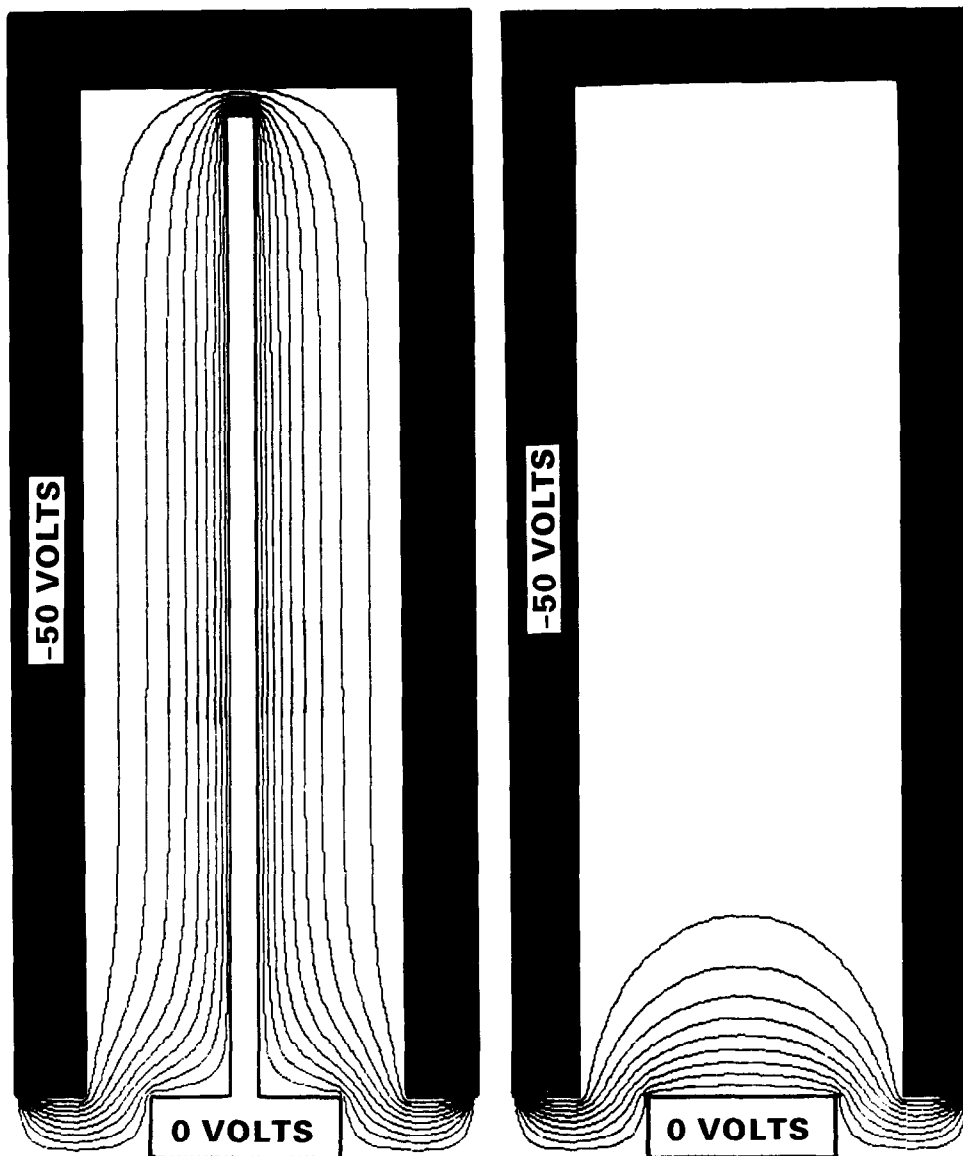


Fig. 11. Equipotential surfaces existing within a concentric cylinders electron-capture detector. Each line corresponds to a decrease of 5 V from the previous line.

Fig. 12. Equipotential surfaces existing within a displaced coaxial cylinders electron-capture detector. Each line corresponds to a decrease of 5 V from the previous line.

electron-capture detector; (2) the direction of the electric field of the contact potential in this particular cell is towards the outer cylinder; (3) the contact potential is located in the region of high electric field gradient; (4) space charge fields primarily direct positive ions to the outer cylinder and have a minor effect on ion collection at the

displaced pin; (5) the electron mobility significantly exceeds positive ion mobility; (6) the effect of ion mobility becomes more apparent at high frequencies.

Connecting the displaced coaxial cylinders electron-capture detector to a capillary column and using a 1075 split injector, a calibration curve was obtained, the cell being operated in the constant current mode (see Fig. 13). The reference current was varied to maintain the same base (sample free) frequency for several voltages. For a  $-10$  V 600 nsec pulse, a reference current of 145 pA was required for a sample free frequency of 1.60 kHz. For a  $-20$  V 600 nsec pulse, a reference current of 214 pA, and for  $-30$  V 600 nsec pulses, a reference current of 256 pA was required to obtain a sample free (base) frequency of 1.60 kHz. These currents reflect the fact that the drift velocity of electrons follows a square root dependence on the electric field strength at constant pressure for sufficiently low electric field intensities, as predicted from kinetic theory based on elastic impacts of thermal electrons. Additionally, the linearity of the electron-capture detector remains the same for all of these extraction voltages. However, the dynamic range decreases for lower extraction voltages due to increased noise. This introduces an interesting concept: the entire cell volume need not be swept free of electrons by the extraction pulse for quantitative analyses. If this is true, then the non-linear response of the electron-capture detector at high concentrations may be due to collection of anions in addition to electrons at high pulse frequencies.

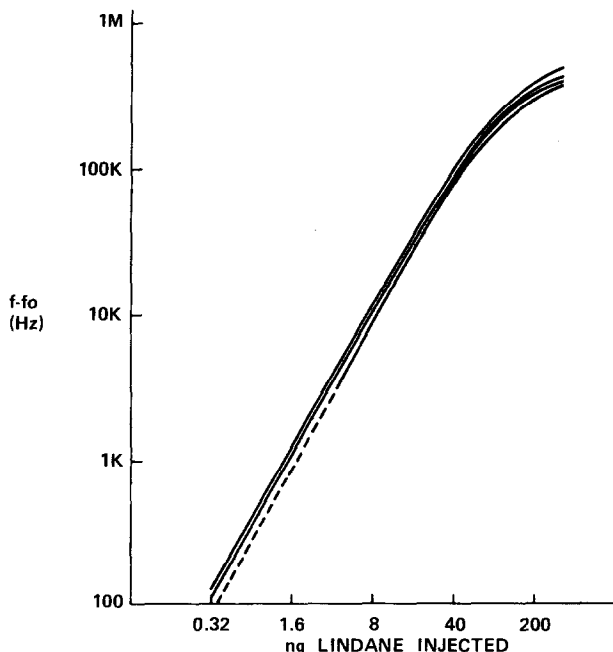


Fig. 13. Change in frequency *versus* concentration of lindane injected. Split ratio 300:1. For  $-40$  V, the reference current was 295 pA. For  $-30$  V, the reference current was 256 pA. For  $-20$  V, the reference current was 214 pA. For  $-10$  V, the reference current was 145 pA. These currents and voltages represent a base frequency of 1.60 kHz. for a coaxial cylinder electron-capture detector, foil pulsed, and displaced pin connected to electrometer.

### Bipolar pulsing

The basic scheme of the bipolar pulser and timing diagram is shown in Fig. 1. The pulse amplitudes and positioning are monitored via an oscilloscope to establish the pulse widths, delay times, and pulse amplitudes of all pulsers. Limitations of this design are due to the positive pulse generator not being capable of providing positive pulses in excess of +40 V at frequencies exceeding 300 kHz.

Noise measured for the bipolar mode was the same as that for the unipolar mode at the same base frequency and negative pulse voltage. A modest increase in base frequency was observed for the bipolar mode which increased as the positive pulse amplitude increased. For a reference current of 275 pA, the (unipolar) base frequency of 1.80 kHz (-50 V, 600 nsec) increased to 1.87 kHz bipolar base frequency (-50 V for 600 nsec, 400 nsec delay, +40 V for 600 nsec).

Examination of the bipolar circuit standing current as a function of pulser voltages were made for several frequencies (see Figs. 14-16). The cell configuration was designed to pulse the outer cylinder (containing the radioactive foil) and to measure the electron-ion current collected by the displaced coaxial cylinder. Here, the feedback circuit was disabled, and a Keithley 616 electrometer was used to measure the current. In a test for -15 V, -25 V and -50 V (600 nsec), followed by a fixed positive voltage pulse (600 nsec, 1  $\mu$ sec delay), a difference was found from the Wentworth model when a displaced coaxial cylinder electron-capture detector was used: either not all of the electrons are being extracted by the application of the initial extraction pulse or the cations have a substantial mobility and are major contributors to the measured current, or both.

Figs. 14-16 indicate that not all the electrons are removed from the active region of the electron-capture detector. Positive ions are not expected to be collected by the displaced coaxial pin, since their displacement in the field generated by the negative pulse should be compensated by a similar displacement in the reverse direction due to the field generated by the positive pulse. This implies that the displaced

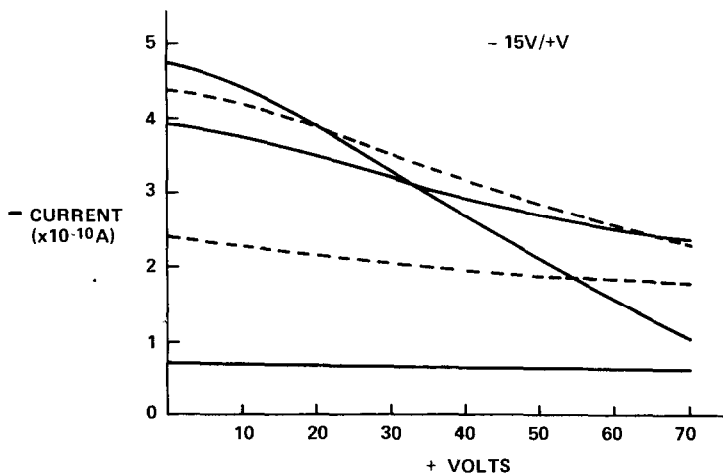


Fig. 14. Current versus positive voltage amplitude for bipolar pulsing. The initial pulse is -15 V for 600 nsec, the delay is 1  $\mu$ sec, and the second pulse is 600 nsec, amplitude is positive.

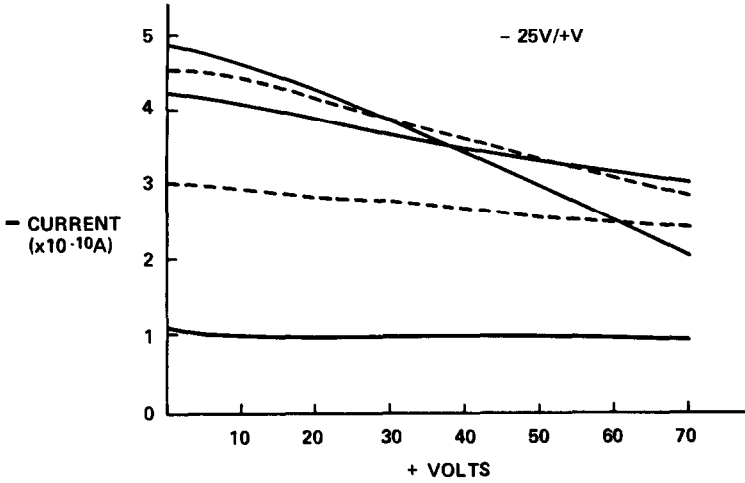


Fig. 15. Current *versus* positive voltage amplitude for bipolar pulsing. The initial pulse is  $-25$  V for 600 nsec, the delay is  $1 \mu\text{sec}$ , and the second pulse is 600 nsec, amplitude is positive.

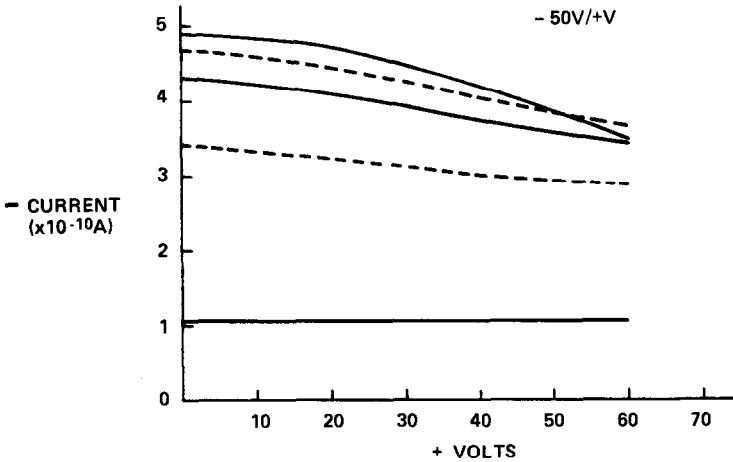


Fig. 16. Current *versus* positive voltage amplitude for bipolar pulsing. The initial pulse is  $-50$  V for 600 nsec, the delay is  $1 \mu\text{sec}$ , and the second pulse is 600 nsec, amplitude is positive.

coaxial cylinders electron-capture detector may be considered to consist of two regions: a) a high electric field region, where all electrons are collected by a pulse; and b) a low electric field region, where electrons move into a region of increased electric field intensity during the application of an extraction pulse, but are not collected during the extraction pulse. The application of a positive pulse immediately following the negative pulse results in moving the electrons out of the high field area, and if the amplitude of the positive pulse is greater than the amplitude of the negative pulse, it will remove electrons from the cell as well as allow positive ions to be collected. The net effect of a bipolar pulse is to decrease the measured electron current. This effect is emphasized at high frequencies due to the lower average electron density in



the cell, and a relatively larger fraction of electrons being removed by the positive pulse. Another interesting point shown is the fact that there is a crossing of constant-frequency lines as a function of increasing positive voltage. Fixed negative and positive pulses show a strong reversal of current as a function of increasing pulser frequency. Using a sufficiently high reference current for a specific bipolar pulse amplitude will generate these profiles in the constant-current mode, and will result in non-linear behavior (*i.e.* increasing sensitivity as a function of increasing analyte concentration).

With the electronics in the configuration shown in Fig. 1, the linearity of the detector operating in the bipolar pulsed, constant-current mode can be examined at low concentrations by simply making a series of injections at constant volume and concentration, the variable investigated being the amplitude of the positive pulser. Fig. 17 reveals that the peaks for a standard constant current mode are of the same shape as those obtained for the various bipolar pulse amplitudes. If these peaks are normalized with respect to peak amplitude, the peak shapes are very nearly identical. At the other extreme, if one examines the response of the electron-capture detector for high concentrations (as shown in Figs. 18 and 19), a significant increase in peak height is observed as a function of increased positive pulse amplitude. The +30 V pulse did not continue the trend observed for the +10 and +20 V pulse, due to the inability of the pulse generator to supply +30 V at frequencies exceeding 300 kHz, but instead, it generated a distorted peak, shown in Fig. 19.

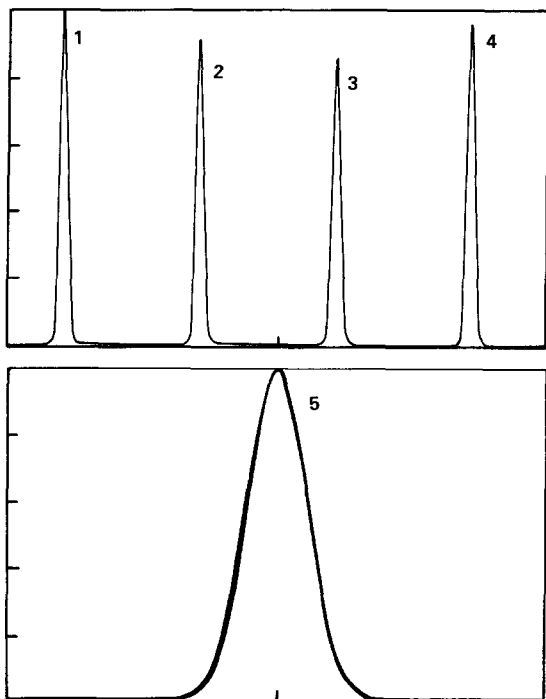


Fig. 17. Low concentrations of Lindane (0.32 ng injected, 300:1 split ratio) for bipolar pulsers, 1.17 kHz base frequency. (1) -50 V; (2) -50 V, +30 V; (3) -50 V, +20 V; (4) -50 V, +10 V; (5) simulated  $W_{1/2} = 1.3$  sec. Lower figure shows all peaks (1-5) plotted with normalized peak heights.

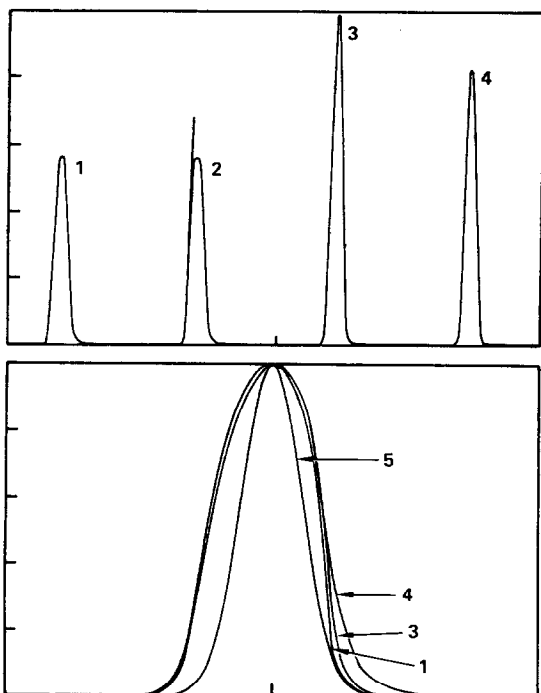


Fig. 18. High concentration of lindane (200 ng injected, 300:1 split ratio) for bipolar pulsers, 1.17 kHz base frequency. (1)  $-50$  V; (2)  $-50$  V,  $+30$  V; (3)  $-50$  V,  $+20$  V; (4)  $-50$  V,  $+10$  V; (5) simulated  $W_{1/2} = 1.3$  sec.

The kinetic model of electron capture<sup>12</sup> reveals a strong temperature dependence on the response of an electron-capture detector with respect to strongly attaching compounds. Due to temperature limitations of the radioactive source, the optimum sensitivity and specificity may not be readily obtained when the standard d.c., constant frequency, or constant current mode is used. Popp *et al.*<sup>13</sup> modified the d.c. mode of operation by applying a fixed radio-frequency voltage (0–600 V, 30 MHz) onto a fixed d.c. offset (0–150 V). The effect of this modification is to pump energy into the free electrons, permitting tuning of their “temperature” to an optimum for electron attachment to a specific molecular species.

While the bipolar pulse does pump some energy into the electron-capture detector (as reflected by charge being extracted from the ionizing region of the electron-capture detector), the long pulse widths, low pulse amplitudes, and relatively long pulse periods more closely resemble a field-free cell with a large amount of time for thermal equilibration of the free electrons. At frequencies where the bipolar pulser begins to linearize the response of the electron-capture detector (*i.e.* above 80 kHz), the cell is still in a field-free condition most of the time. The fact that the displaced coaxial cylinder electron-capture detector becomes non-linear for a multiple of compounds around 80 kHz strongly indicates that another charged species is collected in addition to electrons.

Fig. 20 reveals the response of the electron-capture detector, operated at several different base frequencies (*i.e.* reference currents). At low frequencies, the effect

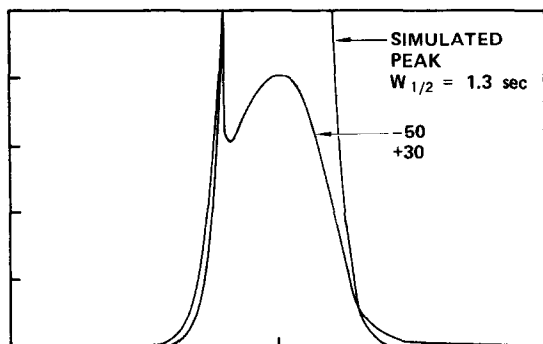


Fig. 19. Simulated Gaussian peak (5 times  $-50$  V pulser only) for 200 ng Lindane injected (split ratio 300:1), 1.17 kHz base frequency. Observed  $-50$  V,  $+30$  V peak has discontinuity due to positive high voltage pulser not being able to pulse at  $+30$  V at frequencies exceeding 300 kHz.

of the bipolar pulser is to increase slightly the sensitivity of the detector. The most notable effect of the bipolar pulser is to linearize the response of the electron-capture detector at high sample concentrations where the cell is normally non-linear. As described above, the geometry of the cell can be described to consist of a high electric field and a low electric field region. For the unipolar constant current mode, the effect of high sample concentration and high frequency is to generate a negative ion sheath which contributes to the measured electron current, and this results in a non-linear response. The action of the bipolar pulse is to cause the motion of the negative ions during the extraction (negative) pulse to be reversed by a positive pulse of equal duration. The effects of the positive pulse are observed primarily when the cell is at relatively high frequencies so that the motion of the negative ions exceeds diffusion by the negative ions during the field free portion of the pulse cycle.

As suggested above, the higher reference currents (or higher base frequencies) generate non-linear behavior at higher concentrations due to an inversion of the current as a function of increasing frequency. The higher reference currents have the additional drawback of increased noise. Together, they combine to decrease the linear dynamic range of the detector.

Similarly, the requirements for maximum sensitivity and coulometric operation are incompatible with capillary gas chromatography. Connor<sup>14,15</sup> and Rosiek *et al.*<sup>16</sup> have presented models for an electron-capture detector, operating in a coulometric mode, which requires large cell volumes, low flow-rates, and large forward electron attachment rate constants. The driving force behind operating an electron-capture detector in the coulometric mode is the difficulty of making calibration standards for the multitude of compounds at sub-picogram levels. The reason for the quantitation difficulties at trace levels has been partially the presence of large metal surfaces and a turbulent cell design (as required by the Wentworth model) which results in sample loss due to adsorption on active metallic sites. These difficulties are exacerbated when hydrogen is used as carrier gas. A recent modification of the displaced coaxial cylinder electron-capture detector<sup>11</sup> showed that sample adsorption on active metallic sites must be minimized. The column effluent must not be allowed to come in contact with metal surfaces prior to entering the ionizing region of the electron-capture detector. An additional requirement is laminar flow through the detector to minimize

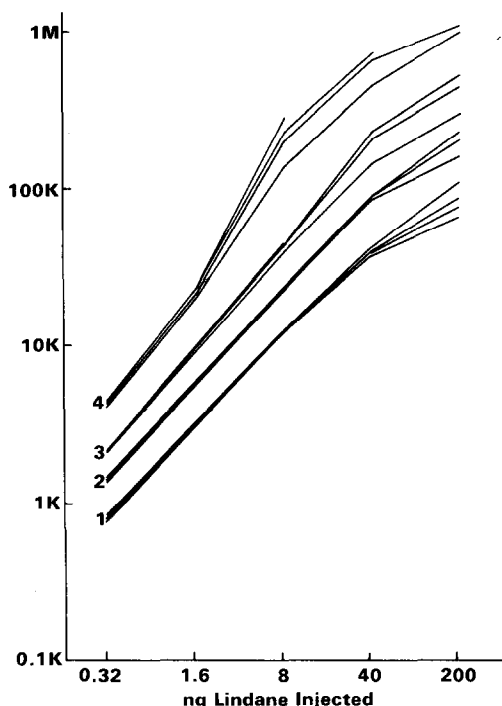


Fig. 20. Change in frequency *versus* lindane injected (split ratio 300:1) for  $-50$  V (600 nsec) followed by  $+0$  V,  $+10$  V,  $+20$  V, and  $+30$  V (600 nsec). Different base frequencies are obtained by changing the reference current. (1) 700 Hz; (2) 1.17 kHz; (3) 1.80 kHz; (4) 3.60 kHz.

not only sample adsorption on the outer walls, but also the time constant of the electron-capture detector for high-speed and high-resolution capillary chromatography.

## CONCLUSIONS

The results presented here show that a bipolar pulsed constant-current electron capture detector can be used to extend the linear dynamic range to higher concentrations. The non-linear behavior observed at high concentrations (high frequency) is attributed to collection of anions as well as electrons. For a displaced coaxial cylinder electron-capture detector, negative ions and electrons contribute to the observed electron-capture detector response. The geometry of the electron-capture detector is important with respect to positive ions being driven onto the electron-capture detector anode by the space charge-generated electric field immediately following the electron extraction pulse. The use of a displaced coaxial electron-capture detector minimizes this effect, as compared with a concentric cylinder design. The action of the bipolar pulser is to reverse the displacement of the ions due to the initial extraction pulse to their original position, thus minimizing the collection of anions.

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