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EVIDENCE FOR MORE THAN ONE RESPONSE MECHANISM IN PULSED ELECTRON-CAPTURE DETECTORS*

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SUMMARY

Evidence has been found for two distinct response modes operating in a laboratory-made and a commercial pulse-driven electron-capture detector. These modes are speculatively associated with a classical "neutralization" process and a recently proposed "space charge" mechanism.

INTRODUCTION

There is little doubt that the electron-capture detector (ECD) rightfully bears its name: Quite a variety of techniques have shown analyte molecules to produce negative ions. Their further fate, however, is less well known: How they make the detector respond has been the subject of some recent debate.

To understand the mechanism of response may be interesting and perhaps even useful for most analytical work. But it becomes essential when physico-chemical data are to be extracted, or when this detector is to be used in an "absolute" measurement such as gas phase coulometry¹⁻⁸. In this technique, the response must accurately reflect the moles of electrons initially captured.

Interestingly enough, one of the pioneer authors that described responses coulometric¹ had actually found one hypercoulometric⁹. This is interesting because the classical ECD mechanism¹⁰ implies a limit: Not more than one electron should appear to be captured by any molecule capable of doing so. Yet, apparent electron molecule ratios as high as 50 F/mol have been measured—even if only under d.c. fields and elevated pressures^{11,12}.

These surprising ratios called for an explanation and prompted us to speculate on an "alternative" response mechanism for d.c.-ECDs¹³. It portrays response as the effect of migrating anions upon the cation-electron recombination rate. In other words, the recorder signal serves no longer as a quantitative measure of initial electron capture, and hypercoulometric behavior becomes possible. Certain predictions of this theory have since been confirmed¹⁴⁻¹⁶.

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To breach the coulometric limit, however, did not necessarily violate the classical ECD theory. The latter had maintained all along that only "field-free" conditions —*i.e.* a pulse regime of short pulse widths and long pulse intervals— could be trusted to provide reliable data. Other regimes, especially d.c., could lead to "erroneous and anomalous responses"¹⁷.

Although hypercoulometric response has not been unknown to pulsed systems^{9,13,18–20}, there always remained the question how closely conditions had approached the field-free ideal; and whether relatively small effects could not have been due to, say, some electron-capturing products of the initial sample²¹ or a recycling species²². Furthermore, conditions such as cell geometry and radioactive range¹³ have a bearing on whether or not hypercoulometric behaviour can be observed —quite apart from the question whether or not the latter does indeed occur on a molecular level. Thus the choice (or happenstance) of detector construction and operation may have been responsible for the presence or absence of hypercoulometric response.

Recently we designed a detector in which the classical ECD response mechanism —the gas-phase neutralization of an analyte-derived anion— could be excluded at will. Under those conditions and in the d.c. mode, the detector exhibited good response¹⁶. A newer, more versatile model behaved likewise²³. Since it could be easily switched between the two configurations that included or excluded the classical cation-anion neutralization, it appealed to us as a potential tool for probing the existence of more than one response mechanism. The probe was not directed at the mechanism of the initial capture of an electron (associative, dissociative, etc.), but at the way in which this initial reaction was translated inside the cell to "response"— *i.e.* the electrical measurement that finally appears as a peak on the recorder chart.

Some of our earlier d.c. experiments seemed to indicate that, even with the classical mechanism allowed, it was the alternative space charge mechanism that produced most of the response^{14,16}. On a formal basis one could even imagine that the two mechanisms opposed one another in their competition for the analyte-derived anion: A neutralized anion no longer contributes to the space charge, while an anion migrating through the unipolar region can no longer find a cation for neutralization. (The d.c. detector in this case is presumed large enough to exhibit bipolar and unipolar regions.)

Obviously these d.c. experiments invited extension to the pulse regime. With the classical mechanism disallowed, would a pulse-driven ECD fail where a d.c.-powered one had worked so well? That seemed unlikely. And, indeed, "clean" conditions —*e.g.* pulses of 1 μ sec width, 360 μ sec period and 60 V amplitude— produced subpicogram responses. That seemed to settle the matter.

However, this was a matter of some importance and so we felt obliged to examine the full range of pulse conditions available to us. That turned out to be a lucky decision because it produced evidence (where before there had been only conjecture) of more than one response mechanism at work.

EXPERIMENTAL

The laboratory-made ECD used in this study is shown in Fig. 1. It can operate at high temperatures²³ and resembles an earlier, low-temperature model¹⁶.

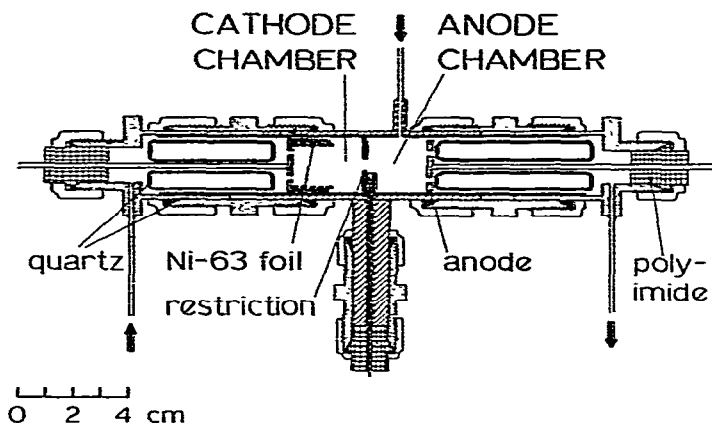


Fig. 1. Two-chamber electron-capture detector for "separated" and "conventional" mode operation.

Repeated here for reader's convenience, this type of ECD uses a restriction that formally divides the detector into cathode chamber (housing the radioactive foil) and anode chamber. The distinguishing feature of this construction is that the column effluent can be routed either to the cathode or to the anode chamber. In the former, "conventional" mode, column effluent and purge gas flow through the whole detector (in Fig. 1 all the way from the left to the right past the blocked central inlet); while in the latter, "separated" mode, the column effluent enters the anode chamber via this central inlet, and meets a fast stream of purge gas sweeping across the restriction from the cathode chamber. In either case, all gases exit at the far right end of the anode chamber. According to arguments made earlier¹⁶, the separated mode prevents the contact of cations with solute-derived anions, thereby precluding the classical neutralization mechanism.

A conventional Tracor ECD pulsing unit (part of the Model 550 electrometer) was used initially. If required, its output was amplified by a laboratory-made circuit. Nominal settings of the pulse power supply were ignored in favor of direct measurements by oscilloscope. Later, a Phillips PM 5705 pulse generator was used in conjunction with the laboratory-made inverting and amplifying circuit shown in Fig. 2. This

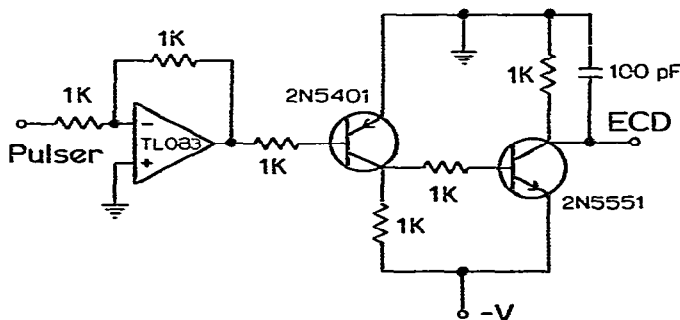


Fig. 2. Inverting and amplifying circuit. K = kΩ.

allowed variation of the pulse width from less than 1 μsec to values approaching the pulse period, *i.e.* d.c. Electrometers were of the varactor type supplied with the Tracor 550 gas chromatograph.

Responses were recorded for lindane (γ -hexachlorocyclohexane) and on occasion 2,4,6-trinitrotoluene (TNT) at different concentrations, different temperatures, and different flows of nitrogen; at different settings of pulse width, period, and amplitude; and in separated and sometimes in conventional mode (see above) —but these measurements were made on a selective rather than on an exhaustive basis.

RESULTS AND DISCUSSION

Similar to the "voltage profile" of the d.c. regime, the "pulse profile" —that is a plot of baseline current over a range of pulse widths— is often considered diagnostic for the state of an ECD. It will tell an experienced analyst how clean the ECD is, what settings to use and what performance to expect.

At first sight, the pulse profiles of this study did not bode any unusual responses. They rose more or less steadily and finally leveled off at long pulse width. The corresponding response curves, however, were most surprising: They clearly exhibited *two* maxima.

This unexpected behavior is illustrated in Fig. 3 for the separated mode. Response peaks strongly in two separate regions, but between these it drops down to rather low levels. For purpose of subsequent referral, we shall name the sharp maximum on the left "A", the broader one on the right "B".

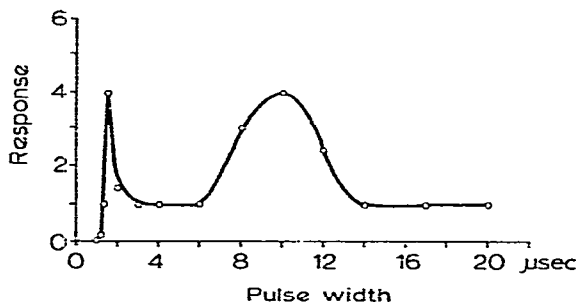


Fig. 3. Typical response maxima in the separated mode. Sample: 10 μg lindane. Column: 3% OV-101 on Carbowax 20M-modified Chromosorb W at 175°C. Flow-rates: column 14, detector purge 200 ml/min. Detector: 280°C, aperture diameter 8 mm. Pulses applied to cathode: amplitude -30 V, period 360 μsec .

These two humps emerged from many measurements, although often in not as pronounced a form. Fig. 4 shows a comparable run in the conventional mode, and includes data taken off a commercial (Tracor) detector. It suggests that the presence of two response maxima is a fairly general phenomenon and not dependent on the use of the separated mode or a particular laboratory-made ECD. One must add, however, that other commercial detectors have not been investigated in this context and that these, if of a different and perhaps smaller geometry, may not produce similarly obvious effects. But that, of course, is speculative.

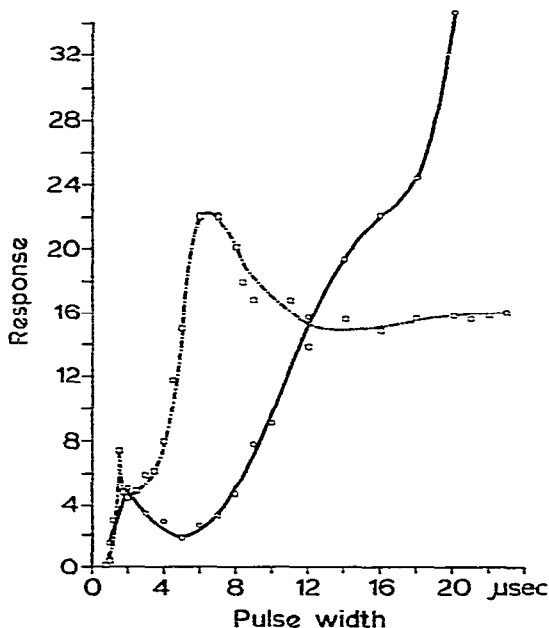


Fig. 4. Response maxima of the conventional mode on the laboratory-made detector (□) and on a commercial (Tracor) ECD (○). Laboratory-made ECD: -60 V pulse amplitude, 360 μ sec period. Tracor ECD: column 17, purge 43 ml/min; 280°C ; -30 V pulse amplitude, 360 μ sec period. Other conditions as in Fig. 3.

A larger number of experiments were performed to follow the behavior of the two response maxima when subjected to a variation of detector parameters. The separated mode was used almost exclusively, since the induced changes were clearer and could therefore be measured over a wider range of operating conditions.

Changing the pulse width was not expected to change the nature of the process in which an electron is initially captured. From that point on, however, it is not clear whether there are two (or more) distinct response mechanisms at work, or whether one and the same response mechanism somehow produces two response maxima owing to, say, the peculiarities of detector geometry. To complicate matters further, one must be aware that the initial electron capture reaction may be similar in nature, but not in extent, at conditions corresponding to the two response maxima: The number of available electrons may be quite different at the two settings.

These caveats noted, it is still reasonable to expect that the behavior of the two response maxima under varying detector conditions would reflect the response mechanism(s) at work: If there was only one, the induced changes would be similar; but with two mechanisms operating, at least some of the changes should be dissimilar. The task then is to look for consonant or dissonant shifts in amplitude and position of the two response maxima.

In regard to the first parameter, the *absolute* response amplitude may not be the best measurement to plot, since it can be influenced by a variety of extraneous factors such as column bleed. The *relative* size of the two maxima, however, should suffer much less from such effects. It is the ratio of response maxima A and B, therefore, which is shown in Fig. 5. Clearly, this ratio varies considerably with circumstances, suggesting that different response mechanisms are at work.

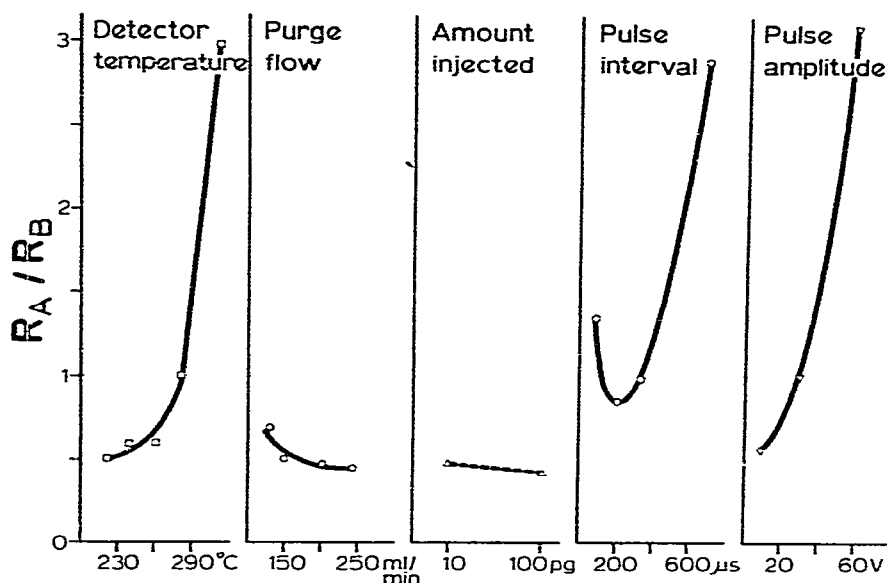


Fig. 5. Relative response (ratio of peak heights) at the two maxima for various experimental conditions.

This appears also indicated by the response profiles of Fig. 6, showing the peak heights for lindane and TNT in conventional mode. It should be added, however, that there appeared very little difference between the two compounds when tested in separated mode, and that no further studies with different compounds were done.

It should also be noted that the *position* of the maxima on the pulse width axis was essentially the same for the two compounds. This is in agreement with information from earlier studies, in which the position of response maxima was generally independent of solute structure.

While the nature of the solute did not appear to influence the position of the response maxima, a variety of detector conditions did. Rather than to present these measurements as mere numbers in a table, the response profile format was chosen to convey the full range of available information.

Fig. 7 presents the profiles of lindane at three different temperatures. Here, as in some other correlations, the measurements were repeated after some weeks in order to confirm the validity of initially established trends. Aside from the shift in relative amplitude discussed earlier, Fig. 7 shows response maximum A shifting to shorter pulsewidths as the temperature is raised, while response maximum B appears to remain more or less stationary.

This is a matter of some interest. The temperature dependence of response has been used as a kinetic probe almost since the ECD's inception. For this and other physico-chemical purposes, the choice at what conditions to measure may have a significant bearing on the results. This is particularly important should there be *two* response mechanisms operating; perhaps in unknown and, during the course of the experiment, changing proportions.

The effects of a change in temperature may be complex. Beyond its influence on the initial capture of the electron, *i.e.* the reaction of much primary interest, tempera-

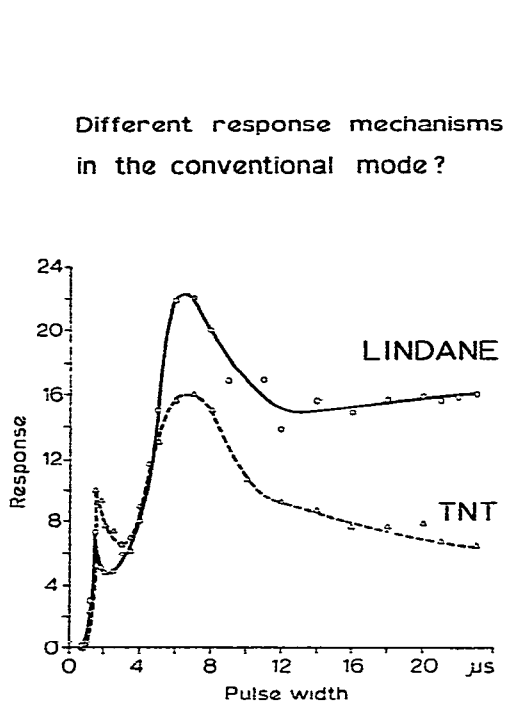


Fig. 6. Simultaneously measured response profiles for lindane and TNT in the conventional mode. Other conditions as in Fig. 4.

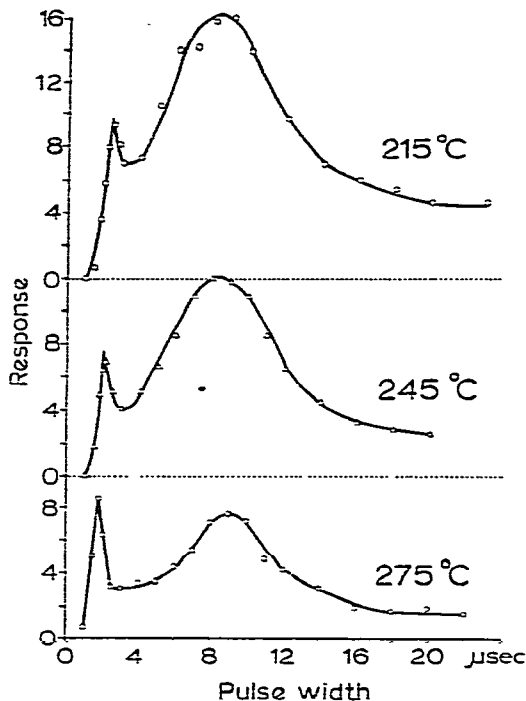


Fig. 7. Variation of lindane response profile with temperature in separated mode. Other conditions as in Fig. 3.

ture can be expected to affect several processes that alter response. For instance, cation–electron recombination is temperature dependent^{24,25}, as is cation–anion neutralization. Furthermore, the cation composition, even in the pure carrier purge gas of the separated mode, may change with temperature. In real-life ECD operation, cations will also arise from carrier gas contamination, stationary-phase bleed and the solute itself. The different equilibria one would expect to exist are again subject to temperature dependence. The formation of various clusters^{26,27} influences not only the distribution of positive charge among several species, but also its overall mobility^{28,29}. A similar argument can be made for anions. One process that has been discussed repeatedly and in different ECD contexts, is the strongly temperature-dependent equilibrium $O_2 + e^- \rightleftharpoons O_2^-$ (refs. 30–33).

Even if one disregards the effects of typical carrier gases, the mobilities—hence concentrations—of charged particles must change with temperature due to the corresponding density change. It may be noted in this context that theoretical predictions of ion mobility are not always consistent with empirical data^{34,35}. The changes in the density of the carrier gas also lead to a different linear flow value and a different range of β radiation, whereby the latter can be strongly influenced by confined detector geometries³⁶.

And then there is always the chance of variable detector cleanliness (e.g. out-gassing effects) and premature analyte decomposition. The latter is particularly dif-

difficult to evaluate and, perhaps for this reason, often ignored. While this is justified under some conditions, under others —e.g. when polyhalogenated species are detected at high temperatures, using a catalytically active ^{63}Ni foil and traces of hydrogen in the carrier gas— the temperature dependence of solute degradation may become the subject of legitimate concern. If and to what extent such processes do influence the finally observed response, remains in most cases unresolved.

The paragraphs above discussed at some length the possibly complex meaning of a seemingly simple experimental result. This was done, *inter alia*, to stress that an observed divergence of two response maxima should be taken only as an indicator, but not as a proof, of two disparate response mechanisms at work. A similar argument applies to later discussions.

In separated mode, the cathode chamber with its radioactive foil is purged by pure nitrogen. The flow of purge gas exerts considerable influence on whether or not two response maxima can be observed: While the latter are completely merged at low values, a high purge flow will make them move apart. Perhaps this has something to do with the change in solute concentration due to dilution by the purge gas, or perhaps the high flow raises the pressure inside the detector. Whatever the reason, it is clear from Fig. 8 that response maximum A moves to lower, but response maximum B to higher pulsewidths as the flow of purge gas is increased.

If solute dilution was responsible for this dissonant shift in the position of the maxima, a similar effect should be observed for changes in analyte concentration. And indeed it is, as can be seen in Fig. 9.

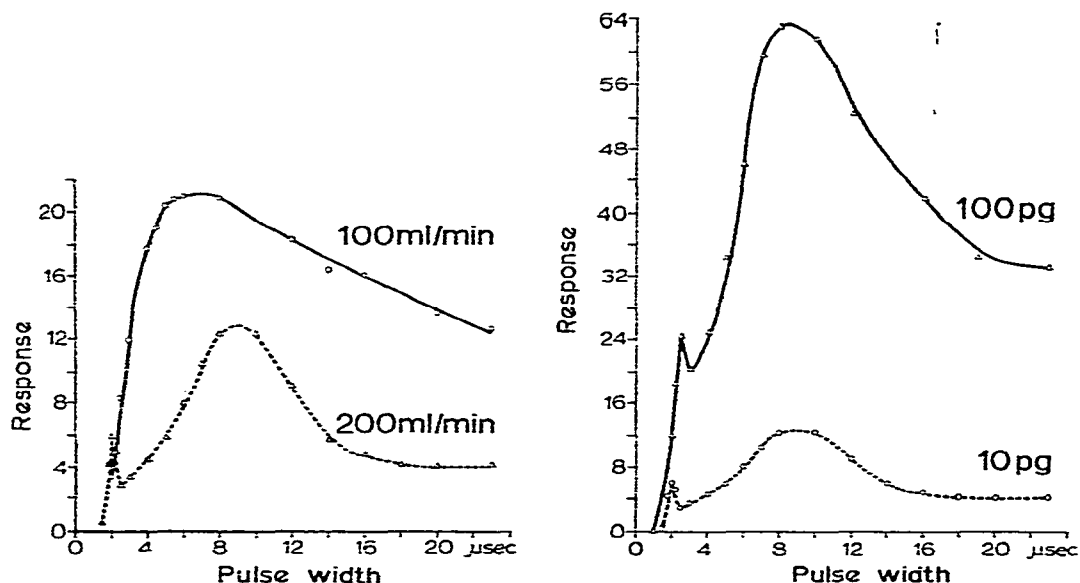


Fig. 8. Variation of response profile with purge flow-rate. Detector temperature 215°C , other conditions as in Fig. 3.

Fig. 9. Variation of response profile with analyte concentration. Detector temperature 215°C , other conditions as in Fig. 3.

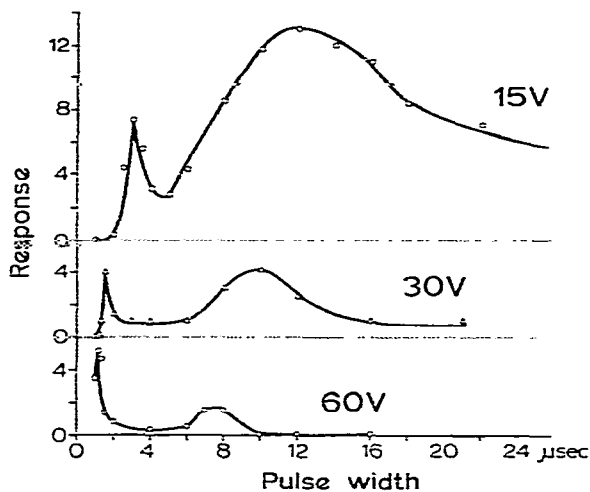


Fig. 10. Variation of response profile with pulse amplitude. Other conditions as in Fig. 3.

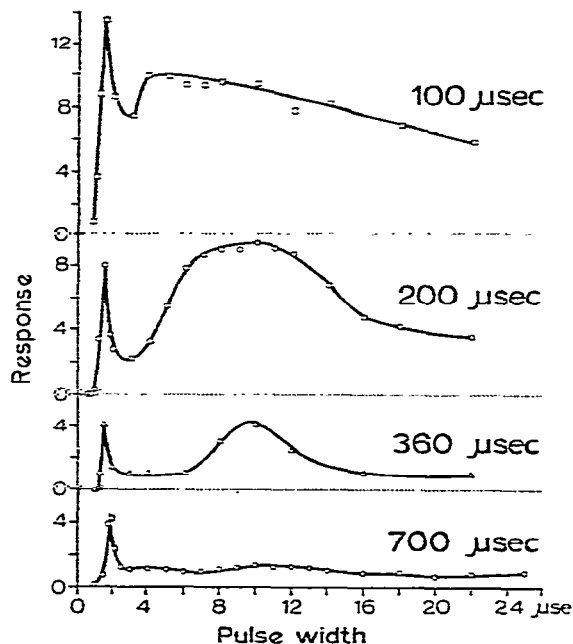


Fig. 11. Variation of response profile with pulse period. Other conditions as in Fig. 3.

Perhaps the effects easiest to predict are those induced by changes in pulse height, duration or interval. If we assume that transport of charged species is involved in producing response, then the crucial parameter, within limits, should be the "effective voltage". This parameter would in the simplest case be the product of pulse amplitude, width and frequency. Not surprisingly, the actual situation is not that simple. The reaction kinetics in the ECD are mostly second order, local field gradients are more or less influenced by space charges, and the pulses can remove charged reagent species in a non-linear fashion. Still, a qualitative relationship of the suggested sort is evident.

For instance, Fig. 10 shows both maxima moving to longer pulse width as the pulse amplitude is decreased. Note that this is a "consonant" shift as opposed to earlier "dissonant" ones. At high amplitudes, the two maxima become very well separated and the valley between them moves close to zero response.

Fig. 11 presents the effects of increasing the pulse interval. It is interesting to note how peak B recedes so that, at low frequencies, peak A becomes the most prominent feature. This happens at conditions close to the field-free ideal.

From the viewpoint of two distinct response mechanisms, it is interesting to compare calibration curves run at the two maxima. To do this, conditions were chosen at which the maxima appeared well separated and maximum A—weaker under most conditions—was considerably larger than maximum B. The fairly predictable results are shown in Fig. 12: maximum A yields a more sensitive analysis but with a shorter linear range. This is a consequence of the very low baseline (about 6 to

7% of the maximum available one): It means decreased fluctuations and a smaller capacity of the information-carrying current; in other words one notices less noise and an earlier cut-off.

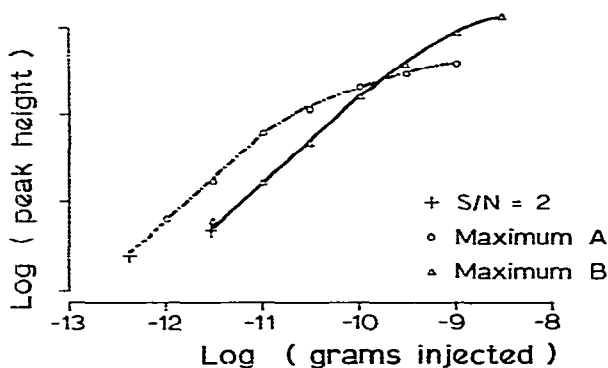


Fig. 12. Calibration plots of lindane. Pulse conditions: amplitude -60 V, period $360 \mu\text{sec}$, width $1 \mu\text{sec}$ for maximum A and $7.5 \mu\text{sec}$ for maximum B. Other conditions as in Fig. 3. S/N = Signal-to-noise ratio.

If the observation of the two response *maxima* was surprising, the assumption of two response *mechanisms* may be disturbing. It was for this reason that our experiments returned to the pulse profile; in order to be sure that no possibly important clue had been overlooked.

Following a common ECD routine, pulse profiles had been run from time to time alongside response profiles. There is a close correlation between baseline and response curves in various modes of electron capture detection; the former are often used as diagnostic tools for the latter.

Given this fact, it seemed highly unusual that (as reported earlier on) the pulse profiles should contain no feature whatsoever correlating with response maximum A. After all, the baseline current carries some continuous "response" (to impurities in the carrier gas, for instance) and, in a manner of speaking, it consists of electrons potentially available for capture.

Very careful measurements were therefore made of the pulse profile I_b , shown as the top trace of Fig. 13. Below it is the response profile R , and the fat arrows pinpoint the precise positions of the two response maxima. A slight distortion may be noticed in I_b at the position of the first maximum. To have a closer look, the slope of the pulse profile, $\Delta I_b / \Delta$ pulse width (p.w.), is plotted at the bottom of Fig. 13. It establishes beyond doubt that the position of response maximum A corresponds to the maximum slope, *i.e.* the point of inflection, of the pulse profile. Maximum B, on the other hand, corresponds to the "knee" position of the pulse profile and that is nothing unusual. Operating at this position often provides the best performance in conventional ECD practice (suggesting that such practice may rely primarily on response mechanism B).

Conventional ECD analysis hardly uses pulse widths beyond those of Fig. 13; yet, the rather unusual circumstances of this study made it advisable to probe further.

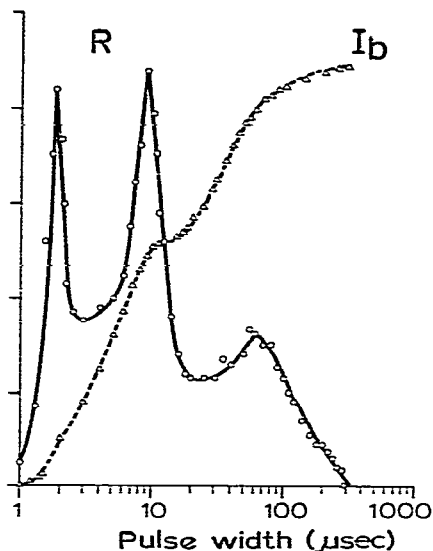
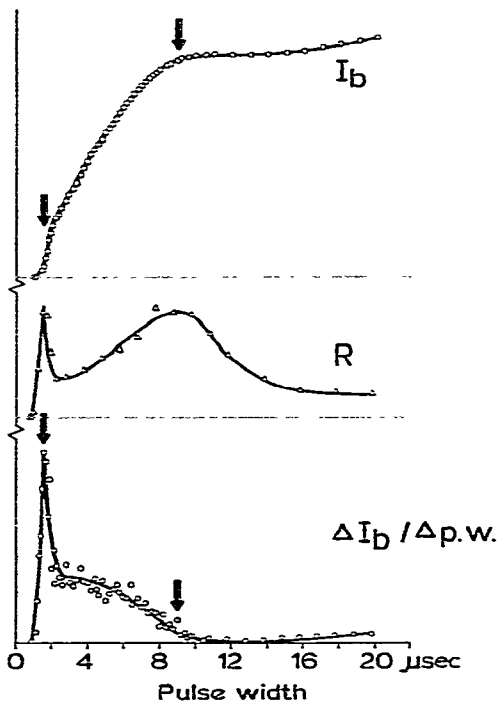


Fig. 13. Correlation of pulse profile (I_b) and response profile (R). Other conditions as in Fig. 3. Bottom trace: Slope of pulse profile. Arrows show the precise position of response maxima. All scales linear.

Fig. 14. Extended response and pulse profiles of lindane. Other conditions as in Fig. 3. Ordinate linear, abscissa logarithmic. Ordinate units are different for different curves.

The results are shown in the (now semi-logarithmic) plot of Fig. 14. Beyond the two strong response maxima, a third, weak one shows up, duly matched by another “knee” in the pulse profile. The size of the maximum was close to the experimental error limit and therefore (besides taking note of this interesting phenomenon) nothing further was done about it.

Still, it appears quite clear that a correlation between the pulse and response profiles does exist. This is also supported by the fact that, when conditions change, respective features of the two profiles move in unison. Of course, it could be argued on a formal basis that this is to be expected since both the baseline current and its temporary decrease known as response, are effects of charge transport processes which, in turn, are influenced by the same geometries and operating conditions.

However, that does not really explain why response maximum A takes a relatively large fraction out of a rather small current, and why, again relatively speaking, the pulse profile shows but a small warp (which was not even noticed the first time around). Judging from the pulse profile—as well as from common sense—there is no reason to assume that the initial electron-capture reaction, while high at positions A and B, but would somehow fail to function between the two maxima. Rather, this appears to be another case where the electron capture proper is improperly represented by the observed response (*cf.*, ref. 15).

When we combined the evidence from all the experiments discussed above, it

seemed to us to constitute reasonable evidence of two (or more) response mechanisms at work. Yet, we could not completely discount the possibility that we had seen but a simple mechanism being split into various maxima by the peculiarities of detector construction.

If the experiments indeed indicate more than one response mechanism at work, the obvious question arises as to the nature of these mechanisms. At this point the question can be answered only by engaging in outright speculation. Before so doing, however, it may be profitable to make some rough estimates of certain transport processes. What one would like to know are the approximate migration rates of charged particles inside the ECD, as brought about by carrier gas flow, diffusion and the electrical field, in order to use them for interpreting pulse and response profiles.

Some estimates

The detector operates generally at 280°C and ambient pressure. If one assumes that anions such as Cl^- , with a reduced mobility K_0 of $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ (ref. 37), are created near the restriction, and, while drifting 2 cm to the anode, pass through a potential difference of 15 V, and if one furthermore neglects space charges, surface charges and field inhomogeneities, the ionic drift speed turns out to be 38 cm/sec during a 30 V rectangular pulse. To take the example of Fig. 3, the pulse is "on" ca. $1.5 \mu\text{sec}$ and ca. $10 \mu\text{sec}$ —out of a $360 \mu\text{sec}$ period—for response maxima A and B, respectively. Therefore the ion would need 13 sec or $3.5 \cdot 10^4$ pulses to reach the anode in the first case, 2 sec or $5.3 \cdot 10^3$ pulses in the second case. This means rather long periods of time and rather many pulses. Furthermore, the estimate ignores effects of coulombic forces such as the "floating-back" of oppositely charged ions during the field-free period.

The average, *i.e.* time-integrated, ion drift speeds are 0.2 and 1 cm/sec for response maxima A and B; somewhat lower than the average gas flow of 2.0 cm/sec (200 ml external) through the anode chamber.

In order to compare these numbers with diffusion effects, a number of simplifying assumptions have again to be made. A rigorous treatment is impossible since the areas of creation, transformation and neutralization of ions would have to be known, not to mention the influence of the detector's peculiar geometry. Pretending diffusion to take place from an infinite plane and taking σ as the distance travelled, one may apply the Einstein equation.

$$\sigma^2 = 2Dt$$

where σ^2 is the variance of a Gaussian distribution and t is the time span of the process³⁸. The diffusion coefficient D may be calculated from the mobility K for the linear regime³⁹ from

$$K/D = 1.16 \cdot 10^4/T$$

and turns out to be $0.24 \text{ cm}^2/\text{sec}$ (T = absolute temperature). Thus the "distance that ions travelled" during 1 sec is calculated as 0.7 cm.

Since drift, flow and diffusion rates turn out to be of the same order of magnitude, the situation is much more complex here than in prior experiments using the d.c.

regime¹⁶. For instance, it is no longer possible to assume, as could be done confidently for d.c. conditions, that cations never enter the anode chamber.

One of the major premises of the classical mechanism is that all free electrons are collected by each pulse (*e.g.*, ref. 40). This is reasonable if one assumes negligible charge interactions, small cell dimensions and strong pulses. Our experiments do not fit these assumptions; thus it becomes necessary to estimate, in analogy to earlier treatments of ionic speed and subject to similar assumptions, the velocities of electrons.

For 30 V/3 cm and ambient pressure, an extrapolation of the measurements by Pack and Phelps⁴¹ to 280°C shows electrons drifting in nitrogen at speed $v = 9 \cdot 10^4$ cm/sec. To traverse the interelectrode distance of *ca.* 3 cm, electrons would need, very roughly, 22 pulses or a total of 8 msec at maximum A, and 3 pulses or 1 msec at maximum B. The fact that the number of pulses is greater than unity even for the second case, is quite interesting.

The gas flow does not play a role in the movement of electrons, but diffusion might. If it is assumed that the mobility equation

$$K = v/E$$

is applicable at $E/p = 10^{-2}$ V cm⁻¹ mmHg⁻¹ (ref. 42) and K is used as has been done above for ions, D turns out to be 430 cm²/sec (E = electric field gradient; p = pressure). From the Einstein equation it can then be estimated that to diffuse 1 cm takes electrons about 1 msec. This compares with drift speeds of about 3 and 0.4 cm/msec. It should be noted in this context that different estimates of diffusion coefficients have been used in the ECD literature, *e.g.* Siegel and McKeown²² assumed values of 0.05 and 50 cm²/sec for positive ions and electrons.

Despite the oversimplifications inherent in our estimates, the results are taken to present a qualitatively accurate picture. Perhaps the most important conclusion is that more than one pulse is needed to collect unimpeded electrons. While the underlying calculations may be subject to doubt, the experimental pulse profiles (*e.g.* that of Fig. 13) support this conclusion.

To see why, one may start by remembering the classical concept of the baseline current (*e.g.*, ref. 43). A pulse profile, in idealized form, exhibits two distinct regions. The initial steep current rise indicates that pulses are too short to clear the cell of electrons. As pulses become wider, most electrons will eventually be removed by a single pulse. From then on, the current rise becomes very shallow, reflecting the collection of electrons generated while the pulse is still on. The transition region between the steep and shallow slopes, the "knee", is therefore supposed to indicate a pulse more or less wide enough to empty the cell of electrons. Off-hand, this does not seem to agree even with calculations for maximum B (located in the knee region) which suggest that not one but three pulses are necessary for an electron to traverse the cell.

However, the calculations are really quite compatible with the experimental data, as the following reasoning will show.

First, the measured pulse profile represents integrated current values. The pulse width at which, say, 50% of the maximum current is collected and the one at which 50% of available electrons are swept from the cell, are not identical: The

former is shorter than the latter. This can be demonstrated by following a train of short pulses, each of which removes the same percentage of electrons from the cell. The residual electrons from the last period are added to the ones newly generated, and imposing the (commonly assumed) second-order recombination rate in an iterative procedure then completes a simulation that supports the argument above.

Second, and perhaps easier to appreciate, is the question what constitutes a "cell" in the present context. If cell means the whole detector volume, then the picture tacitly assumes a "stirred reactor" system, *i.e.* an essentially homogeneous charge environment. However, should the detector contain bipolar and unipolar regions, *i.e.* should cations populate only part of the detector, then a pulse needs to sweep electrons out of only that region—not out of the whole detector—in order to make them escape recombination.

Reality is a bit more complex than this simple picture suggests. Primary ionization decreases in a roughly exponential manner from the radioactive foil. Furthermore, the effects of recombination, not to mention flow and diffusion, need to be considered for a closer definition of the steady-state charge density distribution. Yet, it is quite obvious from recently measured beta ranges³⁶ that most initial ionization occurs within a few mm of the foil. Fig. 1 shows the cylindrical foil occupying about one third of the detector length. Once electrons have escaped this area they have escaped recombination. Now the electrical field gradient is *not* linear (because of the detector geometry and the differences between bipolar and unipolar regions) but as a qualitative description arrived at in hindsight, it seems not unreasonable to look at Fig. 1 and expect electrons to escape the plasma region in about one third of the time it takes them to get all the way across the detector to the anode. If so, the theoretical estimate and the experimental observation are in essential agreement.

The notion that the knee of the pulse profile (and response maximum B) occur in a region where it takes several pulses to transport electrons from the point of generation to the collecting anode, is at first a surprising one. However, it makes sense not only in terms of the baseline current, as discussed above, but also in terms of response.

In the separated configuration, electrons can meet electron-capturing analyte molecules in the anode chamber only. If, however, these electrons are swept through the chamber by a single pulse, electron capture can occur only during a few microseconds out of (if we take the most commonly used pulse period) 360 μ sec. Since response, in whichever mechanistic hypothesis, depends on the initial occurrence of electron capture, it would turn out to be severely depressed under such a condition. On the other hand, the initial electron-capture reaction (though not necessarily response) would clearly attain its highest rate at the highest possible electron concentration in the anode chamber. That would occur at a pulse just wide enough to remove most electrons from recombination in the cathode chamber, but short enough to make these electrons stay for one or perhaps more pulse periods in the anode chamber and be available for capture. Considering these two situations together jives with the experimental observation that response in the separated mode drops off fairly quickly at pulse widths longer than those characteristic of maximum B and the knee position.

In the conventional configuration, on the other hand, electrons may be captured by analyte molecules in both cathode and anode chambers. In fact, under conditions where the pulse width is long enough to sweep electrons all the way

through the anode chamber and restrict capture there to the fraction of time when the pulse is on, capture in the cathode chamber—which is free to occur all of the time—will be the major source of response. From this point of view, response in the conventional mode beyond maximum B and the knee position will drop off much less than in the separated mode. A comparison of the respective modes shown in Figs. 4 and 3 demonstrates that this is indeed the case.

All this, while reasonable, does not yet explain why two response maxima occur and what mechanisms do produce them. At the moment, the only explanation possible is a purely speculative one and the following paragraphs should be viewed in that light.

Some speculations

It is perhaps best to start not with the two response maxima but with the valley between them, taking again the separated mode shown in Fig. 3 as an example. That this valley exists in so pronounced a form is even more surprising than the occurrence of maxima, for there is no doubt that electrons *were* available for capture. As can be seen from the pulse profile, electrons were indeed collected by the anode at pulse widths where the valley occurred; consequently, they must have traversed the anode chamber and met analyte molecules. If there was electron capture, why was there little or no response?

Electron capture results in the formation of an anion, which will drift toward the anode. If detector geometry, flow and effective voltage prevent its contact with a cation—as was mostly the case here—the negative charge cannot be neutralized but must reach the anode. If so, there is no change in current, *i.e.* no response. In other words, the classical response mechanism of neutralization is precluded. But why did the alternative space charge mechanism¹³ also fail to respond?

A qualitative answer, given after the fact, could be as follows: The space charge mechanism relies, obviously, on high charge densities¹⁴. In contrast, the situation here involves a very low electron input into a large-volume chamber flushed by a fast carrier flow. The anion density must therefore be very low and the space charge effect minimal.

If pulse width is increased, however, more electrons are pushed into the anode chamber and become available for capture, and denser space charges form in closer defined regions. As space charges build up, it becomes more difficult to transport anions to the cathode and so the electrical gradient during the pulse steepens in the anode chamber and softens in the cathode chamber. There, cations and electrons now drift slower and their concentration, hence their second-order recombination rate, increases. Thus the detector produces the decrease in current commonly known as electron capture response.

This suggests that maximum B represents a space charge effect. As far as experimental observations are relevant in this context, they tend to support this assignment. In an earlier, d.c.-based study, it was suggested that response increases with higher pressure, lower temperature and a lower voltage gradient, *i.e.* all factors that slow down anion migration¹³. In analogy, response maximum B in this pulsed system also increases when anions travel slower and are more concentrated; be it through lower temperature (= higher density), lower flow, or lower pulse amplitude as shown in Figs. 7, 8 and 10, respectively.

The position of maximum B on the pulse width axis would thus be determined by two factors: On one hand, by the number of electrons available in the anion chamber for capture—a number that first rises, then falls with increasing pulse width; on the other hand, by the relative concentration (inversely related to drift speed) of anions—a number that decreases with increasing pulse width. It is reasonable that this interplay should result in a response maximum situated at the knee of the pulse profile.

In this context it may be interesting to note that commercial pulsed systems often work at or close to the knee position. To consider, furthermore, the fact that in the comparable conventional mode of this study, maximum B is the predominant response (compare Fig. 4 with Fig. 3), raises the question whether a space charge mechanism may not also dominate some commercial pulse-driven ECDs. However, to answer that question is beyond our present means and intentions.

Before moving on to a discussion of maximum A, another possibly controversial matter should be shortly mentioned: Why had we not considered the possible occurrence of ambipolar diffusion (*cf.*, ref. 22)? It is well established that one can estimate the largest possible electron/cation concentration from pulse profiles over a range of frequencies. This limiting value, in our system, is close to $3 \cdot 10^7$ electrons. For, say, the cathode chamber of approximately 8 cm^3 volume, our average limiting electron density of $0.4 \cdot 10^7/\text{cm}^3$ may be compared to a range of 10^7 to $10^8/\text{cm}^3$ quoted by McDaniel for the onset of ambipolar diffusion⁴⁴. Now, an ECD plasma is not homogeneous, but that quoted range would apply only to a layer very close to the radioactive foil, and hence we feel justified in neglecting ambipolar diffusion in the present context.

Response maximum A is undoubtedly the most difficult object of speculation. It occurs at pulse conditions so weak that few electrons are pulled out of the plasma, and the ones that are need several pulses to do it. If one increases pulse width, the baseline current duly increases but response drops, in contrast to any reasonable expectation (*cf.*, Figs. 3 and 13).

A number of scenarios were considered in attempts to explain this unusual behavior, but none was totally convincing. That one that follows is—to stress it again—born of outright speculation.

At the very weak pulse regime of maximum A, as earlier suggested, the nominal ionic drift speed is slower than gas flow or diffusion effects. Not too much can be made of these numbers since they are based on simplifying assumptions and disregard local geometry. However, they are good enough to allow consideration of a scenario in which a limited number of cations would reach the restriction and be carried through it into the anion chamber.

If pulse width is increased, there must come a point where the field is strong enough to hold cations—against diffusion and gas flow—inside the cathode chamber. This change-over from a bipolar to a unipolar anode chamber should be accompanied by some characteristic feature of the pulse profile, since there ought to occur changes in recombination rate, changes in surface charges at the restriction, etc. Fig. 13 does indeed show an undulation in the pulse profile, which coincides with maximum A of the response profile.

Since the detector is in separated configuration, analyte molecules are available only in the anode chamber, and only there can anions be formed. As long as cations

are also able to enter, charge recombination may occur. Although such conditions are not really comparable to those of ECDs described in the literature, the response mechanism suggested here is, in fact, the classical one of enhanced cation-anion neutralization. Incidentally, the electron/molecule ratio for maximum A, about 0.5 F/mol, falls safely below the coulometric limit. Additionally, the presence of slow anions may help to attract nearby cations across the restriction.

As increasing pulse widths prevent cations from reaching the anode chamber, the classical mechanism must cease to operate and response drops to the valley seen in Fig. 3. Response does not drop all the way to zero, but that is reasonable given the diffuse nature of the plasma and the likelihood that some contribution from the space charge mechanism is already present. In conventional configuration, where the classical mechanism is allowed at any pulsewidth, the valley becomes much less pronounced (Fig. 4).

So, taking Fig. 3 as an example, the position of maximum A is on its left side established by the available information-carrying current—current must be collected in order for response to be observed—and on its right side limited by cations receding back into the cathode chamber. To a certain extent, measurements support this assignment. The position of maximum A on the pulse width axis should shift to the right when it becomes more difficult to keep cations, by way of the electric field, inside the cathode chamber. That should occur at lower temperature (*i.e.* higher density), lower pulse amplitude, longer pulse interval, and faster purge flow. Except for the last parameter, the changes are in the predicted direction, as shown in Figs. 7, 10, 11 and 8, respectively. However, the observed changes are small and offer qualified support at best for the proposed scenario.

CONCLUSIONS

The two response maxima seen in particular, pulse-driven ECDs have been speculatively associated with response mechanisms of the "neutralization" and "space charge" type. In doing so, emphasis was placed on transport processes rather than, as usual, on chemical reactions. Obviously it would be interesting to prove or disprove these concepts, and to find out whether and to what extent they operate in more commonly used ECDs. However, this is beyond our means and intentions. That two pronounced maxima appeared in our initial experiments may have been a stroke of luck: As can be seen from several of the figures, these maxima merge or come close to merging under a variety of conditions. "Merged maxima" may also exist under typical operating conditions in some commercially available ECDs. If our speculation linking experimental maxima with theoretical mechanisms is correct, such detectors would translate the initial electron-capture reactions via two or more concurrent response mechanisms into the peaks seen on the chromatogram. That, however, would likely go unnoticed.

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