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ELECTRON-CAPTURE DETECTOR WITH POSITIVE RESPONSE (INCREASE IN CURRENT)*

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SUMMARY

Even though the electron-capture detector is based on the removal of electrons by analyte molecules, and hence responds to these normally by a decrease in cell current, it is possible to utilize the space charge effect, *i.e.* its own response mechanism, to make the detector signal the passage of analyte by an increase in current ("positive" response).

A prototype electron-capture detector was designed to produce such positive response. It was built in three-chamber construction, using a bifurcated current flow to two anodes. One of these is intercepted by analyte molecules, the other is not. The two are coupled with each other, and with cation–electron recombination, via the spatially heterogeneous nitrogen plasma. The anode exposed to gas chromatographic column effluent produces (conventional) negative response, the anode bathed in pure carrier gas provides positive response.

The positive electron-capture response is similar in magnitude to its twin negative response, and to typical response from conventional electron-capture detectors. As is the case with response, noise in the two channels is also coupled through plasma perturbation, and that limits detection to a present minimum of 0.1 pg lindane per second. The importance of this detector resides less in its practical performance, which is unexceptional, than in the fact that it exists at all — and the implications this has for the confirmation of its space-charged based mechanism.

INTRODUCTION

Sometimes it is helpful to ask not what a detector can do but what it can *not* do. The question: "Why can an electron-capture detector not run on a.c. power?" prompted the recent development of an electron-capture detector driven by an alternatingly bipolar regime[1].

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This study was likewise prompted by a seemingly non-sensical question: "Why can an electron-capture detector not give *positive* response (increase in current)?".

That it can not would appear perfectly obvious. An electron-capture detector is based on the capture of electrons by analyte molecules, hence it responds to them by a drop in current (negative response). While this definition is simplified, it is essentially correct and applies, *mutatis mutandis*, to all of the electron-capture literature[2]. In fact, the prevailing concept of the literature, which sees the electron-capture detector as a "stirred reactor", clearly forbids an increase in cell current in response to electron-capturing analyte.

Yet, it should be most interesting to construct a "positive" electron-capture detector: in part just to see how it would perform and whether there were any advantages to operating it in so peculiar a mode; in part because such a detector could, by its very existence, provide some insight into the electron-capture detection (ECD) response mechanism. But, of course, common sense or at least common knowledge argues against the possibility that a detector of this sort could indeed exist.

There are only two, relatively minor reasons to suggest that it may not be impossible after all to construct a positive electron-capture detector. One is theoretical, the other experimental.

The theoretical impetus originates from the space charge theory of ECD response[3]. If migrating anions do, in fact, form a space charge that produces response, and if one of the effects of this space charge is a change in potential gradient across the β-generated plasma, then it should be possible to arrange space charge and gradient such that an increase in current could be registered at a suitably placed electrode.

The experimental impetus originates from an earlier attempt to offer the choice of two anodes to the stream of electrons coming from a typical radioactive ECD cathode. The idea was to monitor any change in the division of current between the two electrodes, *e.g.* when one of the electrodes was made of different metal and thus had a different "contact" potential than the other, when one had a different adsorptivity for column effluents, when one was deliberately covered by an adsorbent, when one was coated with a typical liquid phase, when both were coated but with different liquid phases, etc.[4]. For historical interest, Fig. 1 shows a blueprint of this "sorption electron-capture detector".

While we did expect to see some positive peaks emerging from the "sorption electron-capture detector", we were struck by the fact that these were produced not only by analytes that do not react with electrons, but also by substances known as strong electron capturers. Thus the older, experimental evidence provided some encouragement for attempting the construction of a positively responding electron-capture detector.

For this attempt, some earlier used principles of construction and operation should serve again. Some time ago our group described a two-chamber electron-capture detector, which was used to investigate whether cation–anion neutralization was a necessary condition for observing electron capture response. The two chambers were partially separated by an aperture that allowed the passage of clean carrier gas and electrons. The cathode chamber was flushed with clean carrier, while the gas chromatographic (GC) column effluent passed only through the anode chamber. Although the contact of cations and analyte-derived anions was thus precluded, the

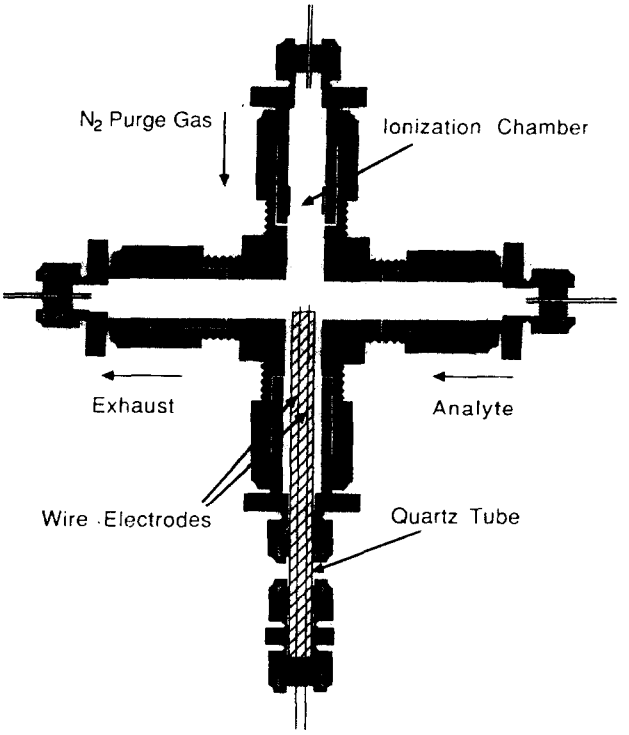


Fig. 1. An attempt to develop a differential "sorption detector" based on electron-capture detector construction elements (not to scale).

detector produced excellent response of high sensitivity[5,6]. While the premise of this detector has been the subject of criticism[7] based on a very large estimate of beta range[8], recent measurements of the spatial plasma distribution adjoining a ^{63}Ni foil under both initial[9] and steady-state[10] conditions have shown it to be valid.

Thus, a similar construction can be used here. However, it is necessary to expand it from a two-chamber to a three-chamber design. The middle or cathode chamber will house the ^{63}Ni radioactive foil and be swept by pure carrier gas. Electrons generated there will have the choice of migrating into either of two anode channels situated on opposite sides of the cylindrical foil. One anode chamber, like the cathode chamber, will be flushed only by pure carrier gas. The other anode chamber will be exposed to column effluent. In accordance with this nomenclature, the two anodes will be referred to as "unexposed" and "exposed", respectively. A picture of the detector is shown in the experimental section.

It may be well at this point to discuss shortly what, if anything, can be expected of such a detection system. We shall do this from different viewpoints, assuming that β radiation would or would not be confined to the cathode chamber; that analyte would or would not be restricted to the exposed anode chamber; and that either neutralization or space charge mechanisms of response, or both, would operate. As will be seen from that discussion, the desired positive response, *i.e.* an increase in

current, can occur only under a specific, narrow set of conditions — while all others lead to the conventional negative response or to no response at all.

To start out, it is quite obvious what will happen when no analyte is present and the detector is filled with pure carrier gas. Using the simplest drive, *i.e.* a negative d.c. potential on the radioactive foil, two streams of electrons will drift toward the two anodes (which, through two electrometers, are on ground potential). If the two interelectrode distances are about the same, and the exposed anode cell is not contaminated, the two currents will be of approximately the same magnitude. This magnitude will rise with the potential applied, up to a limiting value characteristic of the maximum number of collectable electrons — much like in a conventional, single-chamber d.c.-electron-capture detector. Electrons not collected by one of the electrodes will have recombined with cations in the central plasma region. One may expect that, at low voltages *i.e.*, when the collected current is much less than the maximum one, electrons will be withdrawn mainly from the two opposite plasma boundaries, *i.e.* from around the bottom and the top of the radioactive cylinder in the regions of the two apertures.

When an electron-capturing analyte now enters the exposed anode chamber, slow anions are formed there. In essence, the exposed anode chamber (together with the cathode compartment) will act like one of the two-chamber detectors described earlier[5,6], *i.e.* it will produce normal (negative) electron capture response. The fact that cation–anion recombination is largely or totally prevented means that response must be of the "space-charge" type[3]. This mechanism postulates that, following the capture of electrons by analyte molecules, the potential gradient steepens to move the slow anions through the anode chamber, therefore flattening out in the cathode chamber and leading to increased cation–electron residence times (hence recombination rates) in the plasma. The current collected by the exposed electrode drops in conventional, negative response.

Alternatively, though in our opinion not correctly, one could assume that the plasma somehow extends into the anode chamber, or that analyte happens to reach the cathode chamber by diffusion or convection, and that it is therefore classical cation–anion neutralization that reduces the current. In either case, the predicted behaviour of the left detector side is the same.

What will show up on the right side of the detector is much more difficult, but also much more interesting to predict. There are basically three possibilities:

First, plasma and analyte might significantly overlap somewhere in the detector and the classical neutralization mechanism could take place. That would decrease the number of electrons in the plasma, allowing less electrons to migrate to the unexposed electrode. In other words, the unexposed electrode, like the exposed one, would also experience a drop in current, *i.e.* exhibit negative response.

Second, plasma and analyte might not significantly overlap and, so to speak, the right side of the detector would not know what the left side is doing. This should be essentially the case when relatively low currents are drawn from the periphery of the plasma, while its central portions are dominated by recombination. The right side of the plasma would not be affected and, of course, neither would the right anode chamber. In this configuration, the left, exposed electrode would experience a drop in current, *i.e.* normal negative response; while the right, unexposed electrode would not register any change in current, *i.e.* it would provide no response.

Third, plasma and analyte might not overlap, but the two sides of the detector would be effectively coupled by the plasma. This would be primarily the case when there is little recombination occurring in the plasma and the two channels do compete effectively for every electron available. If the space charge theory is correct, then the gradient from the left side will flatten, pulling fewer electrons out of the plasma. Under normal ECD circumstances or in a two-chamber detector, that would simply make more electrons available for recombination. Here, however, the right side, which does not experience the anion-induced changes in the potential gradient, continues to attract with the same force a suddenly increased number of electrons. And that means — if conditions are such that the plasma provides strong coupling between the two channels — that the unexposed electrode will experience an increase in current, *i.e.* that it will produce positive response. (If, on the other hand, the changes in potential gradient postulated by the space charge mechanism were not to exist, then no response should be observed on the unexposed side.)

Thus, interestingly, the only set of conditions under which positive response should be observable by the unexposed electrode are the following: Plasma and analyte do not overlap significantly, a space charge mechanism increases the number of available electrons in the plasma, and the two channels are effectively coupled via the plasma, *i.e.* one channel can make use of the other channel's electrons should these suddenly become available. Thus, the presence or absence of positive response can act as a criterion by which ECD mechanism can be judged.

EXPERIMENTAL

The three-chamber detector is shown in Fig. 2. Its body was constructed from stainless-steel Swagelok fittings: a 1/2-in. bulkhead union, a 1/2- to 1/4-in. reducing

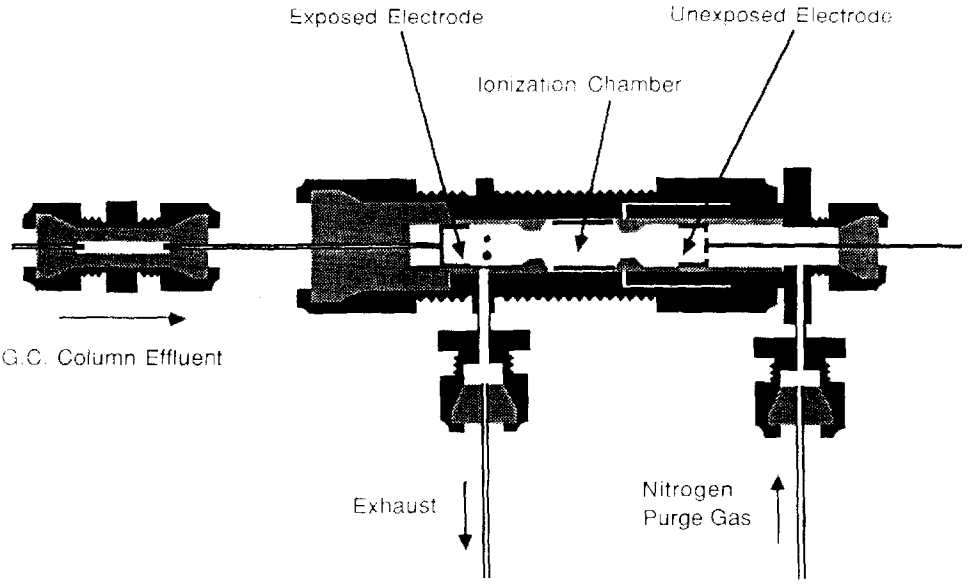


Fig. 2. The three-chamber "positive electron-capture detector" (not to scale).

union, and two 1/4- to 1/8-in. reducing unions. The bulkhead union and the 1/2- to 1/4-in. reducing union were fitted together in the conventional manner, whereas the two 1/4- to 1/8-in. reducing unions were silver-soldered into holes drilled into the main detector body as shown in Fig. 2. Two stainless-steel "cups", mounted on 1/16-in. stainless-steel tubing, served as the electrodes and were held in place by ferrules and sleeves made of polytetrafluoroethylene (PTFE). The "exposed" electrode was drilled through along the axis of the cup to serve as inlet for the GC column effluent. One of the two small reducing unions was used as the purge gas inlet, the other as the outlet line for the combined flows of purge gas and column effluent.

The radioactive source was a cylinder of ^{63}Ni electroplated on gold foil, measuring 30 mm in circumference and 10 mm in length, with an approximate activity of 10 mCi. It fitted firmly inside the bulkhead union with which it was in electrical contact. The foil and the electrodes were held in position by PTFE ferrules and sleeves. The sleeves were not of uniform cross-section, but had constrictions (apertures) which formally divided the assembled detector into three chambers.

The left chamber contained the exposed electrode, through which column effluent entered from the bottom centre of the cup. The effluent left through peripheral openings in the PTFE sleeve. The effluent was confined to the left compartment by a flow of clean carrier gas (nitrogen) coming from the middle chamber through the PTFE constriction, with which it was forced to exist through the 1/8- to 1/4-in. union.

The middle chamber contained the radioactive foil and thus the plasma. This compartment, plus the right chamber housing the "unexposed" second anode, were swept by a flow of clean nitrogen. The carrier and purge gas nitrogen was of "high purity" grade and was further cleaned by passage through a molecular sieve filter and a heated trap for scavenging oxygen and water.

To control the initial distribution of current among the two anodes, the PTFE sleeves were made long enough to allow a spatial adjustment of either electrode toward or away from the middle-chamber cathode.

The whole detector was placed in a heating block made from 1/4-in. aluminium plate and kept electrically insulated by Marinite (Johns Manville) inserts. The block was heated by two cartridges (Watlow) and its temperature was monitored by an iron-constantan thermocouple. This detector assembly was then mounted in a lab-made compartment situated in the side of a Tracor 550 gas chromatograph. Because of its PTFE parts, the maximum detector temperature was limited to 225°C. The effluent transfer line temperature was always kept slightly lower than that of the detector (but, or course, higher than that of the column).

Analytes were chromatographed on a 120 cm × 2 mm I.D. borosilicate column packed with 3% OV-101 on Carbowax 20M–modified Chromosorb W, 60–80 mesh, with a nitrogen carrier gas flow of 8 ml/min. The detector purge flow was adjusted to a level at which no signs of penetration of analyte into the foil chamber could be observed.

The body of the detector and with it the radioactive foil were polarized by a Keithley 240A high-voltage supply for the d.c. mode, by a Tracor 550 ECD power supply for the unipolar pulse mode, and by an Interstate high-voltage function generator for the a.c. mode. The left and right chamber electrodes (the exposed and the unexposed electrode) were connected by screened cables to the two channels of a

Tracor 550 GC dual-channel electrometer with a conventional dual-channel strip chart recorder attached.

RESULTS AND DISCUSSION

The simplest characteristic of an electron-capture detector is its current profile, *i.e.* its I/V plot in d.c. mode under baseline conditions (no analyte). If the two anodes of the three-chamber detector are connected, the summed output looks, not unexpectedly, like a perfectly conventional d.c. electron-capture detector current profile. That is, the current rises non-linearly with rising voltage until it levels off at a constant value when all of the accessible electrons (and cations) are being collected. This plateau is reached at about 15 V, with the exact value depending on interelectrode distances and the cleanliness of both detector and carrier gas.

When the two anodes are monitored separately, as is the purpose of this study, the distribution of current among them can be set by adjusting the interelectrode distances (note that both anodes can be moved forward and backward in relation to the detector body and the common cathode). These distances are deliberately set so that the exposed anode receives the larger baseline current under a d.c. potential, since all predictions agree that this electrode will experience a drop in current when analyte enters the cell.

This adjustment having been made, current profiles can be measured for each anode chamber (channel). The resulting baseline I/V plots are shown in Fig. 3. There is nothing really surprising about them; however, the fact that the individual currents differ from each other, and that they do not reach a constant value at potentials above 15 V (while their sum does) should perhaps be mentioned. This is not too surprising, since the interelectrode distances have been deliberately set such that the exposed chamber would receive the larger portion of the baseline current. This means

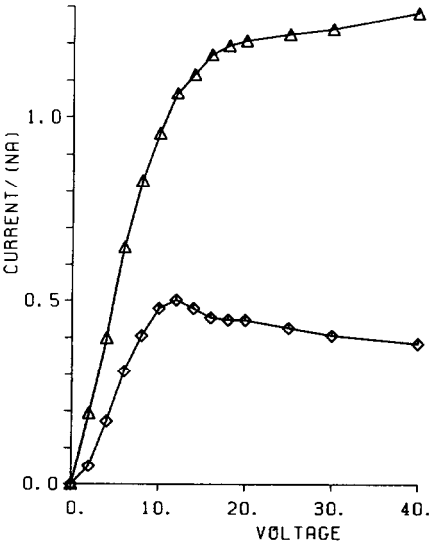


Fig. 3. d.c. current profiles: (△) Exposed electrode; (◇) unexposed electrode.

that the exposed cell is able to draw more current from the beginning, *i.e.* that the potential gradient is steeper across "its" side of the plasma and more electrons are pulled out as a consequence. As the phrasing implies, the competition here is not against the other channel, but against the recombination reaction in the plasma.

As the potential increases, however, and more and more electrons are pulled out of the plasma toward both sides, the plasma density decreases and the second-order recombination reaction effectively shuts down. When the potential reaches about 15 V, all electrons are pulled out and the two channels do now compete against each other.

In this case, the "stronger" channel keeps making further gains, although it is not completely clear what effects determine that outcome and to what extent. Aside from interelectrode distance, the detector is not perfectly symmetrical, both from a structural and a chemical point of view. As regards the latter, the exposed chamber may retain some memory of analytes long passed; and it is bathed in "pure carrier gas" that has, in part, had to come through the chromatographic column. Thus it would not be too surprising if some, however minute traces of electron-capturing substances should be found there. Its impedance would thus depend to some degree on how many anions are formed from this contamination. As the voltage increases, electrons are pulled faster and faster through the exposed chamber and less and less anions are formed. This gives the exposed channel a relative advantage in its competition with the unexposed one.

Differently expressed, it is possible to imagine that the exposed current profile shown in Fig. 3 actually includes a contribution from an analyte and that the imaginary "true" profile would thus be somewhat higher, with the difference between the two reflecting conventional response and therefore being largest in the "knee" region. This "response" now shows up in the unexposed profile as a maximum. While this

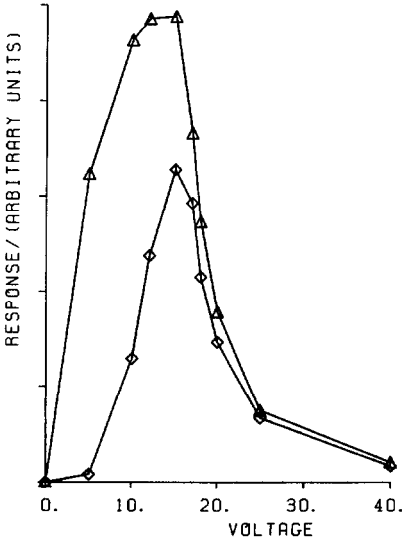


Fig. 4. d.c. response profiles: (△) Exposed electrode, negative response (decrease in current); (◇) unexposed electrode, positive response (increase in current). Analyte: 100 pg lindane.

interpretation is consistent with observation and likely correct, it concerns a minor effect that is of little overall importance and has been mentioned here only for completeness' sake.

More important, of course, are the response profiles of the two chambers. These curves were obtained using 100-pg injections of lindane (in hexane), an amount generally within linear range. They are shown in Fig. 4.

The most striking fact about them is that response is obtained from a channel that is not exposed to analyte, and that this response is positive, *i.e.* an increase in current. Besides providing the raison d'etre for this manuscript, this fact means that plasma and analyte regions do not significantly overlap, and that a space charge mechanism governs the behaviour of this detector. By inference, the latter statement may be true for conventional ECDs as well.

Fig. 4 also demonstrates clearly that positive response from the unexposed electrode comes into its own only at higher voltages, while negative response from the exposed electrode reaches prominence at lower potentials. This is easily explained in light of the previous discussions: The exposed chamber functions like a normal electron-capture detector (though run in a "separated"[5] configuration) and it will show immediately and at any voltage the space-charge effect electron-capturing analytes have on recombination in the plasma. In comparison, there is little or no change at low voltage in the unexposed chamber: Both channels compete for electrons against a still dominant recombination reaction.

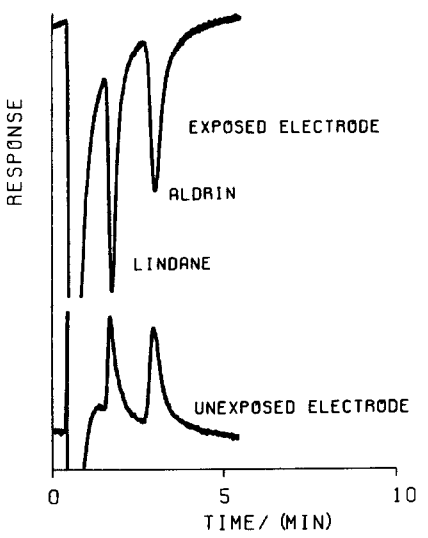
This changes at higher voltages, with the two channels now competing against each other. The exposed channel produces just about as much conventional negative as the unexposed channel produces unconventional positive response.

The difference between the two curves represents the amount of charge that is removed from the gas phase by, mainly if not exclusively, cation–electron recombination in the plasma. A contribution from cation–anion neutralization (resulting from a possible plasma-analyte overlap) cannot be totally ruled out at this stage but would, if it indeed exists, be likely of only minor importance.

Essentially the same type of behaviour as shown by lindane in Fig. 4, is observed for aldrin and nitrobenzene, the former being considered a dissociative, the latter an associative electron capturer. A typical chromatogram of lindane and aldrin is displayed in Fig. 5 and typical calibration curves for these analytes are presented in Fig. 6, both for two-channel detection. Fig. 7, on the other hand, shows lindane calibration curves, measured only in the positive mode but at three different voltages. Overall, the performance of this detector (which wasn't really constructed with optimum performance in mind) is similar to that of a run-of-the-mill d.c. electron-capture detector; displaying perhaps a slightly longer linear range and a slightly lower sensitivity than usual. Both aspects are not too surprising.

Earlier prototype detectors, which had been deliberately designed to favor a space charge mechanism, had at times shown somewhat longer linear ranges. The slightly reduced sensitivity (which is *not* typical of a space-charge driven detector) could be attributed to a construction that serves primarily mechanistic purposes; but there is an additional, and unexpected, effect operating here.

It is apparently caused by the plasma coupling the two channels. A plasma perturbation would send a smaller number of electrons into one, a larger number into the other channel. Considering the competition between the two channels and



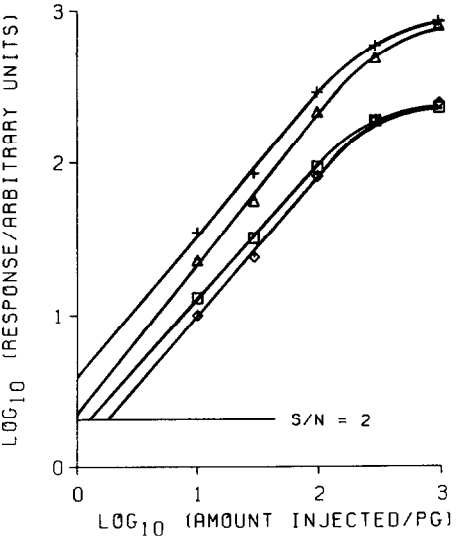
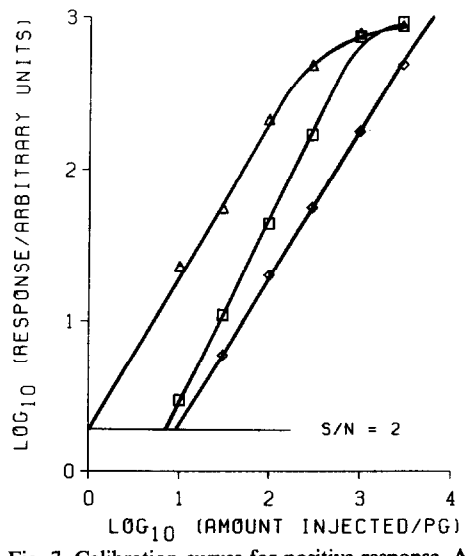


Fig. 5. Simultaneous chromatograms from the three-chamber detector. Analytes: 100 pg each of lindane and aldrin. Voltage: 18 V.

Fig. 6. Calibration curves. Analytes: 100 pg each of lindane and aldrin. Voltage: 12 V. (+) Lindane, exposed electrode, negative response; (△) lindane, unexposed electrode, positive response; (□) aldrin, exposed electrode, negative response; (◇) aldrin, unexposed electrode, positive response.



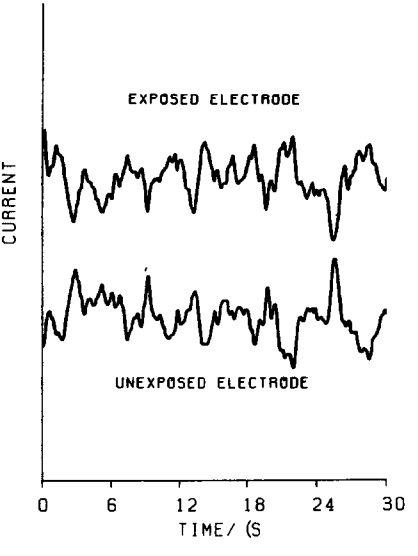


Fig. 7. Calibration curves for positive response. Analyte: 100 pg lindane. Voltage: (△) 12 V, (□) 20 V, (◇) 40 V.

Fig. 8. Amplified simultaneous noise of the two baselines. Voltage: 12 V. Amplifier and recorder time constant: *ca.* 0.5 s.

the particulars of the plasma, the electrical divide must be of a rather shifty nature. This means a larger amount of noise is generated when the two channels are effectively coupled. A high-sensitivity, simultaneous record of the two baselines illustrates this in Fig. 8. Positive deviations on one channel are mirrored by negative deviations on the other, and *vice versa*. If the two baselines are summed, the noise level decreases in spite of the considerably larger total current. Still, even on its relatively high own noise level, the unexposed channel can detect lindane by positive response down to 0.1 pg/s.

With the main purpose of this study thus achieved, attention can focus on two peripheral areas. These are the possible overlap of plasma and analyte regions, and the possible use of bipolar (a.c.) or conventional unipolar pulsing regimes.

The observation of positive response essentially means that little, if any, overlap occurs between plasma and analyte, *i.e.* that the analyte does not diffuse in significant amounts into the plasma or beyond it into the "unexposed" chamber. Of course, the key words in this statement are its modifiers: it is not possible to preclude overlap completely, but it is possible to judge whether this overlap is significant. One of the experimental approaches that allows such a judgement to be made is the variation of purge flow, which has been used here in a manner similar to earlier studies of "separated" chamber designs[5,6]. When the purge flow is reduced in steps, there comes a point when the analyte is able to diffuse in significant amounts into regions where it should not be. This is obvious from the "unexposed" channel signal, which is at first positive, then shows peak distortion and finally changes into negative response as the purge flow is being progressively decreased.

Another approach at demonstrating possible overlap is to use unreasonably large amounts of analyte, *i.e.* to saturate or overwhelm the system. This is shown in the sequence of Fig. 9. Chromatogram a shows positive response to 100 pg of lindane, *i.e.* an amount that is close to the upper end of the linear range. The peak appears undistorted. At 300 pg, in chromatogram b, the later parts of the peak are disturbed (as one would expect from a diffusion–convection process that operates against the flow of pure carrier gas and is comparable in its time scale to peak elution). At 1000 pg, in chromatogram c, a negative signal begins to appear, followed by a time-shifted positive one.

Again, this makes sense: when the peak starts, response is positive. As the concentration grows, diffusion effects grow more noticeable: Significant amounts enter the plasma and the response turns negative. The right side of the detector now functions almost like a conventional electron-capture detector. When the chromatographic peak starts to decline, and as analyte molecules are cleared from the right side of the plasma by pure carrier, the detector returns to its original behaviour. While some remnants of the analyte will still pass through the exposed section (which carries the exit line) the unexposed channel is already clean and again shows a positive response. Note that in order to observe this sequence, the linear range must be exceeded by a large margin.

At 3000 pg, in chromatogram d, the early and the late positive signal stay the same, as expected, while the negative signal shows further growth, in line with increasing amounts of analyte diffusing into areas they should not enter. While this sequence of positive and negative signals is in qualitative agreement with the perceived mechanism, it would be difficult to assess quantitatively how much effective

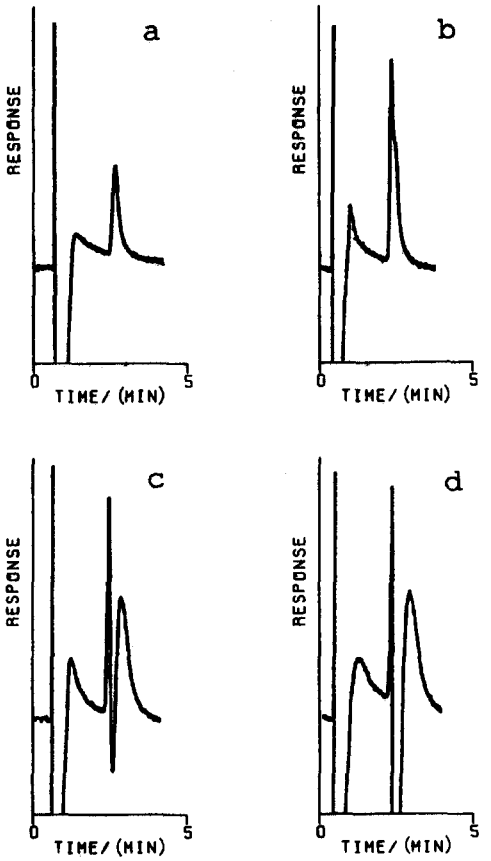


Fig. 9. Overwhelming the system: The effects of plasma/analyte overlap on the "unexposed" channel. Voltage: 18 V. Analyte: 100, 300, 1000 and 3000 pg lindane for chromatograms a, b, c and d, respectively.

overlap exists, *i.e.* how much mechanistic interference is generated. Since a major negative effect occurs only at 3000 pg, some 30 times larger than the upper end of the linear range, the interference is probably on the order of only a few percent. This assures experimental validity for mechanistic deductions, and affirms the questioned geometric premise of earlier work[5,6].

Finally, the effect of drive regimes other than d.c. is interesting to investigate, even though much of it could have been (but was not) deduced from prior experience.

Conventional unipolar pulse regimes include relatively long field-free intervals, during which the electron (and cation) populations build up significantly and their recombination becomes more and more important. Unless the pulse regime were to be an unusually fast one, positive response, if it does occur, should be small. This was precisely what was found by experiment.

Pulsed response was observed at both the exposed and unexposed electrodes. The positive response was much smaller than the negative response. This would indicate that charge is being lost by recombination in the plasma region and response is thus similar to the d.c. response observed at low voltages.

Of somewhat greater interest is the effect of an a.c. regime such as a bipolar, rectangular pulse train. A detailed interpretation of the behaviour of a.c.-driven conventional and lab-made electron-capture detectors has been given[1] and will not be repeated here. However, a short summary may be helpful to serve as a base for the discussion.

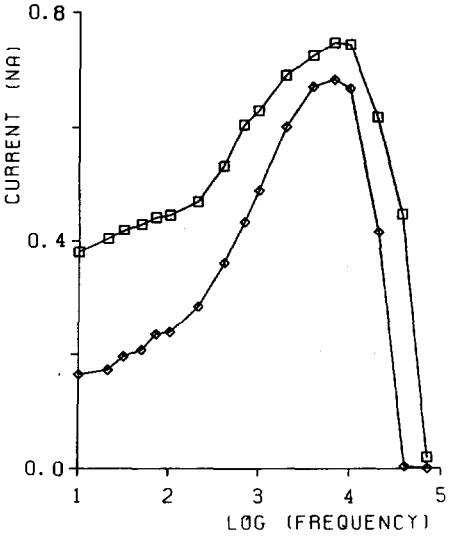
The possibility of a.c. operation is predicated on pronounced plasma heterogeneity, *i.e.* on the system *not* being a "stirred reactor". The current and response profiles (I/f and R/f plots, where f denotes frequency) from an a.c. electron-capture detector are characteristic curves, which can be described, respectively interpreted, as follows:

Starting from low frequency, say 5 Hz, the current is close the half the comparable d.c. current, rising slowly with frequency as steady-state populations of elec trons accumulate during the reversed-field phase and are forwarded to the regular-field phase that follows it. The linear rise in current ends at about 1 kHz, but a continuing and progressively slowing ascent brings the current up to a plateau level, a level that lies just below that of a comparable d.c. system. This means that the radioactive foil is unable to collect electrons during reversed field but must pass them on to the subsequent regular field phase for transport to the counter-electrode. The descent from the plateau, which occurs in or around the 10–100 kHz region, depending on detector dimensions, pulse amplitude, and choice of carrier gas, is caused by the increasing number of oscillating electrons that are no longer capable of reaching the counter-electrode.

The ascent to and the descent from the current plateau are the two regions where an introduction of analyte makes the greatest difference: The response profile shows two distinct maxima there. The maximum at high frequency has been clearly attributed to a space charge effect, but bets on the interpretation of the low-frequency maximum were carefully hedged. While it seemed reasonable to assume that the classical neutralization mechanism played a significant role in the latter, a contribution from some type of space–charge mechanism could not be ruled out and a conclusive definition was deferred until further evidence could be obtained on the relative magnitudes of recombination and neutralization rate constants[1].

This makes the present context even more interesting: If space charges do play a significant role in the low-frequency maximum, then the latter should show up as positive response in the three-chamber detector. The maximum at high frequency, on the other hand, should show up as a matter of course, provided interelectrode distances are not so different as already to shut off current from the unexposed channel at a frequency where the exposed channel is still busy producing its maximum. Overall, of course, the interesting question is whether a.c. does, in fact, produce positive response and, if so, over what frequency range.

In a.c., the reversed-field half cycle behaves much like the field-free interval of a unipolar pulsing regime, *i.e.* electron and cation concentrations build up and recombination becomes significant. Hence one can predict that, particularly at low frequencies, less positive response is expected. On the other hand, a.c. is generally a more powerful regime (the regular-field polarization is imposed half of the time!) than the typical pulsed regime with its long, field-free intervals. That would lead to the expectation that positive a.c. response should generally be less than that of a d.c., but more than that of a pulse system. This, again, is confirmed by the experiment.



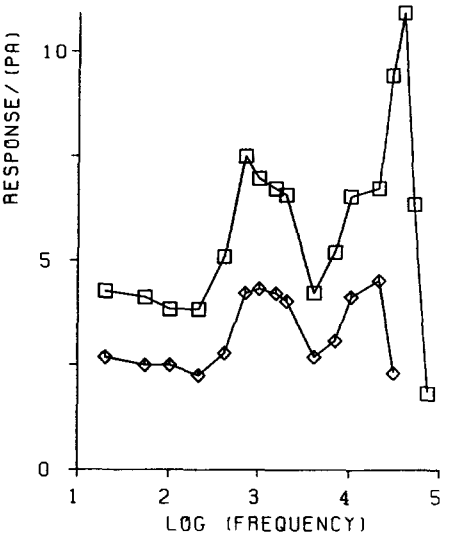


Fig. 10. a.c. current profiles. Rectangular pulses of +/− 20 V amplitude. (□) Exposed electrode, (◇) unexposed electrode.

Fig. 11. a.c. response profiles. Rectangular pulses of +/− 20 V amplitude. Analyte: 100 pg lindane. (□) Exposed electrode, negative response, (◇) unexposed electrode, positive response.

Fig. 10 shows the two currents received by the exposed and unexposed electrodes under baseline conditions. These profiles are very similar to profiles obtained from conventional detectors[1]. The cut-off at high frequency is very sharp, the unexposed channel current has already stopped when the exposed channel is still at about two thirds of its maximum height. This is a function of the relative interelectrode distances (which had already been changed from the d.c. settings in order to allow some current to flow into the unexposed channel).

The effect carries over to Fig. 11, which shows the response profiles for the exposed and unexposed channels. Response in the unexplosed channel is positive throughout, but it is cut short in the region of the high-frequency maximum because much of the signal-carrying current no longer reaches the electrode. The overall shape of the profiles, however, is similar to that produced by conventional electron-capture detectors.

Most important in the light of previous discussions, however, is the fact that the low-frequency maximum can be clearly recognized and that it shows up well in positive response. This means that it must be based, at least in part, on a space-charge mechanism and that, by analogy, the low-frequency maximum found in regular electron-capture detectors should contain a significant contribution of a space–charge based mechanism as well.

Thus, the existence of positive response, in the general order of importance d.c. > a.c. > unipolar pulsed, clearly demonstrates the presence and significance of space–charge mechanisms in all electron-capture detector systems tested so far.

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