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## NON-RADIOACTIVE ELECTRON-CAPTURE DETECTOR

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### SUMMARY

A non-radioactive electron-capture detector is described which uses a thermionic emitter as a source of electrons. The use of this source allows a unique mode of operation which has greatly enhanced sensitivity, yet at the same time allows a large dynamic range. A signal-to-noise ratio of 180 to 1 has been obtained at the 1-pg level, together with a dynamic range of six orders of magnitude. It appears that with this method it is possible to detect femtogram quantities.

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### INTRODUCTION

The electron-capture detector (ECD) has been in existence for almost twenty years. During that time it has evolved from a highly sensitive, yet extremely temperamental detector into a reliable laboratory instrument. During this period, the modes of operation of the detector have changed significantly, extending both the range and the sensitivity of the detector.

But the real principle has barely been changed since its inception, and due to the complexity of the reactions taking place, its operation is still relatively poorly understood. To quote Lovelock<sup>1</sup>, the inventor of this detector: "Perhaps because of the pressure to use the detector in the solution of practical and theoretical problems, it has barely changed since its inception. It is still a simple two-electrode ion-chamber with an internal radiation source, and there is no comprehensive theory of its response which explains numerically the signals it generates."

The radioactive source that is used is at the base of this deceiving physical simplicity, but chemical complexity. Typically, the sources used are  $\beta$ -emitters ranging in energy from 17 keV (max) for tritium (<sup>3</sup>H) to 230 keV for promethium (<sup>147</sup>Pm). As these energetic electrons thermalize by collisions with the molecules of the gas, they produce eventually near thermal electrons. These thermal electrons are used in the reaction with the electrophilic compounds as the cross-section for electron capture of most strong electrophores is maximum near zero energy. However in the process a host of other species such as positive ions, energetic radicals, etc., are created which may react with the electrons, the electrophilic compounds or the negative ions created by electron capture. The complexity of these reactions, coupled with the space charge present in the detector, gives rise to intractable problems<sup>2</sup>. Wentworth *et al.*<sup>3</sup>,

who were responsible for elucidating many of the phenomena taking place in the ECD, have recently reviewed in detail the shortcomings of the radioactive detector<sup>4</sup>. Briefly, these include: (1) contamination of the electron source by column bleed, necessitating frequent cleaning of the detector; (2) irreversible reactions between the source and the electrophilic compounds; (3) upper temperature limitations set by the use of the radioactive foils or platings; and (4) the sources involved require licensing by government agencies.

To these could be added the difficulties of producing small cell volumes. Since the primary  $\beta$  particles have significant energy, their range is substantial, and a large cell volume is required to avoid operation of the cell as a cross-section detector<sup>5</sup>, although newer designs are minimizing the extent of this problem<sup>6</sup>. It has therefore been apparent for a long time that an alternative source for electrons would be very desirable. Wentworth *et al.*<sup>4</sup> in their approach, produce the electrons by photoionization of additives to the effluent (such as triethylamine).

This technique suffers, however, also from a number of deficiencies. The electrons produced are still not truly thermal, as for good ionization efficiency, it is required that the difference between the ionization potential and the ionizing photon energy be at least a few electronvolts. Thermalization, in turn, requires the use of a quenching gas which is unfortunately highly absorbing to the ionizing photons. For this and a variety of other reasons, this approach is presently limited in sensitivity to 50 pg of carbon tetrachloride, a very strong electrophore.

Other approaches in the past have tried to use electrons produced from a gaseous discharge<sup>7</sup>, or photoelectrons provided by metallic photoemitters. It appears, however, somewhat unlikely that a discharge of sufficient stability can be produced to detect picogram quantities.

Similarly, it seems unlikely that a photocathode with sufficient current and with enough stability, unaffected by the effluent of the gas chromatograph, can be found.

Our approach has been to use a thermionic emitter, suitably protected by a guard gas. Thermionic emitters are usually associated with electron emission in vacuum, and their operation (except for some special cathodes such as the Philips cathode) is rapidly and irreversibly destroyed by the presence of small amounts of water or oxygen. In 1967, MacNair<sup>8</sup> developed the barium zirconate cathode, in particular for laser discharges, and it was found to operate suitably in oxidizing atmospheres at low pressure. Although the original current densities quoted by MacNair appear to be somewhat high<sup>9</sup>, the values required for operation as an electron-capture detector are rather minimal, so that the cathode can be operated at low temperature (650–750°C). We found that this cathode, when suitably protected, can also operate very adequately in the atmosphere of the gas chromatograph, with quite acceptable lifetimes. The cathode can be exposed to air and reused without any apparent damage.

It should be remembered that the atmosphere of the gas chromatograph is a rather demanding one. If 3  $\mu$ l of a typical solvent (*e.g.*, isooctane or hexane) are injected at the commonly used flow-rates in chromatographic work, the cell will be filled with almost pure solvent vapor for several seconds. Pure metallic cathodes, such as rhenium or tungsten, working at elevated temperatures (1100–1200°C) oxidize very rapidly. If a suitable material is used to lower the work function, it is found that the

cathode is able to withstand immersion in the solvent vapor, but it takes several minutes for its emission to reach again the preimmersion level.

If the solvent problem could be circumvented, the thermionic emission itself is quite sensitive to the presence of electron capturing compounds, but the recovery constant is inadequately long for faithful detection of chromatographic peaks. In addition, efficient electron emission at atmospheric pressure in inert gases requires a strong electric field, since most of the emitted electrons are "reflected" to the filament by diffusion<sup>10</sup>. This large field is undesirable for efficient electron capture. However, if the filament is shrouded with a guard gas, these problems are all alleviated. The fact that a guard gas is used almost naturally divides the detector into two chambers, a guarded filament chamber used for the production of electrons, and a second chamber where a fraction of the previous electrons is used to react with the electrophores. This allows separate optimization of electron production in the first chamber and optimum conditions for electron capture in the second.

#### PRINCIPLE OF OPERATION

One implementation of a detector using a thermionic emitter is illustrated in Fig. 1. The detector consists of two concentric stainless-steel cylinders, an inner

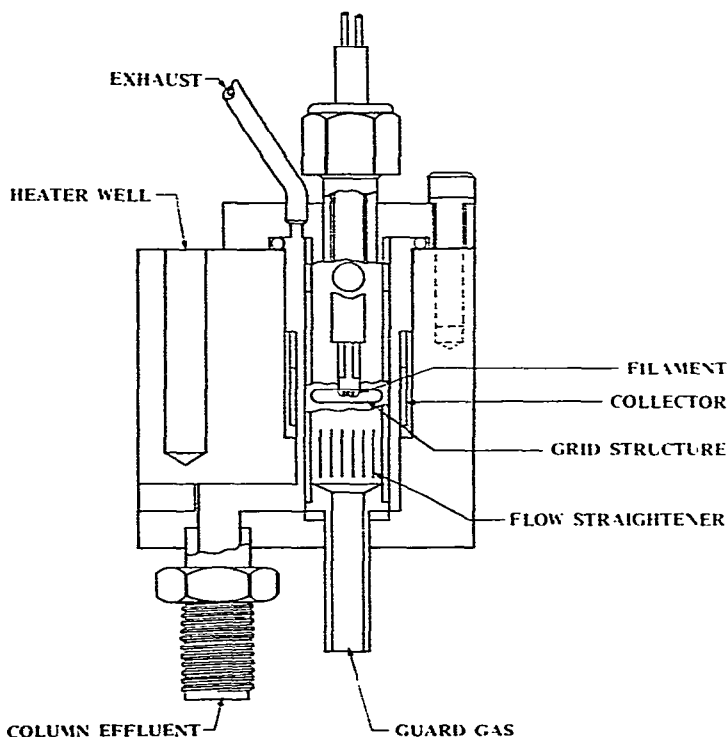


Fig. 1. Schematic illustration of a non-radioactive ECD. A direct heated thermionic cathode supplies electrons which are attracted towards a mesh-like anode. Electrons diffuse through the anode and are attracted with a small potential towards a collector. The column effluent flows in the outer cylinder and a guard gas flows in the inner cylinder. The guard gas prevents excessive penetration of the solvent in the filament chamber. The reaction chamber proper consists of the annulus between both cylinders, and its width is defined by the effective lateral spread of the electron cloud.

cylinder containing the thermionic source and through which the guard gas flows, and an outer one through which the chromatograph effluent flows. Separating the two chambers is a very fine metallic mesh (consisting of nickel or gold), of 80% transmission and about 12  $\mu\text{m}$  thick. The gas flows in both cylinders are colinear and, ideally, laminar and of equal velocity. For this purpose, operation of the detector is usually vertical, so that the thermal plume caused by the hot filament causes minimum disturbance in the outer chamber. Electrons emitted by the filament (which is biased negatively) are attracted toward the inner cylinder which is grounded, and which will be called the anode. Typically, although not necessarily, the electron source is kept at a variable potential by a servoloop to provide a constant current towards the inner cylinder. The current loop is set at a predetermined level, usually on the order of 10  $\mu\text{A}$ , and the voltage required to maintain this current under equilibrium conditions is on the order of 50 V (for a cylinder 12 mm in diameter).

Some of the electrons arriving at the anode pass through the open grid structure and diffuse through to the outer cylinder, which will be referred to as the collector. The potential difference between the collector, C, and the anode, A, is however kept quite small, and in fact operation is possible where the collector is slightly backbiased with respect to the anode.

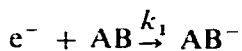
The primary driving force for the electrons to reach the collector is therefore diffusion, not drift. Their own space charge sets up a field opposing their entry in the anode-collector region. The balance between the diffusion force, the space charge field and the applied field results in a current, typically three orders of magnitude smaller than the current in the inner diode. This region of the detector, which is the cell proper, operates therefore in what will be called a diffusion driven, space charge limited mode. As the effluent of the chromatograph flows through the cell, electrophores are converted into negative ions, through reaction with the electrons. Note that with this geometric arrangement, all of the gas flowing through the cell is exposed to the electrons, as the electron path completely traverses the effluent gas (although the effluent is not everywhere exposed to the same electron concentration).

The operation of the detector can now, in a simplified way, be understood as follows. After absorption of an electron by an electrophore, and its conversion into a negative ion, one may assume that another electron is prohibited from entering the cell region, because of the space charge limitation. This condition prevails as long as the ion remains in the cell. As there is only a very weak electric field present in the cell, and the mobility of the negative ion is some three orders of magnitude lower than the electron mobility, the ion is essentially removed by the gas flow, a process which may take a considerable fraction of a second. During the dwell time of the ion, an electron has been prevented from entering the cell. The replacement of an electron by an ionic specimen with largely reduced mobility, generally gives rise to a reduction in current. Since the electron transit time is on the order of a few microseconds, the single ions have effectively prevented the entrance of a large number of electrons so that a gain mechanism is taking place. The gain would be thought of as the ratio of the dwell time of the negative ion to the transit time of the electron, an operation somewhat similar to the gain process observed in photoconductors. It must be realized that this simple model does not hold everywhere, as the effect of a single ion may depend on its position in the cell, since the electron concentration, as will be seen, is highly variable in the cell. However, substantial gain has been measured in this cell.

From this simple outline, it is already possible to discern the advantages of a detector of this type. The electrons in the reaction cell proper are completely thermal (at the most experiencing the weak combination of their self-fields and the applied field). With this low electron energy value, the cross-section for desirable capture reactions with the strong electrophores is maximal, while the undesirable capture of weak electrophores such as oxygen, water and carbon dioxide have low cross-section (their maxima occur near 6.5 eV). The final electrons produced by the ionization shower of  $\beta$  particles have relatively large initial energies (estimated to be on the order of 0–6.5 eV (ref. 4) and therefore are more likely to react with the weakly capturing compounds.

No positive ions or energized radicals are formed in this process, as is the case in the radioactive source. The assimilated polymerization reactions taking place in the effluent, whose deposits eventually coat the radioactive foil are expected to be absent. Hence, frequent cleaning of the detector is not required. Positive ions emitted from the cathode (or the supporting platinum wire), a common phenomenon with most thermionic emitters, are restricted by the field in the inner cylinder from entering the cell proper. Negative ions formed in this region will either be swept out, or discharged on the walls. Overall, the chemistry is a lot cleaner, as there are, in principle, only three specimens present: electrons, electrophores, and negative ions.

The volume of the detector itself can be very small; the volume of the cell here is defined (in the configuration shown) as that section between the two cylinders exposed to electrons. Volumes as small as 50  $\mu$ l have been made and this represents by no means the lower limit. There is, however, a lower limit to the desirability of a small cell size, unless the flow is also reduced. The chemical reaction between the electrons on the electrophores



proceeds with a finite rate constant,  $k_1$ , and assuming a very low initial concentration of electrophores  $[AB]_0 \ll [e^-]$ , we have as a solution:

$$[AB] = [AB]_0 [1 - e^{-t/\tau}] \text{ where } \tau = 1/k_1 [e^-]$$

For most strong electrophores, the value of  $k_1$  is a few times  $10^{-7}$   $\text{cm}^3/\text{sec}$  (refs. 11 and 12), and if we assume an electron concentration of  $10^8$  per  $\text{cm}^3$ , the time constant,  $\tau$ , is around 0.03 sec. If the cell volume is so small that, at the flow-rate under consideration, the dwell time (cell volume/flow-rate) is much smaller than the above time constant, substantial reduction in response will occur.

This detector operates both with argon-methane and nitrogen, without any loss of sensitivity. Cleaning procedures are substantially simplified, and moreover, there is no temperature limit of operation. As another advantage may be listed that the choice of the cell material is vastly enlarged, when no preventive measures against radioactive leakage need to be taken. If necessary, the cell may be fabricated out of Pyrex or fused quartz with metal electrodes (platinum or gold) vacuum deposited in the appropriate places. Glass detectors made this way were found completely satisfactory, and in some ways, superior to stainless-steel detectors.

Note that with this detector there are no basic advantages for the pulse mode, as compared to the d.c. mode of operation. With the radioactive detector, the pulse mode has the advantage over the d.c. mode of operation that in the time between pulses, the electron concentration can build up to a maximum value (set by recombination) since no field is present. The use of the pulse mode is, in fact, dictated by the finite rate of electron production of the source. But with the thermionic emitter, there is no rate limitation of electron production.

If the cell were momentarily pulsed clean of electrons, the electron concentration would be re-established in a matter of microseconds to its previously undisturbed value. The inner chamber provides an almost infinite reservoir of electrons which can fill the cell proper in a very short time. For all practical purposes, the cell always operates in a d.c. mode of operation. There are various ways in which the signal can be retrieved from the detector, depending on whether the collector is operated under a constant voltage mode or under a constant current mode. These modes of operation will be described in more detail in the next section.

#### DESCRIPTION OF THE DETECTOR

Fig. 2 illustrates a cross-section of a detector operating on this principle. It consists of a solid block of stainless steel into which the inner cell is inserted. Column effluent and guard gas are brought in at the same temperature. A glass or ceramic flow straightener is inserted in the inner cell to provide laminar flow, to as good a degree as possible, as turbulent flow can significantly degrade the observed signal-to-noise ratios of the detector.

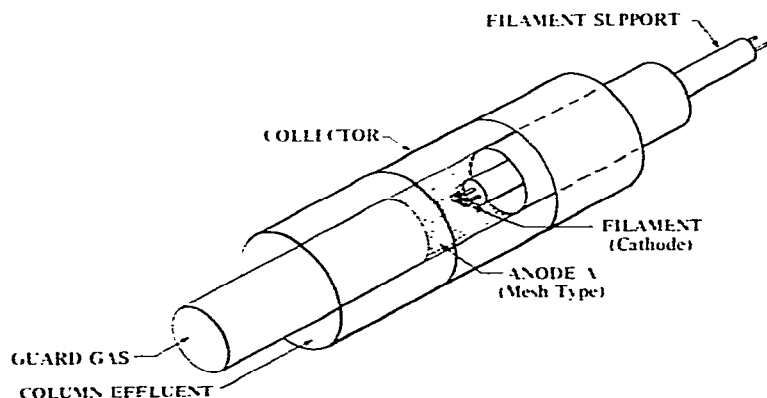


Fig. 2. Schematic illustration of a practical implementation of the non-radioactive ECD. The filament is oriented vertically, so that its thermal plume does not enter the reaction chamber. Provisions are taken so that the flow of both the guard gas and effluent are laminar in the detection chamber, so that a minimum of mixing takes place. All materials are stainless, or ceramic, with silicone rubber O-rings.

The thermionic filament consists of a 0.125 mm thick platinum wire, spirally wound with about ten turns to a length of about 3 mm, and cathodically coated with barium zirconate. The filament is heated by a small floating power supply; a few watts are typically all that is required to keep the filament at the required temperature. The outer diameter of the anode of the cell shown is about 14.8 mm, and the

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inner diameter of the collector 13 mm. The slit through which the electrons diffuse is about 1.3 mm, so that the effective cell volume is on the order of 50  $\mu\text{l}$ . The filament location is adjustable to provide optimum position for emission.

This detector was typically operated with a gas flow through the column of about 60 ml/min. The amount of guard gas required to protect the filament depends upon a number of parameters such as the amount of solvent injection, the diameter of the inner cylinder, and the desired (or acceptable) baseline recovery time.

Injections of 3–5  $\mu\text{l}$  tend to give relatively large penetration in the inner cylinder and require higher gas flow than the injection of 1–2  $\mu\text{l}$ . A large diameter is advantageous, but requires more gas flow if the same linear velocity is to be maintained. For minimum turbulence in the grid zone, it is desirable to have the flow velocities on both sides to be nearly equal, although a certain amount of mismatch can be tolerated. The overriding concern is, of course, an acceptable baseline recovery, before the arrival of the chromatographic peaks. The chromatographic conditions therefore determine to some degree the amount of guard gas required. Guard gas flows on the order of 1–3 ml/sec were typically used. No effect at all was seen on the peak heights when the guard flow was changed over a factor of five from 1 to 5 ml/sec. As stated above, a current loop, set at a predetermined level, keeps the cathode–anode current constant. As the solvent penetrates into the inner region, the voltage required to keep this current constant is generally increased, and may even drive the loop out of control. Small excursions of this control voltage are also noted during the passage of large sample quantities (nanogram or above). The current between the anode and the collector, which is primarily driven by diffusion (at least in equilibrium) can be collected with a constant voltage (typically a couple hundred millivolts) or may be set by another current loop. This secondary current is typically three orders of magnitude smaller than the primary current. For example, a common value for the setting of the primary loop is 10  $\mu\text{A}$ , versus 10 nA for the secondary loop. Control voltages required in the first loop would then be on the order of 40–50 V (depending on the filament condition and the type of gas used), and 100–200 mV for the cell loop.

In the constant-voltage mode of operation of the cell, the current excursion is measured by some electrometer, and generally speaking, the current decreases when the electrophores pass through the cell. In the constant-current mode of operation, an increase in the control voltage is typically needed to keep the current constant, and the incremental voltage is taken as the signal. The latter mode of operation has been used in the particular experiments described here. In this mode any shift in contact potential in the anode–collector region is automatically taken up simply as a shift in the standing voltage, but does not affect the signal amplitude.

In contrast with the constant-voltage mode, the measured value (voltage) tends to increase, rather than decrease with increasing injection of electrophores (versus decreasing current in the constant-voltage mode). As the sample size is increased, the voltage across the cell can always be increased to a value limited only by the design of the servoloop. However, as the voltage across the cell is increased, the cell ceases to operate in a diffusion controlled mode and becomes more and more field controlled. This means that as the sample quantity gets larger, the response factor automatically becomes lower, giving rise to a somewhat compressed range.

## THEORY OF OPERATION

Although a complete and rigorous theory has not yet been attempted, it is possible to describe approximations which give significant insights into the mode of operation. Consider Fig. 3 where the cell is schematically illustrated. A plane geometry has been assumed, since the radius of curvature of the cell is insignificant to the problem. The cylindrical problem is tractable, but offers no new insights into the solution.

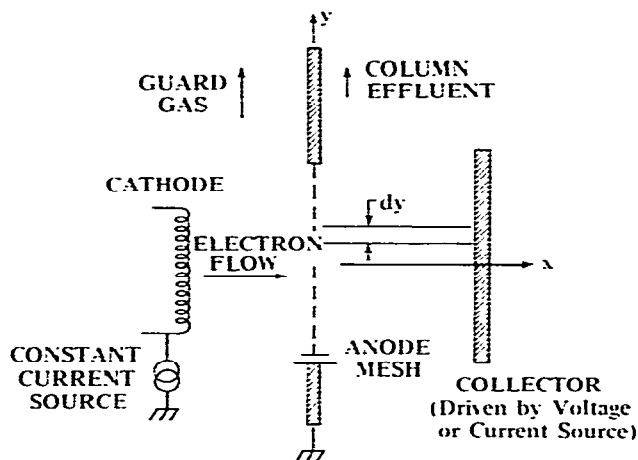


Fig. 3. Schematic illustration of the cell in planar geometry. The cathode current establishes an electron density  $N_e(0)$  at the anode, and due to the mesh-like structure of the latter, an equal electron density exists on the other side of the mesh. Diffusion, aided by a small field, drives the electrons towards the collector, which can be biased either in constant-current or constant-voltage mode.

The primary current from the thermionic filament to the anode establishes an equilibrium electron density at the grid, which can be estimated from the current in the first diode, since this current is dominated at all times by the field. It is assumed that this electron density,  $N_e(0)$ , is kept constant at all times, regardless of the concentration of electrophilics that are present. This assumption is an acceptable approximation, when the electrophilic concentration is small compared to  $N_e(0)$ . It is also assumed that the electron concentration on both sides of the grid is equal. Since the grid is both very open and very thin, this assumption will be always very nearly satisfied. If it were not, a large diffusion current would immediately establish equality. The ionization of an electron capturing compound entering the cell is a function of its rate constant,  $k_1$ , the electron concentration and the dwell time in the cell. Therefore, if a plug  $dy$  of electrophilic material moving along the  $y$  axis is assumed to enter the cell at  $y = 0$ , its ionization will be increasing with increasing  $y$  (and dwell time in the cell). In other terms, the ionization will have both a  $y$  dependence and, as will be seen, a strong  $x$  dependence. The  $y$  dependence is neglected in this approximate theory and replaced by an average ionization dwell time, taken to be half the time for the gas flow to sweep the cell volume.

Almost intuitively, it can be seen that the  $x$  dependence of the ionization will be very strong. From its initial value,  $N_e(0)$  at  $x = 0$ , the electron concentration will



decrease very rapidly with increasing  $x$ , giving rise to a strong diffusive flow. This flow is opposed by the field of the electron space charge. With increasing  $x$ , the space charge field gradually decreases and may change sign, while at the same time, the diffusion gradient decreases and may eventually become negligible.

The elution time for typical chromatographic peaks is much longer than any of the time constants involved, so we will assume that the concentration of unionized electrophilic material entering the cell is constant in time. A time varying peak can be reconstructed by calculating the responses for various static concentrations.

The behavior of the negative particle flow is given by the following equation

$$J = -D_e \frac{\partial N_e}{\partial x} - D_i \frac{\partial N_i}{\partial x} + V_e N_e + V_i N_i \quad (1)$$

where  $J$  is the total charged particle flow,  $D_e$ ,  $D_i$  are the electronic and ionic diffusion constants and  $N_e$ ,  $N_i$ ,  $V_e$ ,  $V_i$  are the electronic and ionic concentrations and velocities.

As the electric field,  $E$ , is quite small, and the cell is working under atmospheric pressure,  $p$ , the parameter  $E/p$  is very small so the velocities can be expressed in terms of their mobilities  $\mu_e$  and  $\mu_i$  as  $V_e = -\mu_e E$ ,  $V_i = -\mu_i E$ . Under equilibrium conditions, the particle flow is constant throughout the cell, or  $\partial J/\partial x = 0$ .

From Gauss' law:

$$\frac{\partial E}{\partial x} = - \frac{(N_e + N_i) e}{\epsilon_0} \quad (2)$$

where  $e$  is the electron charge,  $\epsilon_0$  the permittivity of the gas.

Furthermore, it is assumed that the ion concentration,  $N_i$ , is related to the incoming electrophore concentration ratio by

$$N_i(x) = N_{i0} \{1 - \exp[-N_e(x) k_1 t_1/2]\} \quad (3)$$

where  $N_e(x)$  is the local electron concentration,  $k_1$  the capturing rate constant and  $t_1$  the dwell time in the cell. The rate constant  $k_1$  for electron capture has been assumed in our calculations to be on the order of  $3 \times 10^{-7}$  cm<sup>3</sup>/sec, which is representative of strongly capturing compounds.

This set of equations is numerically solved by trial and error. Under constant-current conditions, the procedure is as follows: since the electron concentration  $N_e(0)$  is known at the boundary, the ion concentration is known there too. The electron gradient,  $\partial N_e/\partial x$ , is guessed at the boundary and the Taylor expansion of  $N_e$  and  $E$  can subsequently be calculated to the second order from eqns. 1 and 2. If the gradient  $\partial N_e/\partial x$  is not guessed right, it is found that the solution either diverges very rapidly, or gives rise to negative electron concentrations. Guessing the right electron derivative is a tedious process, and corresponds to determining the diffusion current at the grid. Since the diffusion current is there much larger than the total current (by typically two orders of magnitude), it is required that the derivative be known to high precision. An acceptable solution for  $N_e$  (and  $E$ ) is such that it neither diverges or yields negative  $N_e$  and matches smoothly with the solution  $J = N_e V_e$  at points far away from the grid, where diffusion has become negligible. (This requires the profile

$\partial N_e/\partial x$  to be convex at all times.) Although this procedure does not yield a unique solution, since these conditions can be met by a set of solutions, in practice it is found that the solution set is very narrowly bracketed, and does allow solutions to diverge only by a few per cent.

The above technique is used when the detector is operating in the constant-current mode. The voltage across the cell is found by integration of the field across the length of the cell. But if the detector is operating in the constant-voltage mode and the voltage found is not equal to the applied voltage, it is necessary to readjust the current value, reiterate the above procedure, integrate the electric field, compare with the applied voltage, readjust the current, etc.

The current-voltage characteristics of planar cells of various size in a nitrogen atmosphere, for different electron concentrations at the boundary are illustrated in Fig. 4. Note the very strong dependence of the current on the length of the cell. For comparison, the space charge limited current, as given by  $J = 9\mu_e V^2 \epsilon_0 / 8l^3$  has also been drawn, where  $\mu_e$  is the electron mobility in nitrogen and  $l$  the cell length. Due to the diffusion, the current always exceeds the space charge limited current, and moreover current is seen to flow for negative bias voltages, where repulsion of the electrons takes place. The cutoff voltage for current is on the order of 50–100 mV for most of the cells of interest.

The electron profile and the electric field across the cell are illustrated in Figs. 5 and 6, for electron fluxes of respectively 0 and  $1 \cdot 10^{11}/\text{cm}^2 \cdot \text{sec}$  (current densities of 0

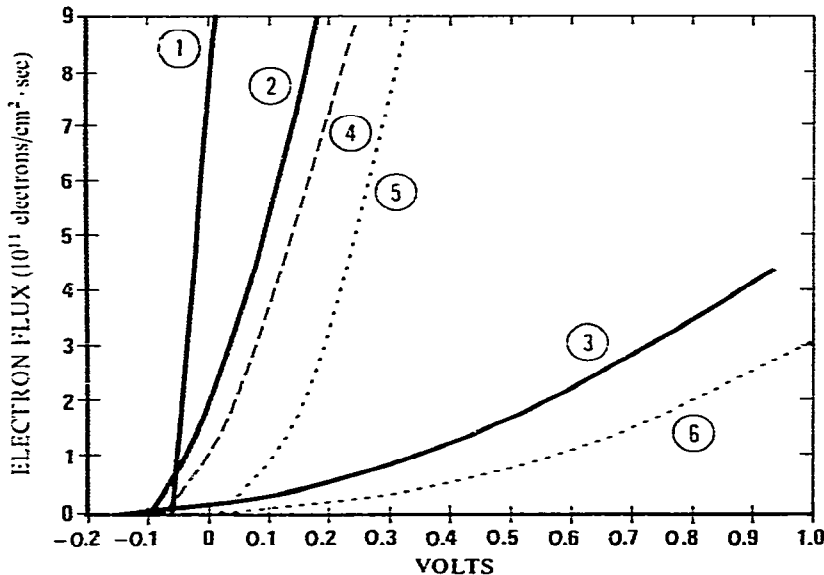


Fig. 4. Current-voltage characteristics of planar diodes, for various electron concentrations  $N_e(0)$  at the anode mesh and various anode-collector spacings,  $L$ . Note that because of the diffusive flow enhancement current can flow even with negative collector bias. With increasing anode-collector separation, the required voltage for a given current increases quite rapidly. The space charge limited current, neglecting diffusion is also illustrated for spacings of 1 and 3 mm. The ambient gas is assumed to be nitrogen. Curves: 1,  $N_e(0) = 2.8 \cdot 10^{14}$  electrons/ $\text{m}^3$ ,  $L = 0.5$  mm; 2,  $N_e(0) = 2.8 \cdot 10^{14}$  electrons/ $\text{m}^3$ ,  $L = 1$  mm; 3,  $N_e(0) = 2.8 \cdot 10^{14}$  electrons/ $\text{m}^3$ ,  $L = 3$  mm; 4,  $N_e(0) = 1 \cdot 10^{14}$  electrons/ $\text{m}^3$ ,  $L = 1$  mm; 5, space charge limited flow,  $L = 1$  mm; 6, space charge limited flow,  $L = 3$  mm.

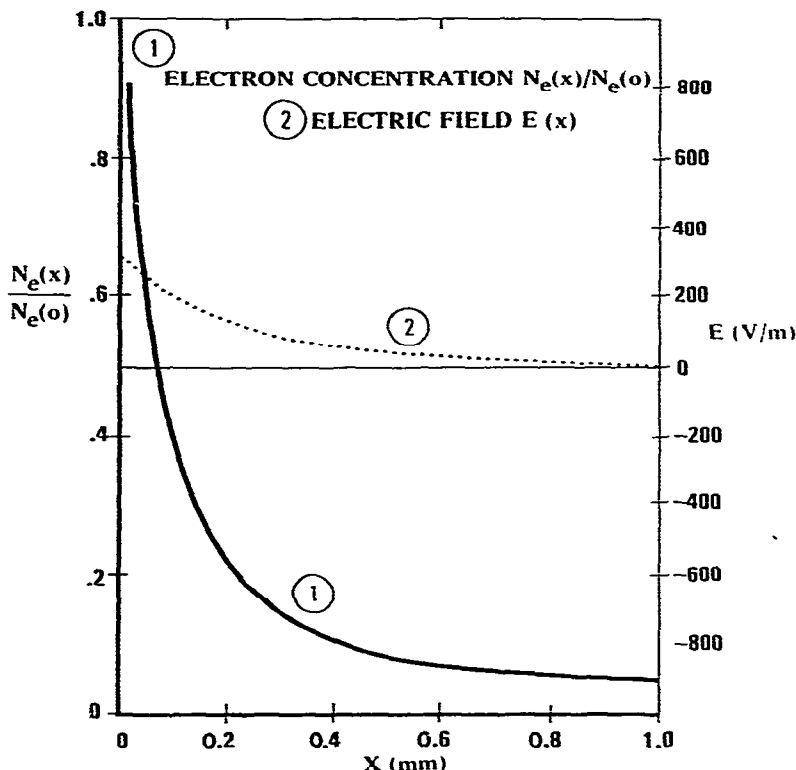


Fig. 5. Normalized electron profile  $N_e(x)/N_e(0)$  and electric field  $E$  across the detection chamber for zero current. The electron density at the anode  $N_e(0)$  is assumed to be  $10^9/\text{cm}^3$ . As the electrons enter the cell, the field opposes their entry: near the collector the diffusion gradient is zero, and so is the field. Nitrogen has been assumed for the carrier gas. Cell bias  $\approx -80$  mV.

and  $1.6 \cdot 10^{-8}$  A/cm<sup>2</sup>). At zero total current, the diffusion and drift current obviously balance each other everywhere, and the electric field will always be positive, opposing the electron motion everywhere since the diffuse flow is always in the same direction.

As the current increases (Fig. 6), the electron concentration in the cell increases, as expected. The electric field is seen to change sign in the cell, opposing the entry of electrons at the grid, and pushing them towards the collector in the collector region. The nature of the current in the cell therefore changes gradually from predominantly a diffuse flow near the anode to drift flow near the collector.

The above characteristics have all assumed the absence of electron capturing compounds in the cell. When the electrophilics are introduced, the field and electron distribution are changed, due to the immobile space charge of the ions (Fig. 7). It has been assumed that the cell is operating under constant-current conditions, and an increase in bias voltage of about 25 mV has been necessary to maintain the same current as before the introduction of electrophores. The unionized electrophilic concentration is assumed to be distributed uniformly across the cell, and equal in magnitude to the electron concentration at the grid. A dwell time of 50 msec has been assumed. Note that the ion concentration is by no means uniform, and follows a

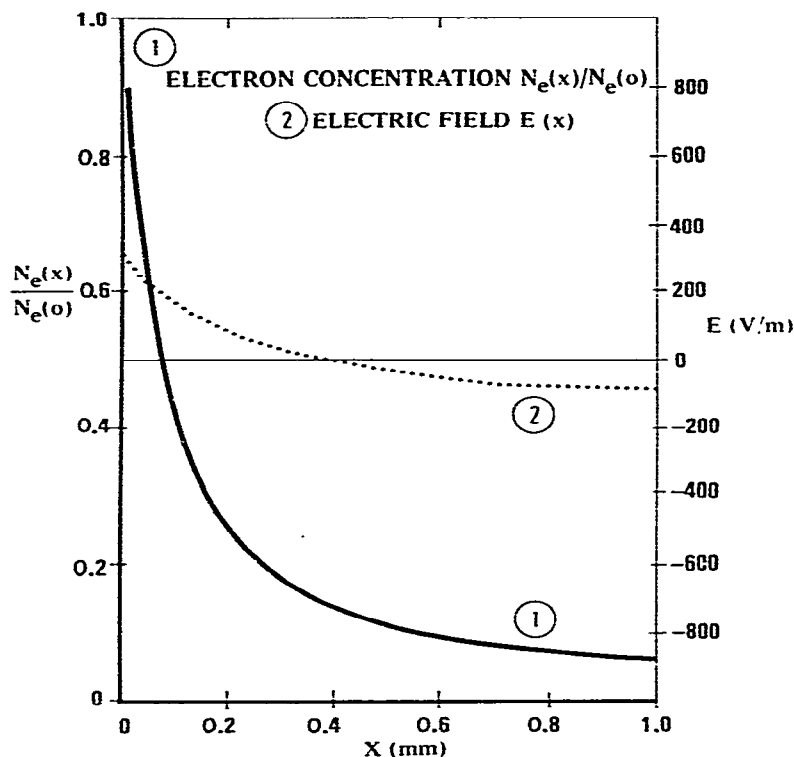


Fig. 6. Normalized electron profile and electric field across the detection chamber for an electron flux of  $5 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{sec}$  ( $j = 8 \cdot 10^{-8} \text{ A. cm}^{-2}$ ). The electron density at the anode is again  $10^8/\text{cm}^3$ . Note the increase in average electron density as compared with Fig. 5. Bias voltage is 130 mV. The electric field now changes sign in the cell, opposing the entrance of electrons at the anode, but aiding diffusion at the collector.

pattern similar to the electron concentration. Moreover, the ionization is far from complete. This is in contrast to the radioactive ECD, where for small concentrations, the ionization may approach 100%.

The response curve, namely the voltage across the cell necessary to keep the current constant, with varying concentrations of electrophilics, is illustrated in Fig. 8. The abscissa represents the electrophore concentration, normalized to the electron concentration at the grid. In this case, the response is nearly linear in the electrophore concentration. Fig. 9 illustrates a similar characteristic with the same equilibrium current, but taken under the condition of constant voltage ( $-4 \text{ mV}$ ). The ordinate now represents the cell current, normalized to the equilibrium value of the undisturbed cell and, as before, the abscissa represents the injected electrophilic compound concentration, normalized to the electron concentration at the grid. The current at first decreases linearly with the injected compound concentration, but becomes rather quickly supralinear.

One particular characteristic of the constant-voltage mode, according to this model, is that over a restricted range the normalized current-concentration characteristic is almost independent of the current value used as long as the cell voltage stays

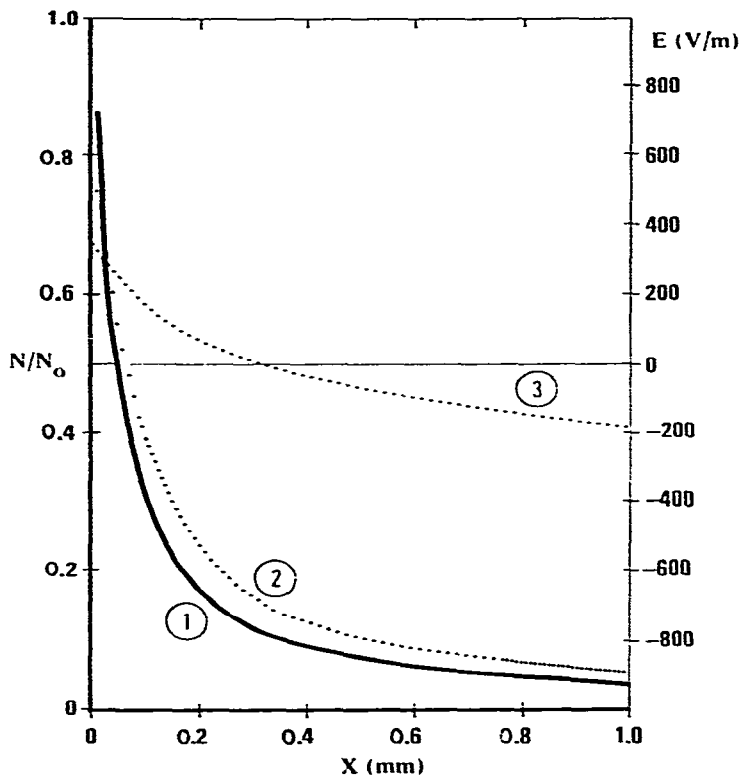


Fig. 7. Electron concentration  $N_e(x)/N_e(0)$  (1), ion concentration  $N_i(x)/N_i(0)$  (2) and electric field  $E_x$  (3) in a planar cell of length 1 mm, electron flux density of  $1 \cdot 10^{11}$  electrons/cm<sup>2</sup>·sec ( $j = 16$  nA/cm<sup>2</sup>). The electron concentration is normalized to the concentration at the grid, and similarly for the ion concentration, both of which are assumed to be  $10^8$ /cm<sup>3</sup>. To accommodate the ionic space charge, the collector voltage has to be raised from  $-4$  mV (in the absence of electrophilics) to 22 mV.

below 200 mV. Doubling the equilibrium current, which requires the voltage to be increased to 40 mV, gives rise to a very much identical characteristic (see Fig. 9).

All of the above characteristics were obtained with nitrogen as the carrier gas, and an electron mobility assumed to be  $1.35 \cdot 10^4$  cm<sup>2</sup>/Vsec (ref. 13). For argon-methane mixtures, (either 5% or 10% methane) the mobility and diffusion coefficient have been assumed to be three times larger<sup>14</sup>. The response of the same physical cell of Fig. 8, with identical electron concentration and operating at the same constant current, but using argon-methane as the carrier gas, is illustrated in Fig. 10.

The equilibrium value of the current can now be maintained with a reverse bias of almost 50 mV. Note however that the response is quite sluggish for low electrophilic concentrations. In fact, the response can even become inverted for low concentrations, that is introduction of an electron capturing compound will reduce the bias signal (under constant-current operation). This anomalous behavior is by no means peculiar to argon-methane mixtures, although it is somewhat more pronounced in them. It is characteristic of the cell behavior, when the operating conditions are

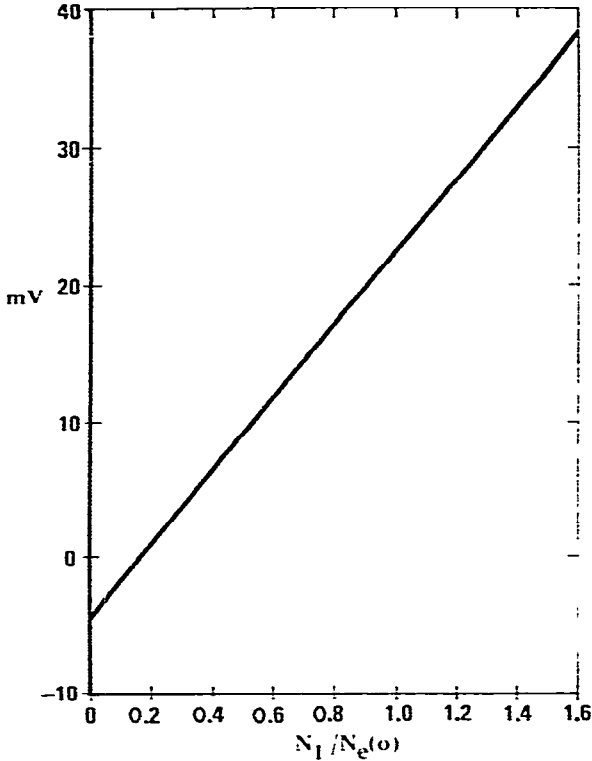


Fig. 8. Calculated response curve for a planar detector operating in the constant-current mode. The conditions are the same as in Fig. 7: electron flux  $1 \cdot 10^{11}$  electrons/cm<sup>2</sup>·sec ( $j = 1.6 \times 10^{-8}$  A/cm<sup>2</sup>), electron concentration  $N_e(0) = 1 \cdot 10^8$ /cm<sup>3</sup>, cell length = 1 mm. Plotted is the voltage across the cell required to keep the current constant as a function of the unionized electrophilic concentration  $N_i$  flowing through the cell. The electrophilic concentration is normalized to  $N_e(0)$ , the electron concentration at the anode.

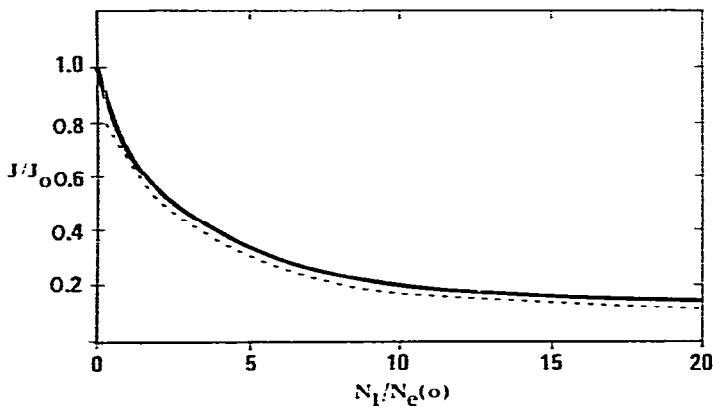


Fig. 9. Calculated response curve for a planar detector operating in the constant-voltage mode. The conditions are similar to Figs. 7 and 8: electron concentration at the anode  $N_e(0) = 1 \cdot 10^8$ /cm<sup>3</sup>, cell length 1 mm, cell-bias voltage  $-4$  mV. At rest, with no electrophilics present, the electron flux  $J_0$  is  $1 \cdot 10^{11}$  electrons/cm<sup>2</sup>·sec ( $j = 1.6 \cdot 10^{-8}$  A/cm<sup>2</sup>). Plotted is the variation of the normalized cell current,  $J/J_0$  as a function of the unionized electrophore concentration  $N_i$  normalized to  $N_e(0)$  introduced in the cell. The dotted line indicates the response curve, when the cell voltage is increased to 40 mV. The electron current at rest doubles. ( $J_0 = 2 \cdot 10^{11}$  electrons/cm<sup>2</sup>·sec) but the normalized graph of current *versus* electrophore concentration is very much identical.

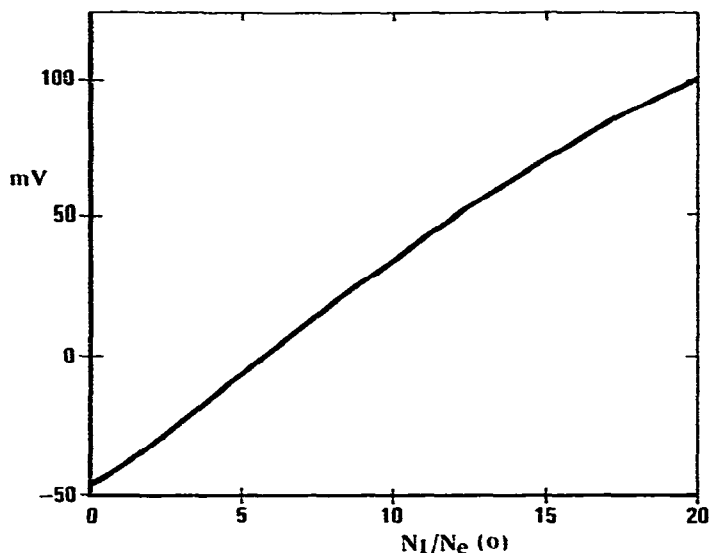


Fig. 10. Calculated response curve for a planar detector operating in the constant-current mode, but using argon-methane (5:95) as the carrier gas, instead of nitrogen. The cell length  $l$  is 1 mm, the electron density  $N_e(0) = 1 \cdot 10^8/\text{cm}^3$ , the constant electron flow  $J_0 = 1 \cdot 10^{11}$  electrons/ $\text{cm}^2 \cdot \text{sec}$  ( $j = 1.6 \cdot 10^{-8}$  A/ $\text{cm}^2$ ). Note the large negative bias voltage at rest, due to the increased electron diffusion and mobility, and the sluggish response for small electrophore concentrations.

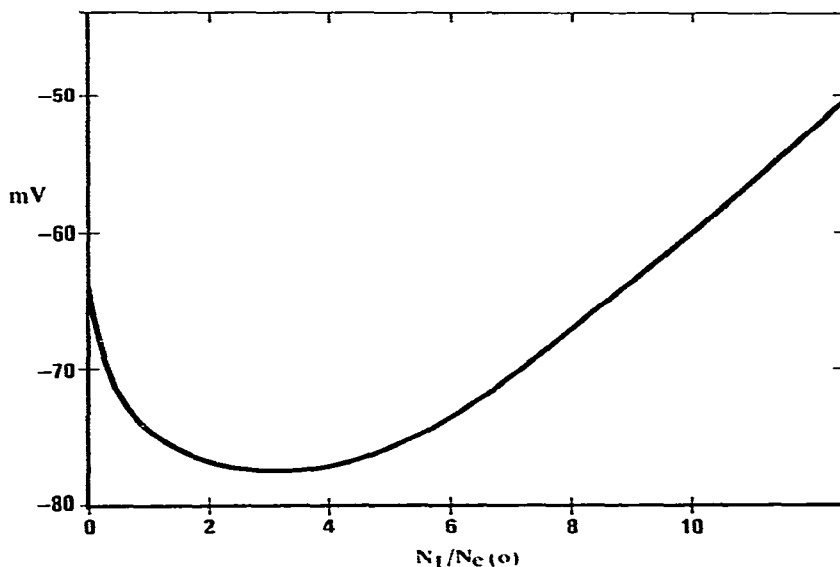


Fig. 11. Calculated response curve for a planar cell, operating in the constant-current mode, with nitrogen as the carrier gas, but with the current reduced by a factor of ten as compared to Fig. 8 ( $L = 1$  mm,  $N_0 = 10^8/\text{cm}^3$ ,  $J_0 = 1 \cdot 10^{10}$  electrons/ $\text{cm}^2 \cdot \text{sec}$ ,  $j = 1.8 \cdot 10^{-9}$  A/ $\text{cm}^2$ ). The response is now seen to be inverted at low electrophore concentrations. In this region, increasing concentrations of electron capturing compounds causes the cell voltage to decrease, rather than increase as is normally expected. This behavior is thought to be due to the predominance of diffusion under the conditions of low current.

chosen such that the cell is operating under reverse bias, which typically corresponds to small current values.

For example, Fig. 11 illustrates the calculated characteristic for the cell, operating under identical conditions as in Fig. 8, operating with nitrogen as the carrier gas, except that the current density has been reduced by a factor of ten. The bias voltage has now become quite strongly negative, at equilibrium, and becomes even more so when electrophores are introduced.

As stated, these inverted responses are found to occur only when the cell is strongly reversed biased. Clearly diffusion is the main driving force under those conditions, and it is perhaps not too surprising that if some electrons are removed (by conversion into ions), that the electron gradient is increased, and that therefore the diffusion current increases. However, as the ion concentration starts building up, the field effects eventually overpower the diffusion effects, and the response reverts to normal.

The effect also occurs in the constant-voltage mode, when a strong negative bias is imposed across the cell, such as to make the current quite small. This is illustrated in Fig. 12, where the current is seen to increase first with increasing electrophore concentrations, until it eventually decreases at higher concentrations.

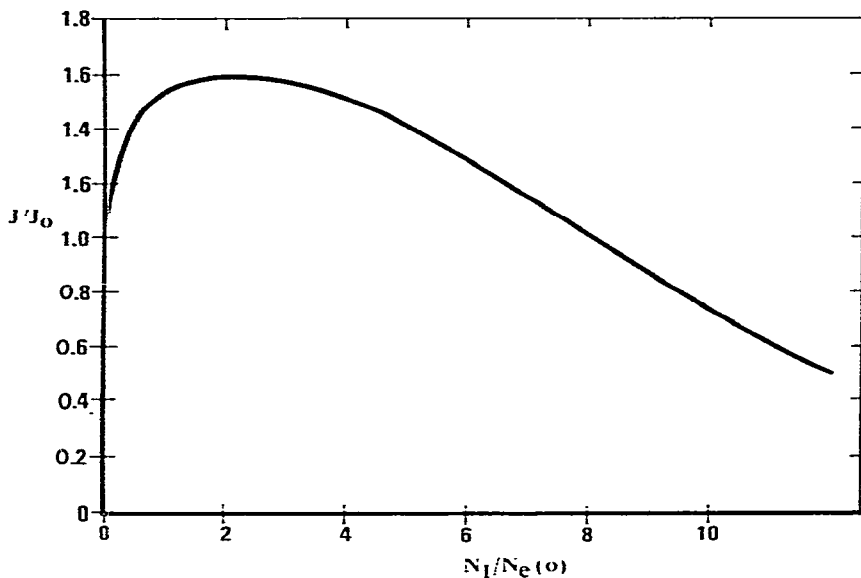


Fig. 12. Calculated response curve for a planar detector, using nitrogen operating under constant voltage with a strongly negative cell bias of  $-64$  mV [ $L = 10^{-3}$ ,  $N_e(0) = 10^8/\text{cm}^3$ , standing current  $J_0 = 1 \cdot 10^{10}$  electrons/ $\text{cm}^2$ -sec]. Plotted is the cell current, normalized to  $J_0$ , as a function of the electrophore concentration in the cell [normalized to  $N_e(0)$ ]. The response is again anomalous, giving an increase in cell current with introduction of the electronegative compounds. At higher concentrations however, the response becomes normal, due to the increasing ionic space charge.

## RESULTS

A typical chromatogram, taken with a detector as illustrated in Fig. 2, is given in Fig. 13. A  $1\text{-}\mu\text{l}$  injection of isooctane was made containing 3 pg of both lindane and



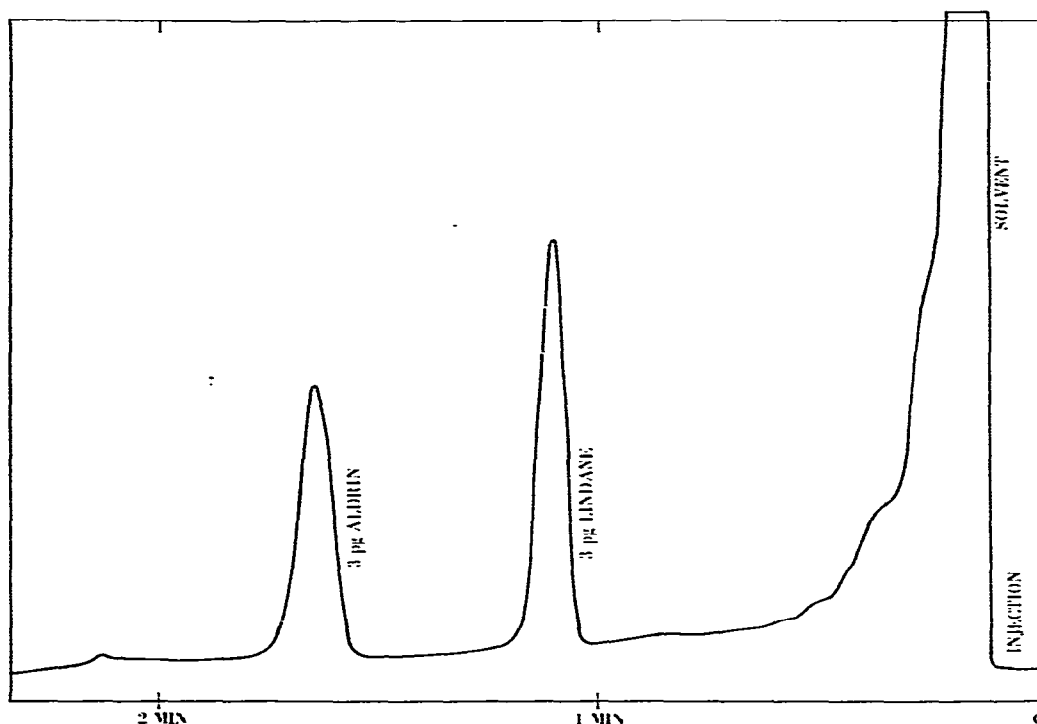


Fig. 13. Typical chromatogram obtained with the non-radioactive ECD for an injection of 1  $\mu$ l of iso-octane containing 3 pg of both lindane and aldrin. The chromatographic conditions were as follows: Hewlett-Packard Type 5710 chromatograph, 6-ft. Supelco column, Type E6806, column temperature 220°C (isothermal), injection port and detector temperature 250°C, nitrogen carrier gas flow 60 ml/min, nitrogen guard gas flow 120 ml/min. Horizontal scale: 15 divisions per min, vertical scale 100 mV. The detector was operated in the constant-current mode with a cathode-anode current of 10  $\mu$ A and an anode-collector current of 10 nA (bias voltage at rest 20 mV).

aldrin, on an HP 5710 chromatograph. A 6-ft. Supelco column, Type E6806, was used in these experiments, with nitrogen as a carrier gas at a flow-rate of 1 ml/sec, and with the guard gas flow set at 2 ml/sec. The column temperature was maintained at 220°C, and both the injection port and the detector were kept at 250°C. Ultra-high-purity carrier gases were used in all the experiments, together with vacuum tight fittings and large well baked out moisture traps and tubing, to provide the cleanest environment possible.

This chromatogram was taken in the constant-current mode with the cathode-anode current fixed at 10  $\mu$ A, and the anode-collector current maintained at 10 nA, at a bias of about 20 mV. Note the very distinct, noise-free signals, even at this low level of injection.

The response curve for lindane, from 1 pg to 1  $\mu$ g, is illustrated in Fig. 14. The incremental signal follows an almost  $\frac{2}{3}$  power law, although not exactly so. If the response were extrapolated with the same slope to lower injections, a signal-to-noise

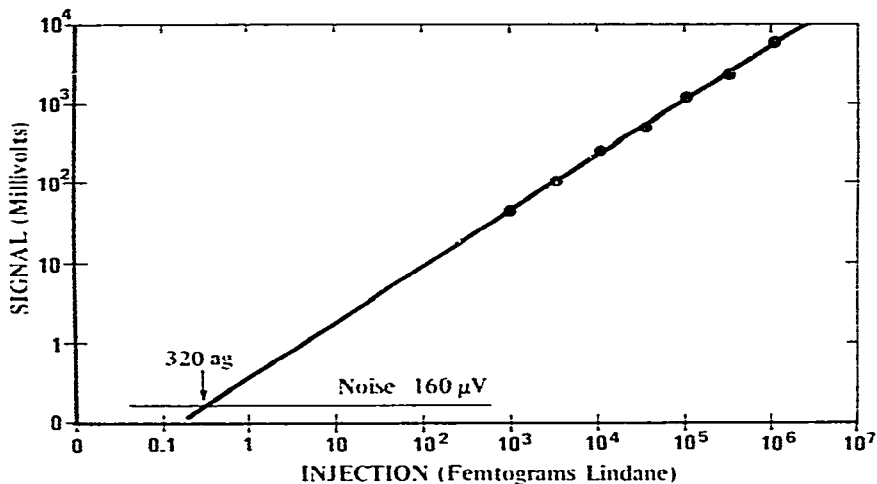


Fig. 14. Peak response curve of the ECD for lindane, measured under the same experimental conditions as Fig. 13. The response follows approximately a two thirds power law. If this response curve were to be extrapolated to the noise, the minimum detectable signal (signal-to-noise ratio = 2) would be 320 ag.

ratio of two (representing the minimum detectable signal) would be obtained at an injection of 320 ag ( $320 \cdot 10^{-18}$  g). It is, however, quite possible that the slope becomes more linear at lower levels; no subpicogram level injections have been attempted because of the difficulty of preparing correct dilutions at this level.

It is interesting to compare the experimental values with the estimates from the theory. Typically, a 1-pg injection of lindane will give a peak signal amplitude of about 30 mV. A total injection of 1 pg of lindane will, under the experimental conditions, give rise to a peak concentration of  $10^8$  atoms per  $\text{cm}^3$  in the detector. The average electron concentration on the anode is subject to some approximations, due to the difficulty of guessing the exact form of the current spreading from cathode to anode. Assuming cylindrical space charge flow, the best estimate is on the order of  $10^8$  electrons per  $\text{cm}^3$  at the anode (for  $10 \mu\text{A}$  of primary current). The ratio of the electrophilic to the electron concentration is therefore close to one, and since the experimental conditions are very close to those illustrated in Fig. 8, with  $N_i/N_e = 1$ , the expected signal is about 25 mV. The agreement is remarkable, and probably fortuitous, in view of the drastic approximations made in the numerical computation. The numerical model, however, does predict a linear concentration behavior in the picogram region, which is not born out by the experiments. On the other hand, it is interesting to note that the negative peaks predicted by the theory are indeed experimentally observed and precisely under those conditions, which indicated by the theory namely strong negative bias and low cell current.

At low injections (picogram) negative peaks are seen; at higher injections (20–30 pg), there is a negative precursor, followed by a positive peak, precisely as would be expected. Results for a similar, although not identical, detector operating in the constant-voltage mode, are illustrated in Fig. 15 again for lindane. Obviously, there will be a decrease in dynamic range if the sensitivity is increased, since the current can hardly be expected to drop below zero. The best observed experimental sensitivity

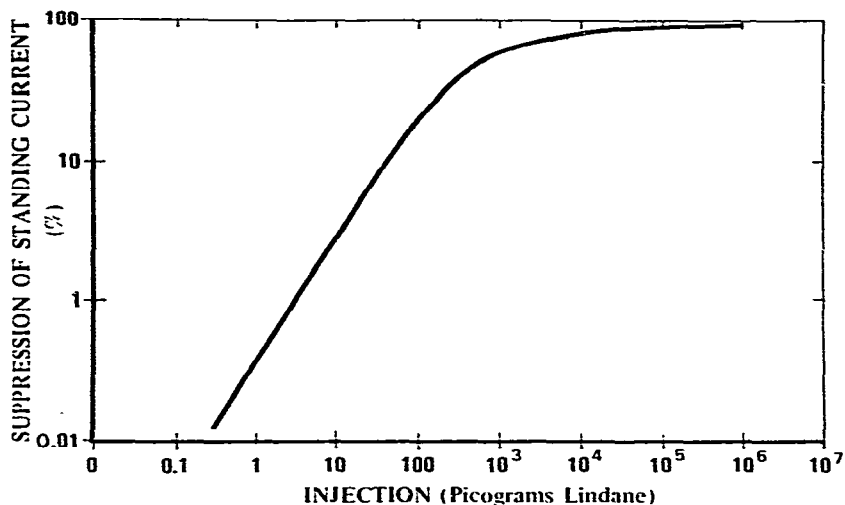


Fig. 15. Response curve for lindane, with the detector operating in the constant-voltage mode of operation. Bias voltage 200 mV, bias current at rest 8.1 nA. Plotted is the percentage suppression of the standing current, *versus* the total amount of lindane injected. The observed response, normalized to the standing current, is experimentally found to be largely independent of the standing current for small bias voltages, as predicted by theory.

was a current reduction of 65% at a 33-pg injection with a bias voltage of 200 mV. If the graph of Fig. 9 is taken to be representative, a 65% reduction in current would be obtained for a 4-pg injection, *versus* the 33 pg observed experimentally. The bias voltage was, however, 200 mV *versus* the -4 mV obtained from the computation, indicating that probably substantial amounts of electrophores were present, even at equilibrium. The independence of the shape of the relative response curve was, however, experimentally verified.

When using the constant-current mode, a slight peak broadening, as yet unexplained, is generally observed at the 10-ng level.

Although only results with lindane and aldrin are represented, the detector was found to be sensitive to any of the common electron-capturing compounds such as Mirex, diazepam, anthraquinone, malathion, etc. Correlation between the observed response in a radioactive detector and this detector is very strong. A 10- $\mu$ l injection of room air containing  $1 \cdot 10^{-14}$  g/ $\mu$ l of carbon tetrachloride, gave signals about 30–40 times above the noise (the column temperature was at 60°C in this case, to provide for sufficient time separation between the air peak and the carbon tetrachloride).

The detector appears to tolerate overloads without prolonged noticeable ill-effects, and seems to require very little clean-up time after removal from the chromatograph. Detectors removed from the chromatograph, stored for a few days in a clean bench and remounted were found to be almost in complete equilibrium in a time span of 2–3 h, whereas a radioactive detector treated the same way, might require at least 1 day.

## CONCLUSION

A new type of ECD has been described which uses a thermionic source of electrons, rather than the usual radioactive source. This allows the use of a sensitive new mode of operation, due to the phenomenon of space charge amplification. It appears that femtogram quantities of capturing compounds may be detected with this detector. A one-dimensional theory of operation has been developed and shows agreement with the experimental results. In view of the simplicity of the reactions taking place, it is hoped that this detector will allow eventually a full theoretical understanding of its operation.

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