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PULSE-MODULATED ELECTRON CAPTURE DETECTION WITH NITROGEN CARRIER GAS

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SUMMARY

In comparison to d.c. operation, pulse-modulated operation of an electron capture detector (ECD) is shown to provide large improvements in linear range and sensitivity. A unique displaced-coaxial-cylinder electron capture cell allows the benefits of pulsed operation to be achieved using nitrogen as the carrier gas. Sample detectivities at the 0.1-pg level are exhibited, as well as linear ranges exceeding 10^4. Dependence of the range of linearity on flow-rate and retention time demonstrates that this ECD functions as a concentration-type detector. The inherent baseline stability of pulse-modulated operation also allows the use of column oven programming techniques in the analysis of samples at the 10-pg level.

INTRODUCTION

In recent years, the traditional d.c. method of operating electron capture detectors (ECDs) has become more and more replaced by a type of electronic operation called the constant-current pulse-modulated method[1,2]. The primary advantage of pulse-modulated operation is that it provides a greatly increased range of linear and dynamic response. In addition, pulsed ECD operation generally provides better detector baseline stabilities compared to d.c. operation for reasons basically described by Lovelock[3].

Previous descriptions of pulse-modulated operation have largely emphasized the use of an argon–methane mixture as the gas chromatographic (GC) carrier gas rather than nitrogen. This results from the requirement for very narrow pulse widths, and the fact that electron drift velocities in argon–methane are much higher than in nitrogen. As a consequence, most conventional ECD cell geometries can be made to function satisfactorily in a pulse-modulated mode if argon–methane is used, but performance with nitrogen is often greatly degraded[2]. Two obvious disadvantages of argon–methane are its added cost compared to nitrogen, and its incompatibility with other commonly used GC detectors.

This paper describes the design of an ECD system developed specifically to operate in a constant current, pulse-modulated mode using nitrogen as the carrier gas. The operating characteristics of this new ECD are described for a variety of

experimental conditions. In addition, an attempt is made to further clarify the pulse-modulated method of operation by pointing out correlations between the pulsed and d.c. modes wherever possible.

EXPERIMENTAL

Data reported in this paper were obtained with a Varian Model 3700 gas chromatograph equipped with a pulse-modulated ECD. The electron capture cell in this instrument is a ceramic–metal assembly capable of operating at temperatures exceeding 400 °C. The cell contains a 7.5 mCi ^{63}Ni foil, and is polarized with negative voltage pulses of 50-V amplitude and 0.64-μsec width. Some d.c. mode data are also reported in this work. These data were obtained using a Keithley Model 240 power supply for a 50-V polarizing voltage, and using the electrometer in the Model 3700 instrument to measure negative currents.

All chromatographic data were obtained using Pyrex columns of dimensions 183 cm × 6 mm O.D. × 2 mm I.D. Column packing materials and operating conditions are indicated where they were used. Nanograde benzene obtained from Mallinckrodt (St. Louis, Mo., U.S.A.) was used as a solvent, and pesticide samples were prepared by dilutions of standard solutions obtained from PolyScience (Niles, Ill., U.S.A.).

PULSE-MODULATED OPERATION

The electronic method of achieving pulse-modulated operation differed slightly in this work from that described by Maggs *et al.*[2]. A block diagram of the pulse-modulated ECD circuit is illustrated in Fig. 1. Included are the basic components common to any method of ECD operation. Namely, there is an EC cell containing a radioactive foil, an ionized gas volume and an electron collector; there is a means of polarizing the cell using a negative voltage; and there is a means of measuring current emanating from the cell. The unique feature of pulse-modulated operation is that

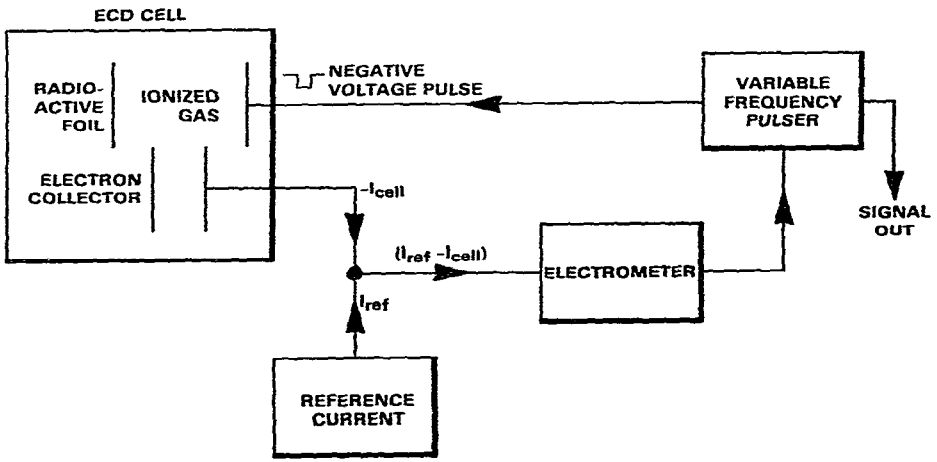

Fig. 1. Block diagram of the electronic components of a constant-current pulse-modulated ECD.

these components are all coupled together to form a closed loop electronic feedback network. Hence, the cell current ($-I_{cell}$) is combined with an external reference current (I_{ref}) such that the difference ($I_{ref} - I_{cell}$) is the input to an electrometer; the electrometer output feeds into the pulse-generating network such that the pulse frequency is determined by the magnitude of the electrometer output; and the frequency of voltage pulses in turn determines the magnitude of I_{cell}. The system works by electronically varying the pulse frequency so as to maintain $I_{cell} = I_{ref}$. Since pulse frequency is the variable quantity in this method of operation the output signal is a voltage proportional to that frequency.

The average current I_{cell} is proportional to the concentration [e] of free electrons in the cell, and the frequency f of the applied voltage pulses as follows:

$$I_{cell} \propto [e]f$$

Hence, when only carrier gas is in the cell, [e] is relatively large and f is low. This pulse frequency with pure carrier gas can be defined as the base frequency f_0 of the system. Typically, f_0 is so low that the time between pulses is about 1000 times longer than the width of each pulse. Hence, for most of the time there is no polarization voltage across the cell. When an electronegative sample enters the EC cell, it converts some of the free electrons in the cell to negative ions. Hence, [e] decreases and f increases in order to keep I_{cell} constant. The passage of an electronegative sample through the electron capture cell produces an output signal with peak height proportional to the frequency difference ($f_A - f_0$) where f_A is the frequency corresponding to a sample concentration [A] within the EC cell. Maggs *et al.*[2] have shown that ($f_A - f_0$) is proportional to [A], so that there is an inherently linear relationship between peak height signal and sample concentration. This linear relationship constitutes a major advantage of pulse-modulated operation in comparison with the previous d.c. method of operation.

Electronically, the maximum possible pulse frequency coincides with the point where adjacent pulses begin to overlap. Hence,

$$f_{max.} = (\text{pulse width})^{-1}$$

At $f_{max.}$, the electron capture cell is in effect polarized by a continuous d.c. voltage equal in magnitude to the pulse amplitude. In order for the pulse-modulated ECD to respond to very large sample concentrations, it is necessary that the pulse width be very narrow so that $f_{max.}$ can extend to large values. Typically, the pulse-modulated method employs pulse widths which are only a fraction of a microsecond wide.

CELL DESIGN CONSIDERATIONS

There are two basic considerations in designing an electron capture cell for optimum pulse-modulated operation. First, there is the requirement that there be minimal electron current at the collector electrode during the time between pulses when the pulse voltage is off. If this is not the case, then there is a contribution to the cell current which does not vary with pulse frequency, and the result is a non-linear response. Sources of this "field-free" background current can be: (a) long-range β

particles from the radioactive foil, (b) electrons diffusing out of the ionized gas volume, (c) convection of electrons if the gas flow is such as to sweep ionized particles into the collector.

With many conventional electron capture cell geometries, the minimization of this "field-free" current necessitates a relatively large cell volume with large separation between the radioactive foil and collector electrode.

The second basic consideration in cell design is the requirement for maximizing the collection of free electrons during the time the pulse voltage is on. Specifically, the free electrons must be able to travel the distance between the radioactive foil and collector electrode within the submicrosecond width of the voltage pulse. This is a principal area of difference between pulsed operation with nitrogen and argon–methane carrier gases. For the electric fields typically used in an ECD, the electron drift velocity in argon–methane is about ten times larger than in nitrogen[4]. Hence, in order to obtain satisfactory pulsed operation with nitrogen, the electron capture cell must have a relatively close spacing between the radioactive foil and the collector electrode.

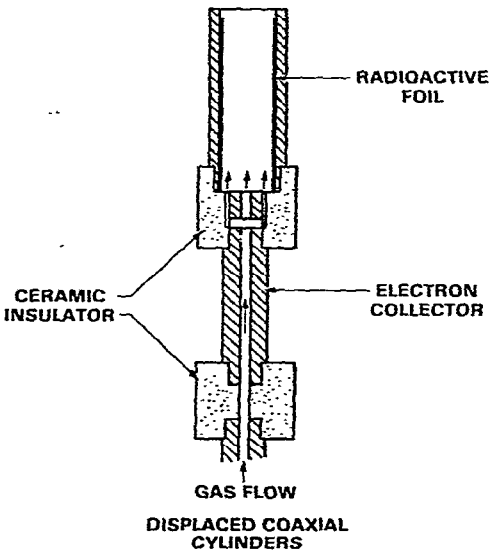

Fig. 2. Schematic illustration of a displaced-coaxial-cylinder electron capture cell.

Fig. 2 shows a schematic illustration of the unique cell geometry used in this work. This cell has a displaced-coaxial-cylinder geometry (sometimes referred to as an asymmetric geometry in previous reports)[3]. The larger cylinder contains the radioactive foil, and a second cylinder of smaller diameter serves as the electron collector. Gas flow from the GC passes through the collector cylinder first, then up through the foil cylinder. By locating the collector cylinder entirely upstream of the ionized gas volume, exposure to long-range β particles is minimal, and gas flow minimizes diffusion and convection of electrons into the collector. However, the free electrons are mobile enough that modest pulse voltages (*e.g.*, 50 V) are adequate to cause the electrons to move against the gas flow and to be collected during the time the pulse is

on. This geometry has allowed the construction of an electron capture cell of very low volume (300 μl) for increased detectivity of samples. Also, a relatively small separation between the collector electrode and the ionized gas volume is achieved, so that efficient electron collection is realized even with nitrogen carrier gas.

RESULTS AND DISCUSSION

Correlations between pulsed and d.c. operation

Fig. 3 illustrates a basic set of operating curves describing pulsed and d.c. operation of an ECD. These operating curves consist of plots of cell current *versus* pulse frequency. There exists one curve for pure carrier gas and one curve each for carrier plus sample in increasing amounts. The family of curves shown in Fig. 3 correspond to a displaced-coaxial-cylinder cell geometry, operating with nitrogen carrier gas, using a pulse width of 0.6 μsec, and a pulse amplitude of 50 V. The relative positions of the curves change if a different cell geometry, carrier gas, or pulse parameters are used.

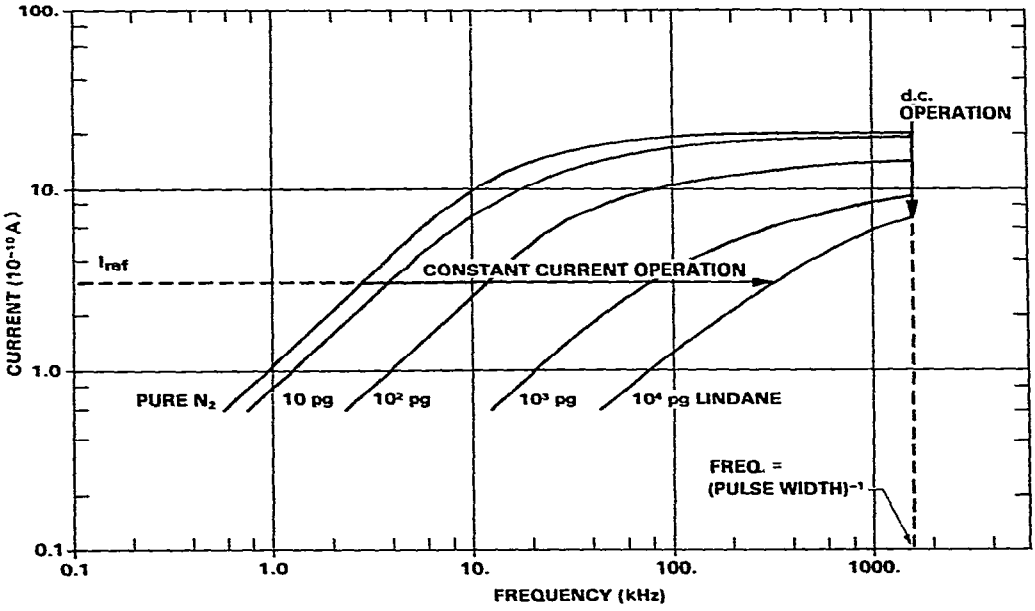

Fig. 3. Basic current *versus* frequency operating curves illustrating operation in a constant-current pulse-modulated mode and in a d.c. mode.

The d.c. operation is represented in Fig. 3 by current changes along a vertical line at the point where $f =$ (pulse width)$^{-1}$. In the d.c. mode, the cell exhibits its characteristic standing current with pure nitrogen present, and additions of sample cause decreases in the cell current. Operation in the constant-current pulse-modulated mode is represented in Fig. 3 by frequency changes along a horizontal current level corresponding to I_{ref}. With pure nitrogen, the cell operates at its characteristic base frequency f_0, and additions of sample cause increases in the frequency.

Measurements of the base frequency f_0 are the pulsed analog of d.c. measurements of standing current. Just as a contaminated foil, a high column bleed, or an impure carrier gas cause a decrease in standing current in the d.c. mode, they also cause an increase in base frequency in the pulsed mode. Hence, the magnitude of f_0 can be used to monitor the cleanliness of the ECD system. From variations in nitrogen flow-rate and detector temperature, f_0 was also found to vary as the inverse of gas density in the electron capture cell.

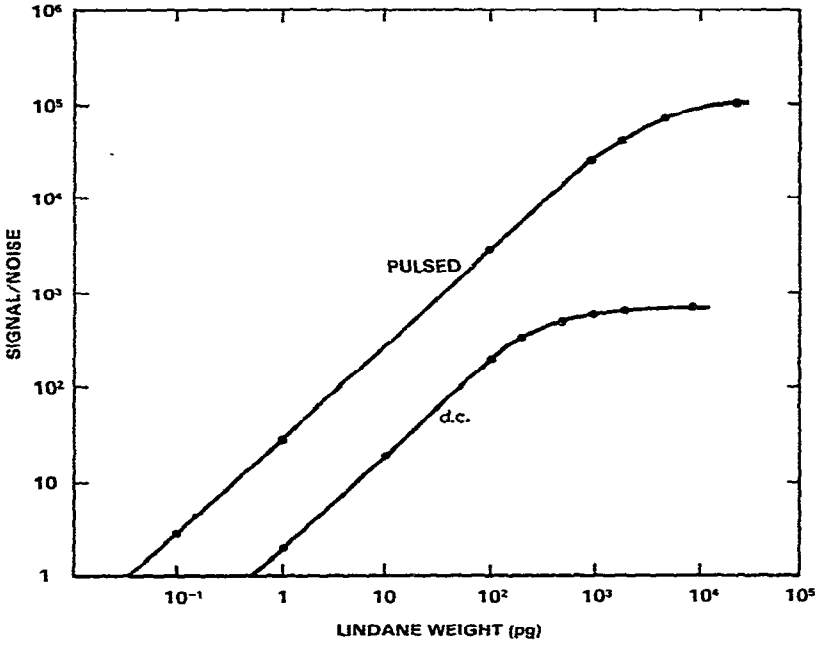

Fig. 4. Comparison of pulse-modulated and d.c. sample responses for the same ECD.

Fig. 4 shows a comparison of sample response for the same ECD cell operated in both the pulse-modulated mode and in a d.c. mode. Since the d.c. output signal is a current, and the pulse-modulated output signal is a frequency, the signal-to-noise ratio is used to compare the two modes of operation. Not only does the pulsed mode provide greater linear and dynamic response, but it also provides greater sensitivity. The latter property is probably the result of higher [e] in the pulsed mode.

Detectivity and linear range

Fig. 5 provides an illustration of ECD detectivity at the 0.1-pg level that was achieved in this work. Shown is the ECD response to a GC injection of pure benzene solvent followed by an injection of trace pesticides in benzene. To achieve this kind of detectivity, it is essential that the entire GC system be functioning well. In addition to a well-conditioned low-bleed column, it was necessary to employ high-temperature low-bleed septa of the type commonly recommended for GC–mass spectrometry in order to obtain solvent injections free of spurious peaks.

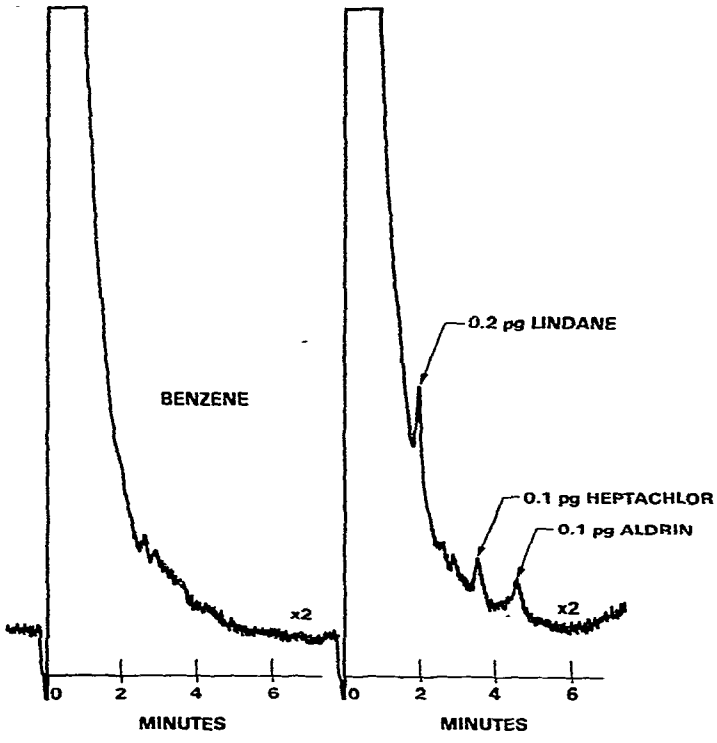

Fig. 5. Chromatograms showing injections of pure benzene solvent and benzene containing trace amounts of pesticides. Conditions: column packing, 3% OV-1 on Gas-Chrom Q, 80–100 mesh; flow-rate, 36 ml/min nitrogen; column temperature, 180°C; injector temperature, 210°C; detector temperature, 270°C; I_{cell}, 3×10^{-10} A.

Fig. 6 shows the linear and dynamic range using nitrogen as the carrier gas and lindane as the test substance. Both peak height and peak area sensitivity are plotted *versus* lindane weight. Defining the minimum detectable signal as twice the noise, the peak height response is linear within a $\pm 5\%$ band for a range of 1.3×10^4 in lindane weight. The dynamic range for peak height response extends to the point where the peak height sensitivity extrapolates to zero and covers a range of 7×10^5 in lindane weight. When the same data are plotted in terms of peak area rather than peak height, the upper limits of both linear and dynamic ranges are extended to higher lindane weights by about a factor of two. This is because the sample residence time within the ECD is small compared to the sample peak width coming off the GC column. Hence, the ECD senses only a small portion of the total GC peak at any given time. In this situation, non-linear sample concentrations are reached first in the peak centers, while the wings of the peak still give linear response.

Fig. 7 illustrates the effect on linear range caused by varying detector flow-rate. The top plot shows the peak height sensitivity for a flow-rate of 30 ml/min through the column. The bottom plot is the peak height sensitivity for the same column flow-rate plus an additional 70 ml/min make-up gas at the detector. At the higher detector flow-rate, the entire linear range is shifted toward higher sample weights. This is

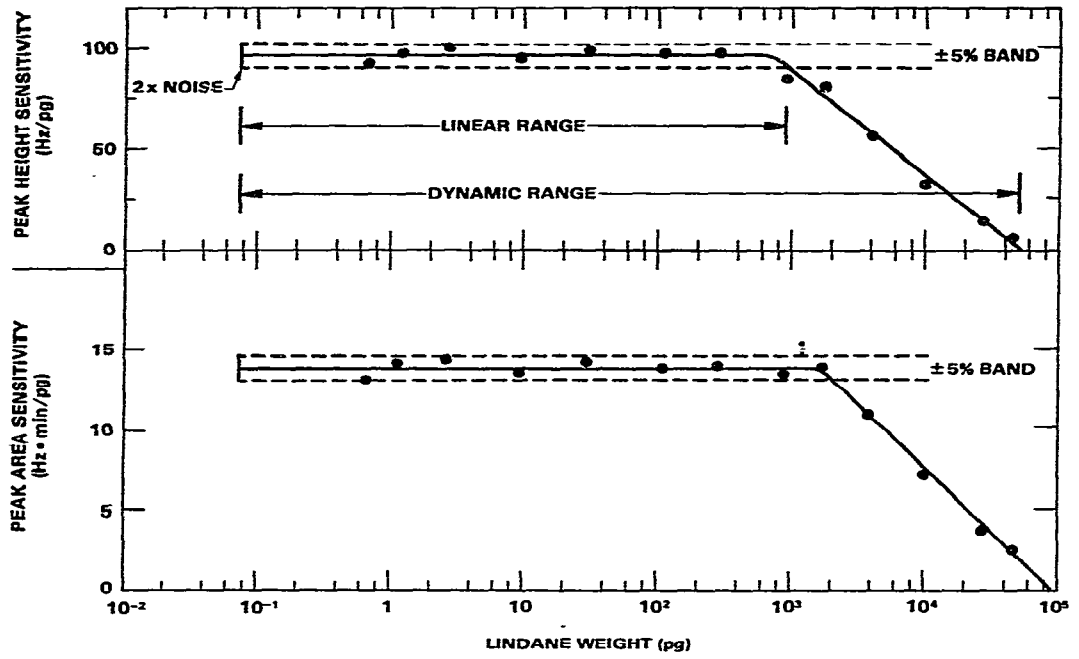

Fig. 6. Illustration of ranges of linear and dynamic response for lindane. Both peak height and peak area sensitivities are plotted for comparison. Conditions: column, same as Fig. 5; flow-rate, 37 ml/min nitrogen; column temperature, 190°C; injector temperature, 210°C; detector temperature, 300°C; I_{cell}, 3×10^{-10} A.

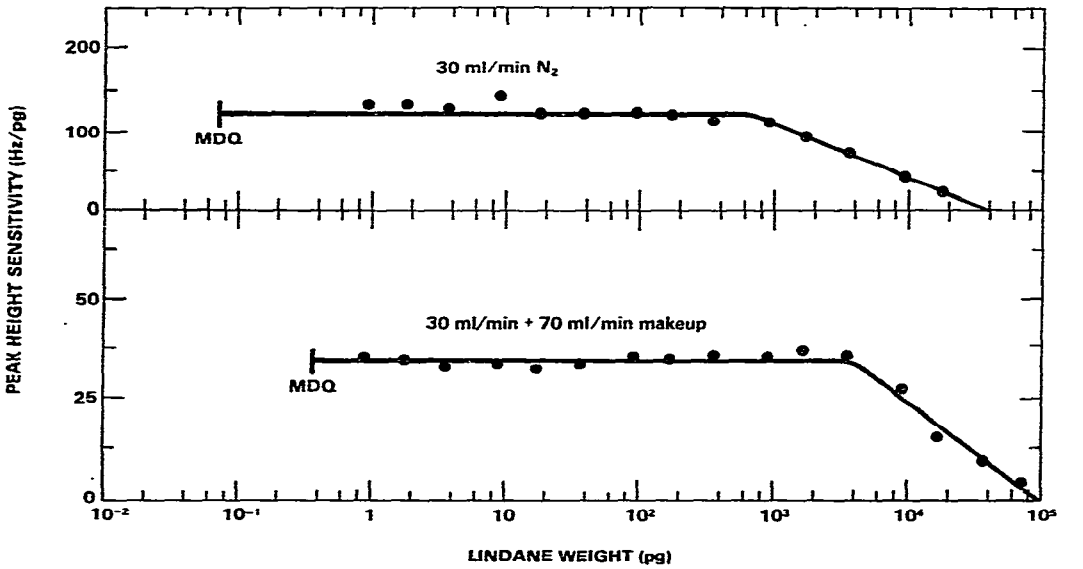

Fig. 7. Dependence of range of linearity on detector flow-rate. Both curves represent a flow-rate of 30 ml/min nitrogen through the column. The bottom curve has additional 70 ml/min nitrogen make-up gas added at the detector. MDQ = Minimum detectable quantity.

exactly the behavior expected for a detector that is a concentration-type detector. The concentration that is important is again the sample concentration within the detector volume at any given time. A similar effect of shifting the range of linearity can be accomplished by varying the retention time of the sample. Hence, the longer the retention time, the more the linear range is shifted toward higher sample weights. As a result, judicious selections of flow-rate and/or retention time can be used to shift the entire linear range by about an order magnitude toward either higher or lower sample weights, thereby tailoring the response of the ECD to suit a particular analysis.

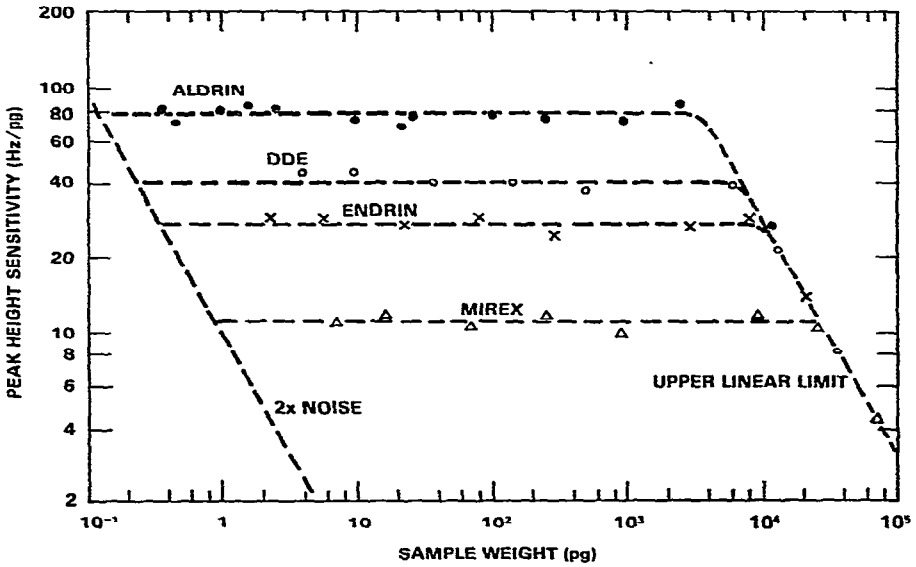

Fig. 8. Plot of the linear ranges of response of aldrin, DDE, endrin and mirex. Diagonal lines labeled "2 × noise" and "upper linear limit" represent lines of constant frequency. Conditions: column packing, 3% QF-1 + 1% DC-200 on Gas-Chrom Q, 100–120 mesh; flow-rate, 36 ml/min nitrogen; column temperature, 190°C; injector temperature, 220°C; detector temperature, 300°C; I_{cell}, 1.5×10^{-10} A. Retention times: aldrin, 2.5 min; DDE, 4.9 min; endrin, 7.1 min; mirex, 12 min.

Fig. 8 shows a plot of the linear ranges of the four pesticides aldrin, DDE, endrin and mirex, using a relatively high bleed column. These data are bounded at small weights by a diagonal line corresponding to a constant frequency equal to twice the noise. The data also define a similar diagonal line of almost constant frequency corresponding to the upper linear limit of the ECD. It is interesting that each of these different sample compounds begin giving a non-linear response when the sample peak height reaches about the same frequency. Combining that frequency (3×10^5 Hz) with the magnitude of the cell current (1.5×10^{-10} A), the number of free electrons collected per pulse can be calculated as follows:

$$6.2 \times 10^{18} \cdot I_{cell}/f = 3100 \text{ electrons per pulse}$$

With pure nitrogen in the cell, the number of electrons per pulse was 6×10^5. Hence, it appears to be a basic characteristic of this ECD, that dynamic response to samples

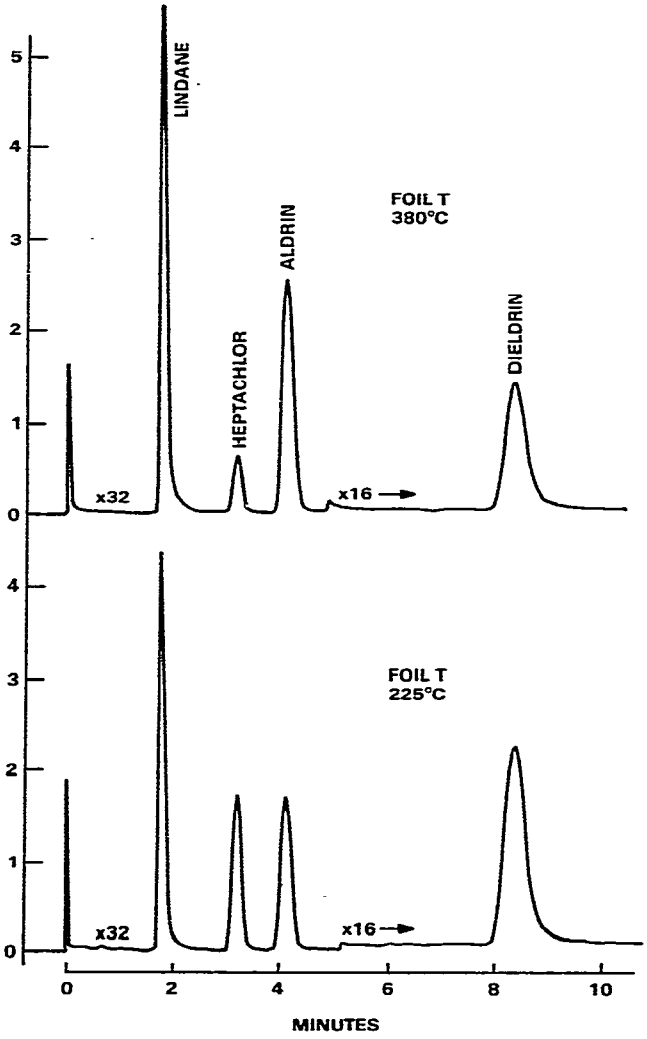

Fig. 9. Pesticide analysis at two different detector temperatures. Sample amounts are 221 pg for lindane and 123 pg each for heptachlor, aldrin and dieldrin. Conditions: column packing, 3% OV-101 on Varaport 30, 100–120 mesh; flow-rate, 50 ml/min nitrogen; column temperature, 170°C; injector temperature, 200°C; I_{cell}, 3×10^{-10} A.

tends to be lost whenever the electron density is reduced to less than 0.5% of its original magnitude.

Response versus detector temperature

It is well known that electron capturing compounds can have widely varying responses as a function of detector temperature[5,6]. A major advantage of using a ^{63}Ni source in the ECD instead of a ^{3}H source is that detector operating temperatures can range to much higher values. As a result, adjustments of detector temperature can be employed as a further means of enhancing certain sample responses. Fig. 9 provides

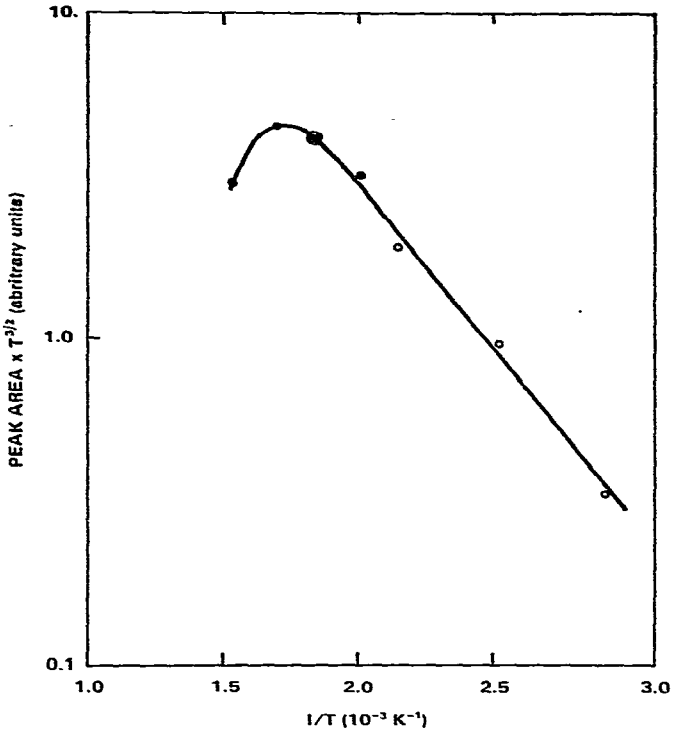

Fig. 10. Temperature dependence of electron attachment to dieldrin. Data of the present experiment (●) are normalized to agree with previous data (○) of Maggs *et al.*[2] at $1/T = 1.8 \times 10^{-3}\ ^{\circ}K^{-1}$.

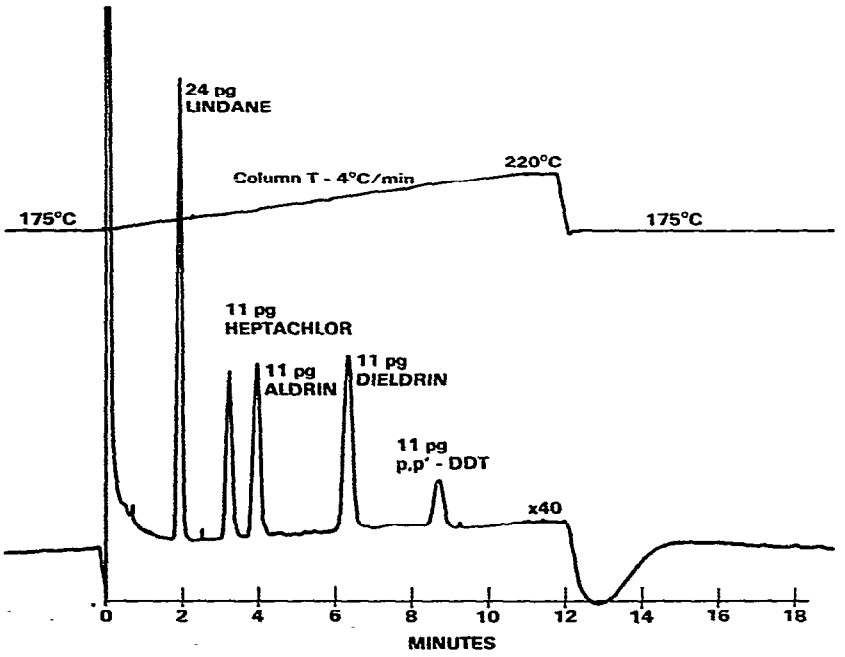

Fig. 11. Analysis of pesticides in benzene solvent using column oven programming. Conditions: detector temperature, 300°C; column temperature, programmed 175°C–220°C at 4°C/min with 1 min final hold at 220°C; other conditions same as Fig. 5.

an illustration of two chromatograms obtained at two different foil temperatures. It is clear that at 380 °C the lindane and aldrin peaks have been enhanced, while the heptachlor and dieldrin peaks are suppressed. Previous data on the temperature dependence of dieldrin response have been reported by Maggs *et al.*[2]. Their data are combined with the results of the present work in the plot of log (peak area $\times T^{3/2}$) *versus* $1/T$ that is shown in Fig. 10. As pointed out by Maggs *et al.*[2], the negative slope of the data at temperatures below 300 °C ($1/T = 1.75 \times 10^{-3}$ °K^{-1}) is indicative of a dissociative electron attachment mechanism. The reversal of slope at temperatures above 300 °C indicates a change in the electron attachment mechanism or possibly the onset of thermal decomposition of the neutral compound.

Column oven programming

Pulse-modulated operation of an ECD provides an inherently more stable baseline than d.c. operation. As a consequence, it is possible to use column oven programming techniques to improve peak shapes and reduce analysis times[7]. Fig. 11 provides an illustration that column oven programming with pesticide samples at the 10-pg level is clearly feasible. Since the GC used in this work was equipped with flow controllers, the small increase in baseline with increasing column temperature is essentially due to increased column bleed. At the end of the column oven program, the baseline upset exhibited in Fig. 11 is mostly due to transient flow changes caused by rapid cooling of the column and subsequent re-equilibration to the original column oven temperature.

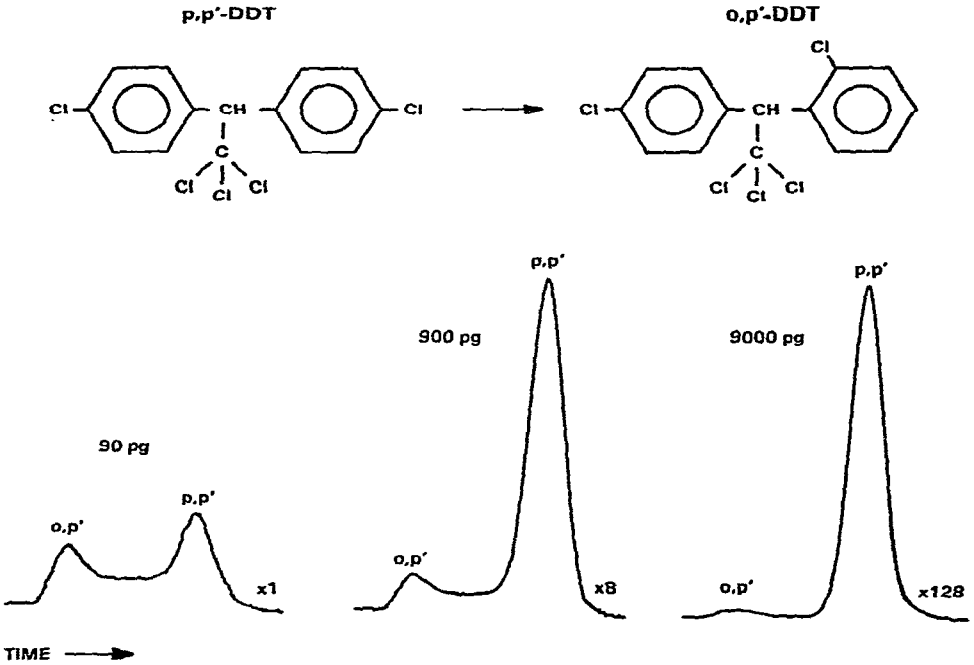

Fig. 12. Illustration of the conversion of *p,p'*-DDT isomer to *o,p'*-DDT isomer in interaction with GC column. Injected sample contained only *p,p'*-DDT. Conditions: column packing, 10% OV-1 on Chromosorb W, 60–80 mesh; flow-rate, 60 ml/min nitrogen; column temperature, 205°C; injector temperature, 220°C; detector temperature, 300°C.

Diagnosing other GC effects

The high sensitivity and large range of dynamic response offered by pulse-modulated ECD operation allow this detector to be used as a diagnostic tool to examine effects occurring in other parts of the GC system. A good example of this is the interaction of *p,p'*-DDT with the GC column. Peak height responses of this DDT isomer were found to often exhibit a non-linear response as a function of sample weight. A similar observation was mentioned previously by Fenimore and Davis[8]. In the present work, the degree of non-linearity was observed to depend on the column that was used. Chromatograms from the worst column (10% OV-1 on Chromosorb W, 60–80 mesh) are exhibited in Fig. 12. These data demonstrate the conversion of the *p,p'*-DDT isomer to the *o,p'*-DDT isomer while in transit through the column. The fact that the interaction is occurring on the column is evidenced by sample that arrives at the detector at times intermediate between the *o,p'*- and *p,p'*-DDT retention times, and also by the fact that the same samples injected onto other columns showed much less sample at the *o,p'*-DDT retention time. This DDT column interaction is apparently the result of a limited number of active sites on the column, since the relative magnitude of sample at the *o,p'*-DDT retention time diminishes as the total sample weight increases. The situation illustrated in Fig. 12 represents an especially severe interaction. With the column employed for the data shown in Fig. 11, it is clear that the effect is much diminished, although not completely eliminated. No effort was made in the present work to systematically correlate the observed column interaction with the type of column, column preparation or column conditioning. However, it is evident that the pulse-modulated ECD could be very usefully employed in studies of this type.

ACKNOWLEDGEMENTS

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