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STUDIES AND SPECULATIONS ON AN ALTERNATIVE MECHANISM FOR THE RESPONSE OF DIRECT-CURRENT ELECTRON-CAPTURE DETECTORS*

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SUMMARY

The classical theory of electron-capture detection does not allow for hypercoulometric response such as has been found recently under conditions of elevated pressure in some electron-capture detectors (ECDs), nor does it predict certain other experimental observations. In an effort to understand why and how hypercoulometric performance can occur, measurements have been made of the ionization region and characteristic current-voltage relationships in real and simulated ECDs. The centre-of-ionization was found much closer to the foil than is commonly assumed, namely at approximately 1 mm for ^{63}Ni and approximately 0.2 mm for ^3H in nitrogen at ambient conditions. A hypothetical response mechanism, alternative and, in certain ways, complementary to the classical theory was therefore developed. It sees detector response, distinct from the initial electron-capture reaction, as the effect of a space charge formed by migrating negative ions, which decrease the field gradient (and therefore increase electron-positive ion recombination) in the ionization region. Estimates of the counterfield established by the migration of anions show that it can indeed produce hypercoulometric response and that, in agreement with experimental observations, increased pressure leads to higher response. Some simple experimental tests of the proposed mechanism have been carried out and others, more crucial ones, are suggested for future investigation.

INTRODUCTION

It is commonly accepted that the drop in cell current seen as a chromatographic peak in electron-capture detectors (ECDs) is due to a removal of free electrons from the ionized gas by solute molecules (for an extensive review of the "classical" theory of electron-capture detection, see ref. 1). Thus an upper limit of

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response should exist in ECDs; defined, in essence, by each solute molecule removing one electron. This coulometric limit has indeed been observed². If the ratio of captured electrons to solute molecules in the detector cell is accurately reflected by the ratio of peak area (in faradays) to the amount injected (in moles) then the latter should, in general, not exceed 1.

THEORETICAL

"Hypercoulometric" response in the d.c. mode

A ratio of, say, 2 or 3 would still be considered possible if electron-capturing products were formed from the ionized solute. (Such products may be formed³ and have, in fact, been used to confirm the structure of parent molecules⁴). It was, however, surprising for us to find ratios far in excess of this number for many compounds⁵. This "hypercoulometric" response was obtained from a commercial Tracor (Mikrotek) ⁶³Ni ECD operating at up to 5 atm pressure in the d.c. mode; *i.e.* under less than conventional conditions. As pressure increased, so did response⁶.

There are caveats in the literature concerning the various disturbing side effects incurred by operating the ECD with a constant potential⁷, and these include the influence of space charges. Yet, a response 50 times the coulometric limit—with even higher numbers likely to be attained by higher pressures—and minimum detectable amounts almost a decade below the "theoretical detection limit" of $3.3 \cdot 10^{-16}$ mole⁴, suggested the possibility that a response mode other than the commonly accepted one was at work. If that mode was based on space charges, then one may consider promoting it from a disturbing side effect to a bona fide mechanism. While we have assumed such type of processes to be operative⁸, other possibilities for explaining hypercoulometric response do exist, *e.g.* one based on the "recycling neutral" suggested by Siegel and McKeown⁹.

Hypercoulometric response in the pulse mode?

Whenever hypercoulometric response in the d.c. mode has been discussed, comments of referees and conference audiences alike revolved around one theme: Does the same effect occur in pulse mode?

It is obvious why this question is being asked. In general, the d.c. mode is considered outdated and, compared to the pulse modes, less sensitive and much more prone to error. Only the pulse mode under "clean" conditions is considered reliable enough to produce data for mechanistic conclusions. And it would appear a simple matter indeed to repeat certain measurements in a pulse system. However, for us this was neither technically nor conceptually that simple.

Technically, increasing the pressure requires much faster pulsing if most of the available current is to be sampled (the rate of the second-order recombination quadruples with doubled pressure). In order to keep the cell field-free most of the time, pulse widths have to be very short and pulse amplitudes very high. The design of the Tracor pulse power supply (Model 113639 with board 113793 as well as various replacement boards), when tested by oscilloscope at full power output (60 V) proved inadequate: a slow rise-time restricted the amplitude of short pulses to small fractions of what it should have been (typically to less than half at 1 μ sec); furthermore, wide pulses and short intervals produced grossly distorted waveforms.

Better pulsing equipment exists, of course, but would rarely be used with ECDs because of its cost. Hence, rather than to invest in expensive instrumentation for what we considered to be a sideline pursuit, the problem was brought into experimental range by modifying ECD geometry. A specially designed, coaxial ^3H ECD of small dimensions made it possible to use arbitrary but still fairly reasonable pulse conditions through a limited pressure range. Response in this pulse mode proved somewhat similar to that in the d.c. mode run for comparison, as shown in Fig. 1. Both are hypercoulometric and increase with increasing pressure, although the effect is less pronounced in the pulse mode.

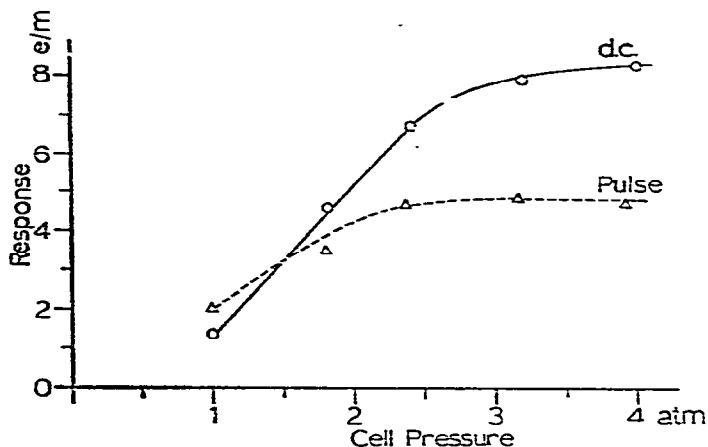


Fig. 1. Occurrence of hypercoulometric response in a co-axial ^3H ECD at elevated pressures, in both d.c. and "pulsed" modes. e/m = faradays peak area/moles substance injected.

Yet, the change in pulse conditions required by the increase in pressure did not allow any firm conclusions to be drawn. It is easy to see why: in the d.c. mode, the only variable is voltage, and it can simply be set for each pressure so as to produce maximum response. If the criterion of maximum response is used for setting pulse parameters, however, some settings may approach too closely those of d.c. and can therefore not be considered typical of pulsed operation; other, less sensitive settings must then be used.

There is little doubt, however, that hypercoulometric response can be found under conventional pulsed conditions. This was shown by Leggett¹⁰ as well as by ourselves. Whether hypercoulometric response can also occur under rigorously "pure" pulse conditions (short, strong pulses, relatively long intervals) would be interesting to investigate. However, since this relies heavily on the definition of an "acceptable" pulse condition, the matter may be considered somewhat academic and its solution remains beyond our present means and intentions.

Reversed-field effect

Besides hypercoulometric response, we encountered another effect in d.c. mode which we found difficult to reconcile with accepted theory. It concerned reversal of the electric field.

In common electron-capture practice, the radioactive foil is negatively polar-

ized and the counter electrode is essentially at ground potential, collecting electrons (or heavy negative ions). No essential change in detector performance occurs, of course, if the role of the two electrodes is reversed, *i.e.* if the counter electrode is positively polarized and the radioactive foil, now collecting positive ions, is connected to the amplifier.

In both cases, the direction of the electric field remains the same—positive particles migrating to the radioactive foil (plus any conducting parts that happen to have the same potential); electrons to the counter electrode. Here the ECD can simply be considered a variable, non-linear impedance device, whose impedance increases with the introduction of electron-capturing gas chromatographic (GC) solutes. The picture changes, however, when the direction of the electric field is reversed—either by using a positively polarized foil or a negatively polarized counter electrode. In typical ECDs, the impedance increases considerably or, differently expressed, it takes a much higher voltage to reach the plateau of the “voltage profile”¹¹.

By how much the impedance changes depends on the ECD's particular geometry, radioactive source and operating conditions. Our studies involving hypercoulometric response^{5,6,11} had been carried out on a Tracor (Mikrotek) ⁶³Ni unit and the construction of this particular ECD, as it turns out, produces a very large difference in impedance between regular and reversed-field conditions. Also, it is remarkably adapt at producing hypercoulometric response. (The two qualities are related as shall be shown later.) Since the Tracor's construction differs somewhat from that of other ECDs, and since that very construction lends itself particularly well to subsequent discussions, its important elements shall be shortly described here.

This ECD consists of cylindrical upper and lower chambers, which are connected by a much narrower channel. (As an estimate from the Tracor manual, the radii and heights in mm are as follows: upper chamber $r = 3.7$, $h = 8.5$; channel $r = 1.8$, $h = 8.0$; lower chamber $r = 3.7$, $h = 6.2$). The upper (ionization) chamber houses the cylindrical ⁶³Ni–Au foil (normally negatively polarized); the lower one a cylindrical counter-electrode (normally connected to the amplifier). The non-conductive parts of the two chambers and the vertical channel between them are made from boron nitride. In recommended operation, the column effluent enters from the top and leaves from the bottom.

This ECD then, when clean and under nitrogen at ambient pressure and temperature, needs about 5 V to pass through 50% of the maximum current in regular field configuration. With the field reversed, about 10³ V are necessary. (These values, especially the first one, can vary considerably depending on detector conditions.)

The difference in impedance between regular and reversed-field modes can be attributed to the different mobility of positive ions and electrons and their different distance of travel from generation to collection. If positive ions have to travel the longer way in reversed-field condition (and this way is especially long in the Tracor ECD) the impedance of the ECD will be higher. (It should be noted that the term “impedance” is used here as a convenient way of describing the voltage-current relationship. In one sense it can be considered a “chemical” impedance; *i.e.* charge neutralization impeding charge collection.)

In this detector, then, a curious phenomenon was first noted (and later found in other ECD constructions as well): under reversed-field conditions, essentially no

electron-capture response occurs. It should be added for fairness that occasional wiggles were observed in the baseline; however, even if one would consider these to be bona fide peaks, they were several orders of magnitude off the mark. Now this is curious because classical electron-capture theory would predict that some response should have been noticed.

In classical theory, the GC peak results from capture of electrons by solute molecules, followed by positive ion-negative ion neutralization. If, as will be shown below, the capture and neutralization rates (at equal baseline currents) are comparable in regular and reversed-field conditions, then electron-capture response should be apparent in both modes.

The capture and neutralization rates are determined by the concentrations of reactants and these, for all charged species, depend on the electrical field gradient. We know the voltage imposed across the two electrodes, of course, but we do not, off hand, know the gradient in the area where negative and positive species co-exist, *i.e.* the ionization region in the upper chamber. Yet, we can make a comparison based on voltage profiles (*i.e.*, current (*v.s.*)–potential ($I-V$) plots without peak).

At equal current, say 50% of maximum, half the charges reach the electrodes and half the charges are lost by recombination. To account for 50% recombination in either regular or reversed-field modes, the concentrations of positive ions and electrons in the ionization region must be the same, hence the field gradient there must be the same (even though the imposed potentials are very different). If we assume that this situation does not change too drastically with the passage of a small peak, capture and neutralization rates should be comparable in both field directions, hence response should be observed for both of them.

It may be difficult to accept that electron-capture rates should be comparable for very different operating voltages (but equal background currents) in the two modes. Yet there exists experimental backing: one can estimate the extent of the electron capture reaction by determining how much of the original compound survives¹¹. Data on various pesticides showed that, as the voltage profile shifted to higher values in reversed mode, so did the characteristic S-curve of residual analyte. For instance, at $\approx 50\%$ current the electron-capture reaction of 10 pg dieldrin was 93% complete in regular, 73% complete in reversed field condition. However, had the same high voltage necessary for the reversed mode been used for the regular one, the reaction would have been essentially shut off.

With electron capture and, by inference, neutralization operative in reversed mode, why was no significant response observed? Differently stated, why is electron capture a necessary but not a sufficient condition for response? Why are the electron-capture reaction and the response mechanism separate, though related, entities?

Apparently, the predominant response mechanism under these conditions is different from the classical one and, since it shares this distinction with the mechanism responsible for hypercoulometric peaks, perhaps the two are identical. If so, it need to be explained how hypercoulometric response can come about and why it can come about in one field direction only.

Various processes could conceivably contribute to hypercoulometric response, only one of which will be considered here. It deals with the migration of negative ions, particularly those that reach the anode.

A response mechanism based on negative ion migration

Negative ions can be formed from suitable solute molecules along the path of electron travel, from generation to collection. Some are formed in the primary ionization region where positive ions abound, others may be formed in a region where few, if any, positive ions are available (as, for instance, in the lower chamber of the Tracor ECD). When electrons are being replaced by negative ions, the impedance of the ECD will increase and, with constant voltage, the current will drop. (The increase in impedance could be compared to that caused by an equal number of positive ions travelling the long way under reversed-field conditions.)

If, in a regular d.c. ECD system, the negative ions formed are migrating to the anode, they will set up an opposing or counter field. Thereby they will bring about a drop in the field gradient (and thus slow down charged particles) in the ionization region. Increasing residence times (concentrations) increases the neutralization rate of positive ions with electrons (as well as with negative ions). A drop in current results, similar to moving to the left on a typical voltage profile.

It is obvious that such a picture requires knowledge of the location of the ionization region in relation to the two electrodes: Only if this region is situated close to the (negatively polarized) radioactive foil, but far away from the counter electrode, is this mechanism likely to work with any reasonable efficiency.

Where is the ionization region?

There are large differences in the literature on the range of β radiation from the commonly used emitters like ^3H and ^{63}Ni in form, and under conditions typical of GC detectors. For instance, a maximum range is given in a monograph on detectors for ^3H in air as 5–10 mm (ref. 12), but 0.2 mm were found in an actual measurement¹³. Pellizzari's review¹ quotes 2 mm for ^3H in argon.

For ^{63}Ni , Jentzsch and Otte¹² quote *ca.* 6 cm, Pellizzari¹ 6–8 mm. The latter reviewer adds the generally accepted conclusion: "This important property determines the minimum electrode spacing in ECDs".

Judging from commonly used ECD dimensions, then, 1–2 mm for ^3H and 6–8 mm for ^{63}Ni seem to represent more or less accepted values. Thus, for most constructions—the Tracor ECD being an exception—the detector cell volume would be considered a largely "bipolar" region (*i.e.* both positive and negative species occur throughout the cell) and this has also been a generally accepted view. It may be noted that some early ^{63}Ni models were constructed with smaller dimensions and their poor performance contributed much to the acceptance of the 6–8-mm limit quoted above. While the correctness of these values would matter little in terms of the classical neutralization theory, it would represent a major factor in considerations concerning the migration of negative ions.

The distance to know, however, is not the maximum β range but the distance from the radioactive foil to the "centre-of-charge" for positive ions or electrons in the moment of generation. If one imagines a detector with this centre-of-charge halfway between the two electrodes, a characteristic situation results. First, the voltage profiles (I - V curves for the background current) should be the same for regular and reversed-field conditions: the positive ions, which essentially determine the impedance, must on the average migrate the same distance to either electrode. Second, such a device should work well as an electron capture detector (save for

possible noise problems) from the viewpoint of classical neutralization theory, but it should show relatively low efficiency if response were mainly due to increased impedance caused by the conversion of electrons to (heavy) negative ions. To make any reasonable estimate of response as dependent on ions migrating under various conditions, the location of this centre-of-charge and, by inference, that of the ionization region, must be known with at least a modicum of accuracy.

Measurement of the centre-of-charge

It was therefore incumbent upon this study to make some appropriate measurements. These were based on the following assumption: when the centre-of-charge is located precisely between two electrodes, the impedance of the device becomes independent of field direction. Thus one can use a simulated, parallel-plate ECD with adjustable electrode spacing and determine, at various pressures, the distances at which the same voltage is needed to obtain the same current. For instance, measurements can be made of V_{50}^+ and V_{50}^- (defined as the voltages necessary to collect 50% of the maximum available current in either reversed field (V^+) or regular field (V^-) configuration). When the centre-of-charge is situated roughly in the middle between the two electrodes—roughly because the electrodes are not really equivalent since only one carries the radioactive foil—then

$$V_{50}^+ = V_{50}^- \quad \text{or} \quad \frac{V_{50}^+}{V_{50}^-} = 1.$$

Obviously, any reasonable current setting could be used depending on convenience; 50% happens to be a quantity that can be easily and relatively precisely measured from standard voltage profiles for both field directions under all but the most extreme distance and pressure conditions.

EXPERIMENTAL

Fig. 2 shows the device used for the distance measurement. One of the parallel-plate electrodes carries a ^{63}Ni foil (New England Nuclear) or Sc^3H_3 foil (U.S. Radium) flat on its surface. The threaded rods are held by PTFE plugs in a leak-tight seal and the distance between the parallel plates can be easily changed by turning the rods. The two openings in the cylindrical glass enclosure serve to sweep the cell with pure nitrogen at various pressures. (A similar device, but with a wider and longer enclosure, was used during later parts of this study to cut down on field distortion effects.)

For measurements at a particular distance and pressure, voltage profiles were recorded for both field directions and the two voltages determined which gave 50% of maximum available current. For measurements requiring the presence of an electron-capturing substance in the cell (simulating the passage of a peak through an ECD), the nitrogen gas was passed over the surface of pentachloronitrobenzene (PCNB) or tetrachloronitrobenzene (TCNB) before entering the cell.

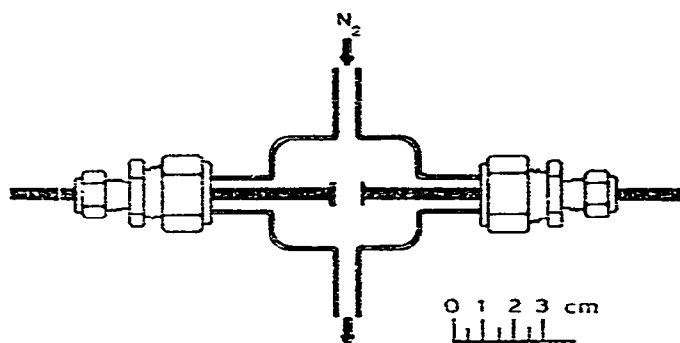


Fig. 2. Device for measuring the position of the "centre-of-charge", and simulating ECD behavior. See text for explanation.

RESULTS AND DISCUSSION

Determination of the centre-of-charge

Fig. 3 shows a typical run, measuring V_{50} values at various electrode distances under regular (V^-) and reversed (V^+) field conditions at 2 atm total pressure. As the electrodes get very close to each other, measurements become unreliable for a variety of reasons, e.g. the impinging of radiation on the counter electrode. It is therefore better to extrapolate to the point where the two curves cross.

It may be asked what shape one would expect for such curves. A V_{50} measurement is, in essence, a measure of the impedance under particular conditions. The impedance can be considered the sum of individual impedances for cations and electrons and these, for the sake of this argument, can be considered inversely pro-

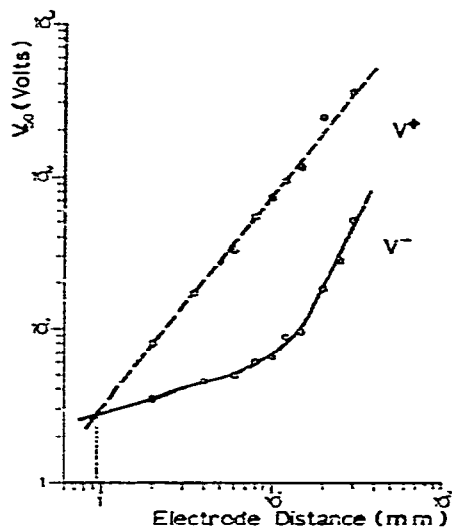


Fig. 3. Measurements of voltage necessary to collect 50% of maximum available current at regular (^{63}Ni foil as cathode, V^-) and reversed-field (V^+) conditions. Nitrogen at 2 atm total.

portional to the respective mobilities. Now the mobility of positive ions should be more than 10^3 times slower than that of the electron and, at shorter distances, the total impedance would therefore be determined mainly by the distance the *cations* have to travel (assuming the complete absence of electron-capturing substances, of course). As electrode spacings increase, longer distances must be traversed by cations in the V^+ measurement, by electrons in the V^- measurement. Hence V_{50}^+ should rise sharply with distance, V_{50}^- slowly, and this is indeed what happens. (At much longer distances, the V^- measurement should eventually rise and become parallel with the V^+ measurement; reflecting, in an idealized setting, the relative mobilities of the species involved. It must be noted, though, that in this as in other measurements with the device shown in Fig. 2, data taken at very long distances may be increasingly distorted by the effects of the insulating glass enclosure and of very small amounts of electron-capturing contaminants, which are difficult to remove from a source that cannot be baked out.) The extrapolation to the point where $V_{50}^+ = V_{50}^-$, however, should be accurate enough for the aims of this study.

When a number of electrode-spacings, where this occurs, are determined at different pressures, the expected hyperbolic relationship between pressure and electrode distance is obtained (Fig. 4). For atmospheric pressure, this distance is approximately 2 mm and the distance of the centre (plane) of charge from the radioactive foil therefore half that value, *i.e.* 1 mm. (For ^3H , which presents more of an experimental problem because of this β emitter's short reach, the latter distance is approximately 0.2 mm.)

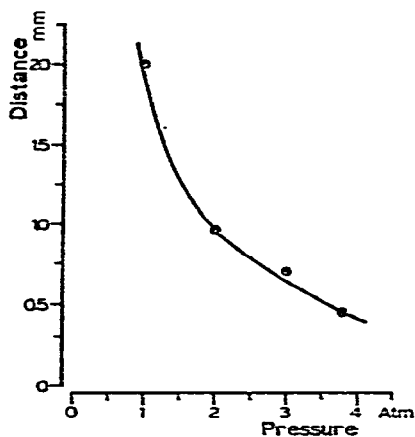


Fig. 4. Plot of electrode spacings for which $V_{50}^+ = V_{50}^-$ at various pressures.

These values are quite a bit shorter than commonly assumed. They permit the consideration of a mechanism that is based on the differences in detector impedance for migrating electrons *vs.* migrating ions.

The device shown in Fig. 2 lacks certain qualities demanded of an operational ECD, but it can be used nicely for converting electrons to heavier anions and observing the concomitant changes in impedance. For this purpose larger amounts of electron-capturing substances (TCNB or PCNB) are introduced with the sweep

gas, so that one may assume that most electrons have been converted to anions and the system is "saturated".

Saturation experiments

What should one expect from such an experiment? The answer differs depending on whether one consults the classical theory or the response mechanism being developed here.

According to classical theory; *i.e.* electron capture followed by rapid neutralization of negative ions, the effect of PCNB should be to reduce the number of positive ions and electrons by equal amounts. The ionic species that are pulled away from reaction (by a potential set to keep the current at 50% of maximum) must therefore be positive ions and electrons. (The negative ions would not be expected to exist too long in a bipolar region if "recombination of ions occurs 10^5 – 10^8 times faster than the recombination of free electrons and positive ions"¹.) Thus both V_{50}^+ and V_{50}^- should rise to higher values, but otherwise maintain their general appearance. If, alternatively, the ratio V_{50}^+/V_{50}^- is plotted against interelectrode distance, essentially the same curve should be obtained with or without added PCNB.

(This conclusion is formulated as one of two extremes for sake of a clear distinction; however, it is perhaps unfair in that it adopts the common assumption of a bipolar cell volume. It also must be pointed out that consideration of the finding by Siegel and McKeown⁹ of equal densities of positive and negative ions in a saturated API source would have led to a different, and correct, conclusion in this context.)

What does the response mechanism of *this* study predict? If all electrons are converted to negative ions—and assuming that the positive and negative ions in this state have approximately the same mobility—there should be little difference in impedance between regular and reversed-field conditions. The V_{50}^+ and V_{50}^- dependences on electrode spacing should be nearly the same; being somewhat higher than, but otherwise resembling, the V_{50}^+ dependence in the undoped state. Alternatively, if the V_{50}^+/V_{50}^- ratio is plotted vs. distance, it should remain constant and close to a value of one.

The former presentation is employed in Fig. 5, which shows the results of an experiment with a ³H foil. The latter plot is used in Fig. 6, this time with a ⁶³Ni foil. Both agree with expectations formulated above.

In fact, if a doped system at regular field conditions behaves similar to an undoped system at reversed-field, the complete voltage profiles should reflect the same trend, and indeed they do. Fig. 7 shows this for a PCNB-doped run, using a ⁶³Ni foil and 15 mm interelectrode distance, taken from a different set of experiments than the one shown in Fig. 5.

While the saturation experiments thus favor a response mechanism based on migrating negative ions, it must be emphasized that the conceptual alternatives have been extremely, perhaps unduly, simplified; that the reasoning applies to d.c. operation; and that the system used is not the "cleanest" one possible in either a chemical or a physical sense, not to mention its disparity from a typical GC set-up.

The experiments, then, simply state the following: this simulated ECD shows, under undoped conditions, very different impedances in regular and reversed-field

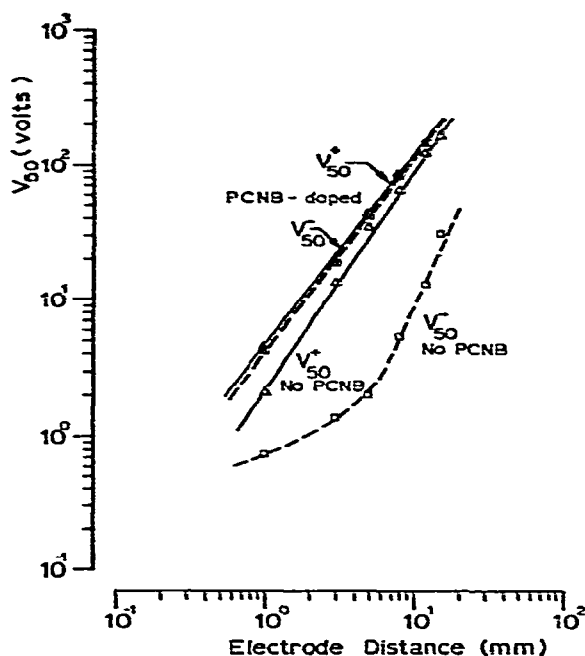


Fig. 5. V_{50} values with and without PCNB doping. Nitrogen at 1 atm (ambient pressure), ^3H foil.

modes; however, when an electron-capturing compound is introduced, the two impedances become similar. The correlation of these two states with, respectively, migrating positive ions and electrons, and migrating positive ions and negative ions, would appear reasonable.

As alluded to before, there is a geometric component implicit in the pictures used to describe the alternative mechanisms. Stated with gross oversimplification, the classical picture of electron capture (with detector dimensions generally reflecting the

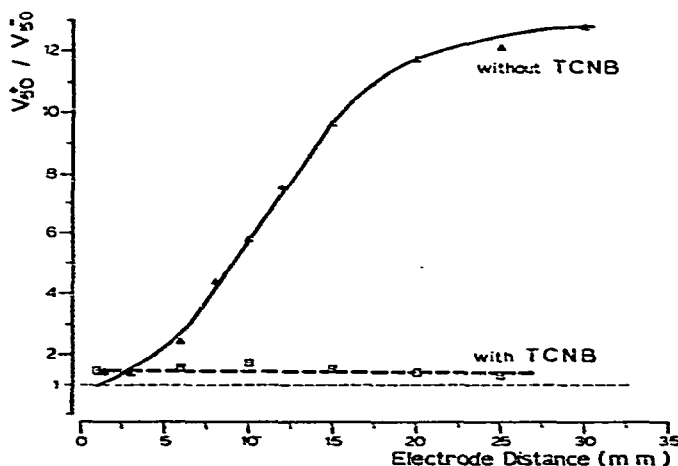


Fig. 6. V_{50}^+ / V_{50}^- ratios with and without TCNB doping. Nitrogen at 1 atm, ^{63}Ni foil.

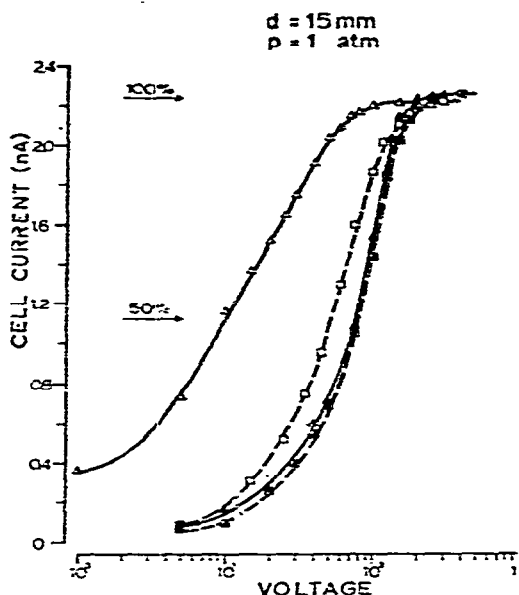


Fig. 7. Voltage profiles with and without PCNB doping. Electrode spacing 15 mm, nitrogen at 1 atm (ambient), ^{63}Ni foil. Δ , Regular field, undoped; \square , reversed field, undoped; \blacktriangle , regular field, doped; \blacksquare , reversed field, doped.

assumed maximum range of β radiation) views primary ionization (and, in the case of pulsed electron capture, plasma distribution) as fairly homogeneous through most of the detector cell; this view is shared by Siegel and McKeown⁹ who, furthermore, view most of the plasma as governed by ambipolar diffusion. In contrast, the view taken in this paper uses a definite ionization region, from where migration of electrons (and negative ions) occurs over a relatively long distance, similar to the bipolar and unipolar zones in ionization-type particulate detectors¹⁴. This brings up questions of diffusion vs. lifetime and drift time of ionic species, and explains why the however approximate determination of the ionization region was considered so important. As has been pointed out before, literature values on the range of particular β radiations vary by more than an order of magnitude and, probably due to the fact that the classical electron-capture mechanism is not overly dependent on this factor, one generally notices a conspicuous scarcity of experimental data.

Thus we have to compare our values on the centre-of-charge, 1 mm for ^{63}Ni and 0.2 mm for ^3H at ambient conditions in nitrogen, with commonly accepted estimates for the maximum range or the ionization zone of 6–8 mm for ^{63}Ni and 2 mm for ^3H in argon¹ as well as with a measured value for the latter of 0.2 mm in air¹³. Now, it would be quite erroneous to assume that, say, the ionization region covers about double the centre-of-charge distance. Ionization cross sections depend on energy and, furthermore, the distribution of ^{63}Ni atoms on and below the surface of a particular foil influences one type of measurement but not the other. Yet, there still appears to be a definite and, in the context of this paper, crucial discrepancy between the commonly accepted estimates and the experimental data presented herein.

Based on the latter, we presume it permissible to proceed with developing a mechanism critically dependent on a narrow ionization sheath situated close to one (and far from the other) electrode.

A bit of speculation may be added aside this point. Since GC detectors need to be constructed so as to keep peak broadening within reasonable limits, a typical ^{63}Ni ECD shows probably a higher ratio of ionization zone thickness to electrode spacing than does a typical ^3H ECD. Since a higher ratio, at least in our view, results in lower response, it would appear fair to speculate that perhaps some of the lower responses reported repeatedly for ^{63}Ni vs. ^3H detectors may be related to this simple geometric factor. On this ground, a point can also be made for running narrowly-dimensioned ^{63}Ni ECDs under elevated pressure to improve response.

The slow travel of heavy negative ions over longer distances will create a counterfield, *i.e.* a field that opposes the originally imposed one, thereby weakening the field gradient in the ionization region and increasing there the concentration of reactive, charged species. The picture of a counterfield due to a space charge may be compared to similar models in electrophoresis or gaseous discharges; but, for the present purpose, it is perhaps best portrayed in the treatment by Simon and Axmark¹⁴ of bi- and unipolar regions in particulate detectors. In fact, their conclusions in regard to the influence of electrode spacing on the sensitivity of smoke detectors closely parallels ours on the same effect in ECDs.

The obvious question is whether the space charge can weaken the originally imposed field enough to be of practical significance as a response mechanism and, furthermore, whether it can do this to the extent that the detector will produce hypercoulometric response. The geometry of the Tracor ECD would be very difficult to handle in this regard and therefore, for a first try, the device shown in Fig. 2 under the conditions of Fig. 7, is substituted. Even there, we shall dispense with iterative calculations and be satisfied with an order-of-magnitude estimate.

Estimation of the counterfield

Be it assumed, quite erroneously, that *ab initio* the field is homogeneous, the gradient linear, ions don't diffuse outside this linear field (*i.e.* they stay within a cylinder with the cross section given by the two electrodes), and no counterfield exists. Under 1 atm nitrogen and 25°, it takes about 50 V in reversed-field condition to collect 50% of the cations. Their distribution depends on the purity of carrier and detector but, for the sake of argument, an average reduced mobility K_0 of 2.5 cm²/V·sec (ref. 15) is assumed. Since

$$v = K_0 \cdot \frac{V}{\text{cm}} \cdot \frac{760}{p \text{ (torr)}} \cdot \frac{T}{273}$$

the cation speed calculates as

$$v^+ = 2.5 \cdot \frac{50}{1.5} \cdot \frac{760}{760} \cdot \frac{298}{273} = 91 \text{ cm/sec}$$

Cations would therefore spend 1.4 cm/91 cm/sec = 15 msec travelling from generation to collection.

Fifty percent of the available current is 1.1 nA or, during 15 msec, $1.6 \cdot 10^{-11}$ C. If, again wildly erroneous, these ions are considered present as part of an "infinite plane of charge"¹⁶ on the same area as the electrode area, 50 mm², then the field

$$E = \frac{\sigma}{2\epsilon_0}$$

where σ is the charge density in C/m² and $\epsilon_0 = 9 \cdot 10^{-12}$ C/m·V. Thus

$$E = \frac{1.6 \cdot 10^{-11} \text{ C}}{50 \cdot 10^{-6} \text{ m}^2} \cdot \frac{1}{2 \cdot 9 \cdot 10^{-12} \text{ C/m} \cdot \text{V}} = 1.8 \cdot 10^4 \text{ V/m}$$

which corresponds to 270 V/15 mm. Such a counterfield is impossible since there are only 50 V imposed on the system. The main reason for this discrepancy (besides the obvious fact that these ions are not part of an infinite plane) is that the electric field lines bulge out between the electrodes and the actual cross section is much larger than the electrode area. What emerges clearly from this estimate, however, is that the counterfield can indeed attain significant strength and must be reckoned with. (This point is nothing new, having been made for positive ions many years ago by Levelock himself⁷.)

In a regular ECD with constricted geometry, say the Tracor ECD, a similar calculation using the channel cross section 10 mm², and assuming 15 mm as field length, shows that, if $1.1 \cdot 10^3$ V are necessary to collect 50% (= 3 nA) of the current, the counterfield calculated in the same order-of-magnitude manner as above corresponds to 175 V/15 mm; still a sizeable fraction of the originally imposed 1100 V. While better calculations would be highly desirable, the earlier point that space charges have a major influence on response, remains valid.

If this is correct, then it is an *actual* field gradient (imposed field minus counterfield) in the ionization region that determines the speed, hence the second-order recombination rate of positive ions and electrons. Impedance to the passage of a particular current fraction is thus related to pulling the required number of charges away from recombination.

So far our speculation has pertained to a rather unusual situation, *i.e.* the baseline current under reversed-field conditions. Of greater interest, however, is the cell current during passage of a peak, with the detector operating under regular field conditions.

For that case, consider that voltage has been set at $\approx 90\%$ of standing current (a common setting) and that, as the peak apex passes, there is a 10% drop in that current (*i.e.* 9% of all available electrons appear to have been "captured"). If the hypothetical assumption is made that all of the negative ions generated reach the counterelectrode and the likely assumption that these ions possess approximately the same mobility as the positive ions in the system (while the much faster electrons are excluded from consideration), then the counterfield generated by the migrating negative ions would be 10% of that generated by positive migrating ions (from a baseline current of the same magnitude in a reversed-field situation). Thus, a connection is established between the easily measured *I-V* curve at reversed field and the proposed migration of negative ions. Hence it is possible to arrive at an order-of-

magnitude estimate for the counterfield owing to this migration and, obviously, it also must turn out to be a sizeable fraction of the originally imposed one. It is clear, therefore, that, for this effect alone, the current must drop.

Before the effects of this counterfield on the cell current are closer evaluated, the above assumption of negative ions travelling all the way to collection needs to be further discussed. To provide for an efficient response mechanism, it must be shown that larger numbers of negative ions are indeed likely to reach the anode. (Classical theory predicts that they do not; maintaining—quite correctly if space charge effects are neglected—that collected negative ions would decrease response.)

Migrating negative ions?

According to classical theory, recombination rates of positive and negative ions are 10^5 – 10^8 times greater than those of positive ions and electrons¹. Off hand this would seem to rule out any significant negative ion migration from a bipolar region.

According to Siegel and McKeown⁹, however, rates are generally of the same magnitude; in fact, one of the authors mentioned a particular measurement using an API source lower than that of positive ions and electrons¹⁷. Saturation experiments with CCl_4 by Grimsrud *et al.*¹⁸ also support this view. Off hand, this would seem to allow significant negative ion migration.

It may be noted, parenthetically, that part of this seemingly very large discrepancy arises because rates, in contrast to rate constants, have to take into account the residence times of ions and electrons; and these, in turn, depend on the extent to which ambipolar diffusion is thought to occur. While Siegel and McKeown⁹ assume ambipolar diffusion based on E/p values, Lovelock and Watson¹⁹ do not and have presented experimental evidence for unimpeded electron transport.

Off hand, then, it would seem that an answer to this current discussion be required for this study. Fortunately, this is not the case. Recombination rates are important only for a region where *both* positive and negative species occur in significant amounts; *i.e.* the bipolar ionization region. Although the boundaries of this region are by no means defined, the experiments of this study suggest that, in the cases at hand, this region occupies but a small part of the detector volume. Since electrons migrate through all of the volume, negative ions can be formed in regions where no positive ions are available for neutralization. Thus, a counterfield can be assumed to exist or, more precisely, the consideration of a mechanism based on a counterfield formed by migrating negative ions can proceed even in the absence of information on recombination rates.

The case of the Tracor ECD

Even if the ionization region were larger than our experimental data indicate, the two-chamber construction of the Tracor ECD, on which the largest hypercoulometric responses were found, clearly rules out the presence of significant numbers of positive ions in the lower chamber. First, β rays cannot reach this chamber. Second, positive ions are unlikely to be swept into the chamber by the carrier gas flow.

To wit, even with 100 ml/min carrier flowing down through the narrow channel, the linear gas velocity there is still an order of magnitude lower than a typical ion

velocity. Furthermore, it is possible to operate this ECD with gas flows reversed. (Interestingly enough, the response then increases by a factor of two—conceivably because of a different distribution of negative ions—and this flow configuration has therefore been used in the hypercoulometric response experiments^{5,6}.) And, it has proven impossible to bring about significant changes in $I-V$ profiles (measured on the unit shown in Fig. 2) by blowing gas streams of up to 1 l/min between the two electrodes, perpendicular to the electrical field²⁰.

Thus the absence of positive ions in the lower chamber can be taken for granted. Since electrons must travel through this chamber to be collected, their capture there would result in a negative-ion region separate from the ionization region. It only remains to be demonstrated that they are indeed captured there.

Capture outside the ionization region

Literature on the ECD indicates that, at higher voltages, the electron-capture reaction may cease because electrons acquire too much energy from the field and, as is well known, electron-capture cross sections are highly energy-dependent. If this effect would play a major role, then one could argue that, perhaps due to a softer field gradient across the ionization range and a steeper one through other parts of the detector (an improbable situation, as will be shown later), negative ions should not be formed in the latter region. It is well known, of course, that d.c. ECD response shows a definite maximum and can drop off rather precipitously at voltages higher than the optimum one. In classical theory, "response" is often implicitly viewed as being synonymous with "the extent of electron capture"; and a drop in response would thus appear to imply that this reaction ceases at higher voltages. Our own experiments on residual analyte and products show that the reaction rate is very low indeed at high voltages, although there is some evidence of reaction with good capturers even at 1000 V and the correlation of response with the extent of electron capture is far from perfect¹¹. Conventional kinetic modeling shows, however, that much (though not all) of the drop can be attributed simply to decreased electron residence time.

In fact, it is most unlikely that the increase in electron energy should be responsible for the reaction shutting off at higher fields. The electron capture spectra of many compounds have been determined by various means and, generally, stretch broadly over the 0–5 eV range and beyond (the sharp SF_6^- resonance being an exception). While, obviously, increase in energy can bring about increase or decrease in electron-capture response (see, for instance, ref. 21 and earlier literature cited therein) it should not lead to a reaction shutting off. The thermal electron energy is about 0.03 eV and conventional ECD potentials will not raise it significantly. For instance, the 30 km/sec drift speed of electrons measured by Lovelock and Watson¹⁹ in argon–10% methane with a parallel plane detector at 30 V/cm added a mere 0.003 eV in kinetic energy to the ambient level. Of course, in a cylindrical detector higher values can be found around a point or wire-type anode²². However, it is probably fair to assume that in most electron-capture systems, reactions can be pretty well "shut off" by voltages that confer less than 0.1 eV on the electrons.

This point is also supported by the fact that, in d.c. ECDs, the response of many compounds of different chemical structure follows a similar dependence on voltage¹¹.

If larger changes in electron energy would occur, substances should strongly differ from each other in this respect²¹. The similarity of response profiles ($R-V$ curves) has long been common knowledge among pesticide residue analysts and was reinforced for us by a study of hypercoulometric response requiring the measurement of response profiles for a wide variety of substances⁵. We realize that profiles of different compounds peaking at different voltages have been published; however, it should be noted that profiles depend to a great extent on contamination and column bleed, hence column temperature. Even when the same compound is run at exactly the same conditions but with three different amounts injected, three profiles will result which peak at somewhat different voltages, a fact predicted by the modeling mentioned above and demonstrated, for general interest, in Fig. 8.

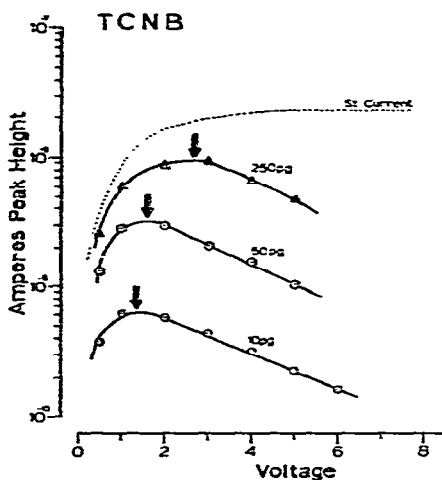


Fig. 8. d.c. response profiles for different amounts of tetrachloronitrobenzene. Lab-made ECD with ^3H foil.

Thus it appears that the main effect of varying the speed of electrons relates to their concentration, not their energy. This raises the question whether electrons could acquire enough speed in the lower (collection) chamber of the Tracor ECD to escape capture. This is unlikely to happen, since a rather large ring electrode is used to collect them. A guess of the field gradients involved suggests, in fact, that, while the electrons speed up considerably coming through the channel, they slow down again as they enter the large collection chamber and drift radially outwards towards the cylindrical anode. It should be noted at this point that in a co-axial ECD design, electrons rather speed up as they approach the anode. The fact that the latter can shut off a reaction completely at 100 V d.c.² and that, in our hands, the former geometry only came close to doing so at 1000 V d.c., but gave consistently higher hypercoulometric response than the latter, may be related to such field effects.

So sum up, it seems reasonable to assume that electrons can be captured in unipolar regions to a significant extent. For the resulting negative ions, neutralization can then occur only by contact with the counter electrode or any other conducting surface. Considering the low mobility of heavy ions as compared to electrons, a significant counterfield should result.

Having established the likelihood of a negative ion space charge being formed, how does response come about? Or, differently expressed: if negative ions are collected instead of being neutralized, why does the current decrease?

In particular, how does the hypercoulometric effect come about? Its definition implies that for every negative ion reaching the anode, more than one electron has to be prevented from getting there.

Estimate of a hypercoulometric response

To demonstrate that this is possible, a short, very approximate calculation is in order. Any of a number of voltage profiles could be used for illustration, however, we have chosen here, employing it for double duty, a plot from the saturation experiment series which is similar to the one shown in Fig. 7, but uses an ^3H foil and a 5-mm electrode spacing.

Let us assume, for convenient display in the plot shown in Fig. 9, that a large peak, $\approx 12\%$ of baseline current, is produced by the system running at 10 V d.c. The peak height (marked ΔI) is 1 nA.

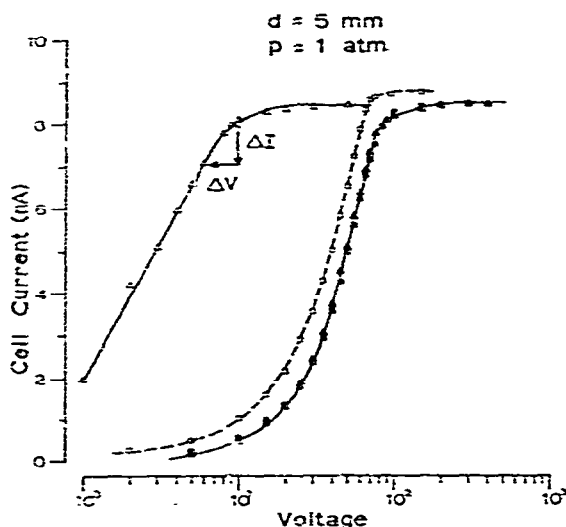


Fig. 9. Voltage profiles with and without PCNB doping. Similar to Fig. 7, but electrode spacing 5 mm and ^3H foil.

To decrease the current by the same amount *without* introducing a peak, the voltage would have to be lowered to 6 V, leading to increased neutralization of electrons in the bipolar region. But one could imagine the same decrease $\Delta V = 4$ V being brought about by a suitable number of negative ions, travelling to the anode. Without bothering with iterative procedures, again, and subject to a variety of simplifying assumptions, one can calculate the necessary number of ions. Assume the negative charges in a 50-mm^2 portion of an "infinite plane of charges" with $E = 4$ V/5 mm field strength. In meters and coulombs,

$$\text{charge} = \frac{4 \text{ V}}{5 \cdot 10^{-3} \text{ m}} \cdot 2.9 \cdot 10^{-12} \frac{\text{C}}{\text{V} \cdot \text{m}} \cdot 50 \cdot 10^{-6} \text{ m}^2 = 7.2 \cdot 10^{-13} \text{ C}$$

This charge, then, produces a drop in current of $1 \cdot 10^{-9}$ A while migrating, on average, 2.4 mm (half the distance from the centre-of-charge to the anode). The time for this migration

$$\tau = \frac{d}{K_0} \cdot \frac{1}{E} \cdot \frac{p}{760} \cdot \frac{273}{T}$$

For, say, Cl^- with a reduced mobility $K_0 = 2.9 \text{ cm}^2/\text{V} \cdot \text{sec}$ at 760 mm and 298 °K

$$\tau = \frac{0.24 \text{ cm}}{2.9 \frac{\text{cm}^2}{\text{V} \cdot \text{sec}}} \cdot \frac{0.5 \text{ cm}}{6 \text{ V}} \cdot 1 \cdot \frac{273^\circ \text{ K}}{298^\circ \text{ K}} = 6.3 \cdot 10^{-3} \text{ sec}$$

Therefore, the charge prevented from reaching the anode during this time slice is $6.3 \cdot 10^{-12}$ C and, for every electron truly captured by an analyte molecule, the outside measurement would indicate about nine (8.75) "captured" electrons.

Clearly, that response is hypercoulometric. If we call the nine-to-one ratio R_{HC} and consider it worthy of maximization, it may be well to follow the calculation above and combine the variables, leaving constants aside

$$R_{\text{HC}} \propto \frac{1}{V} \cdot \frac{\Delta I}{\Delta V} \cdot \frac{p}{T} \cdot d' \cdot \frac{d^2}{a} \cdot \frac{1}{K_0}$$

where d' is the distance between the centre of ionization and the anode, d is the interelectrode distance, a is the cross section of the cell perpendicular to the ion beam, and all other symbols have their usual meaning.

It is obvious that some parameters are interrelated, *e.g.* d' depends on pressure (controlling the range of β rays), and the magnitude of V in a reasonable system depends both on pressure p and on cell geometry d^2/a . These caveats in mind, one can go about considering how to maximize the contribution of this particular response mechanism.

What influences response?

The terms $1/V$ and $\Delta I/\Delta V$ indicate that, other parameters being equal, the voltage of maximum response (usually close to that required to give 90% of maximum current) should be as low, and the slope of the I - V curve as steep, as possible. In practical terms, that amounts to saying that detector and carrier gas should be as clean as possible. And indeed, a clean system, hence one that operates at lower voltage, gives larger peaks. While this is one of the oldest experiences in electron capture detection in general, and while there are also good kinetic reasons why that should be so, it may be revealing that this fact turns up in the present context.

The term p/T suggests that higher pressure and lower temperature (but only in the sense that it influences ion mobility) lead to increased response. As far as pressure is concerned, this is definitely true. We found strong hypercoulometric response in a (for other purposes) pressurized system to start with⁵; and we have later shown response to increase drastically with pressure⁶. While specifics of this increase depend on detector geometry, we have never failed to find it in clean, optimized d.c. systems.

Whether a decrease in temperature leads to increased response cannot be established with certainty at this moment; besides, it would not be expected to exceed a factor of two. To test this relationship, one would have to find a compound whose electron capture and consequent degradation mechanism were independent of temperature (otherwise one measures the effects of temperature on, say, associative or dissociative capture rather than on the mobility of a given number of ions) and one would have to exclude certain other, temperature-sensitive parameters such as the cleanliness of the detector and the presence of trace levels of oxygen in the carrier.

The term d' suggests that a long distance between electrodes, and a short reach of β rays, *i.e.* factors that give rise to a long unipolar region, are beneficial. This criterion would prefer ^{55}Fe over ^3H over ^{63}Ni (quite apart from the lower noise level of the softer emission²³). The effect of β -range would be particularly noticeable in detectors with short electrode gaps.

The term d^2/a suggests that electrodes should be far apart, with a small cross section of the available space in between, to maximize the counterfield from a given number of ions. While there are obvious limits, *e.g.* those given by voltage, to using geometry this way, it is interesting to note that the Tracor ECD could have been (but most likely was not) conceived along these lines.

Finally, the term $1/K_0$ suggests that heavy (slow) ions increase response; and a survey of the range of K_0 data from plasma chromatography¹⁵ indicates that the effects should generally not exceed a factor of two. It may be interesting to speculate in certain cases whether relatively long lifetimes of molecular anions²⁴ may have some bearing on that question. Our own results suggest that there may be certain differences between, say, nitro and halo compounds in terms of the concentration dependence of hypercoulometric response⁵, but the data are neither precise nor numerous enough to allow firm conclusions. Besides, the questions of associative *vs.* dissociative behaviour, and the possibility of multiple electron capture (*e.g.* loss of more than one chlorine) enter this picture. A factor of two, in any case, is exceedingly small compared to, say, the several orders of magnitude difference found in electron capture coefficients.

A clean detector of suitable geometry, operated in d.c. mode under elevated pressure, does thus appear to meet the major conditions for obtaining hypercoulometric response. Not surprisingly, it was precisely such a system in which the phenomenon was first observed.

It may be noted that these conditions are mostly physical in nature and do not necessarily reflect on certain chemical aspects involved in coulometric or, for that matter, hypercoulometric response (compare ref. 25).

Before proceeding further it may be well to recall the physicochemical difference between the classical mechanism of electron capture and the one assumed to contribute to d.c. ECD performance in this paper. In both concepts response is due to the increased neutralization of electrons. In classical theory, however, this occurs via the intermediary negative ions being neutralized; while here the recombination of electrons and positive ions in the ionization region is increased due to migrating negative ions outside this region. Thus the latter approach allows, while the former denies, hypercoulometric response.

(It should be obvious that the latter approach does not completely rule out some neutralization via negative ions; nor does the former rule out the existence of

negative space charges. Also, one can envision a counterfield set up by ions within reach of the ionization zone, where both mechanisms may operate and influence the observed response. The fact that a negative ion may eventually be neutralized by a positive ion does not mean that, earlier on, its mere presence in a particular spot could not have contributed in some degree to increased positive ion/electron neutralization.)

The increase in recombination due to migrating negative ions can be roughly envisioned by considering the changes in the field gradient during the passage of a peak. Fig. 10 shows this based on the ideal picture of a parallel-plate ^3H ECD with homogenous field, run at constant voltage. (To facilitate orientation, Fig. 10 was made to conform approximately to Fig. 9; however, the gradients are imaginary and schematic, and should not be assumed to reflect the solution of the respective field and kinetic equations.)

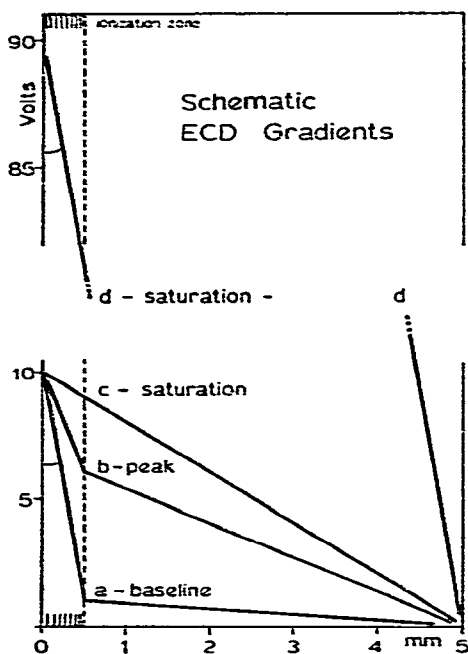


Fig. 10. Schematic of assumed field gradients under various conditions. a, Baseline; b, peak; c, saturation; all at the same voltage. d, saturation, at the same current as a.

Curve a reflects the baseline state, with the charge carriers being cations and electrons. In part relating to their mobility, the gradient is very steep in the ionization region, very gentle in other parts of the detector. Curve c, on the other hand, describes the saturation state, where the charge carriers are cations and anions and the gradient therefore remains roughly similar throughout the cell. The intermediate curve b, then, characterizes the passage of a peak. The gradient outside the ionization zone becomes steeper because of anions being formed, consequently the gradient inside the zone becomes less steep, bringing about longer residence times of cations and electrons and, in turn, higher recombination rates.

Several aspects of this simple picture may be noteworthy. First, the second-order recombination

$$r \propto [e^-] \cdot [M^+] \propto \frac{1}{E^2}$$

is inversely proportional to the square of the gradient. (This does not mean that response is likewise a square function of the amount injected, since the now increased field outside the ionization zone leads to a reduction in the number of electrons captured.) Also, response (change in gradient) is largest when the baseline gradient is as steep as possible in the ionization zone, *i.e.* when the detector is as clean as possible.

Second, the gradient in the ionization region is much steeper than in the rest of the detector (given typical analytical conditions). Therefore the chances of an analyte molecule capturing an electron are much lower in the bipolar as compared to the unipolar region. This adds further support to earlier considerations of the probability of electron capture outside the ionization sheath.

Third, if one would want to work at constant current (as opposed to the constant voltage implied above), the gradient in the ionization zone would have to remain the same. Thus a saturation experiment, for instance, which is to be run at the same current as the baseline (a), may be characterized by the more or less straight line d; both curves showing the same slope in the ionization zone.

If response is determined by the numbers and the extent of negative ions migrating, then it should be possible, at least in theory, to calculate its values under various circumstances. The effective number of migrating negative ions depends on two closely interrelated parameters: the total number of negative ions generated, *i.e.* the number of analyte molecules capturing electrons, and the voltage (as well as the geometry) of the detector. The voltage determines the residence time of electrons (hence their reaction rate with analyte molecules and their recombination rate with cations) and the residence time of negative ions (hence their contribution to the counterfield, as well as their neutralization rate by positive ions in the ionization zone). Experimentally, the number of negative ions generated can be determined from a measurement of residual analyte¹¹ if it is assumed that no analyte molecule survives intact the capture of an electron and the ensuing processes—neutralization by positive species or on an electrode, charge transfer, etc. (This assumption is certainly reasonable in the case of dissociative electron capture, where it is unlikely that larger amounts of the analyte could be re-formed. Of course, more than one ion could be formed from one analyte molecule of suitable structure—*e.g.* polychlorinated compounds have been shown to lose several of their chlorines³, presumably sequentially and as Cl⁻—but the major contribution to ECD response can still be assumed to stem from the initial capture under most circumstances.)

If the anions thus produced are then presumed migrating, and their effect on the electron/positive ion neutralization rate is estimated graphically using the reversed-field profile, the maximum response can be successfully simulated; however, the fit is otherwise less than satisfactory.

A major difficulty in improved forms of calculation would appear to be the need to know the distribution of speed, hence local concentrations, for any ion species throughout the detector. The major information wanted, of course, is the

integrated influence of migrating negative ions on the field gradient in the recombination region for cations and electrons, in order to calculate concentrations for use in rate equations. Even without such quantitative backing, however, it appears possible to make some predictions that are based on the proposed detector mechanism and could be subjected to experimental verification.

Suggested further experiments

First, the nature of the proposed mechanism should make it possible to divorce the electron capture proper from the concomitant process that provides the response. This could be done in two ways. Either the two are physically separated, or they are allowed to proceed together but are manipulated independently, *e.g.* such that one is varied while the other is being held constant. The obvious question then, of course, is whether such a separation of processes is indeed possible and, furthermore, whether it leads to observable "electron-capture response" in cases where classical theory suggests that it should not. Attempts are now underway to probe the relationship of the two processes.

Second, it should be possible to correlate the response of an ECD with certain other of its characteristics. It may be difficult to do computations based on migrating negative species, but it is very easy, experimentally, to use migrating positive ones instead and thus let the system itself provide the information.

This is simply done by reversing the field and forcing the positive species to travel the long way, in order to simulate the behavior of negative ions. (Or, the profiles of saturation experiments could be used, but there may be reasons for wanting to stay with a "clean" system). Admittedly, such a comparison does neglect certain aspects of the system. For instance, different species start their travel from different origins, cations are formed only in the ionization zone, anions, as suggested, all over the detector. But generally, the behavior of positive ions under these reversed-field conditions should give a good indication of what the negative ones would do under a regular field. Detectors that show a high impedance to the travel of positive ions should do likewise for the negative ones.

In terms of I - V plots: the more difference there is between a voltage profile under regular and one under reversed-field conditions (at the *same* current), the greater will be the effect of migrating negative ions and hence the response. This leads to the prediction that $(V^+ - V^-)_I$, *i.e.* the difference in voltage necessary to collect the same current in regular and reversed-field conditions, should correlate with the response of the detector. It is often difficult to measure the reversed-field profile in the region where I is 90 or 95% of maximum, but other, arbitrary values (*e.g.* 50%) should give comparable data. Again, classical theory would not predict such a correlation to exist.

CONCLUSIONS

From the mechanism developed here for d.c. ECD as an alternative or, perhaps, a supplement to the classical theory, the two disturbing experimental findings—first, no response under reversed-field conditions and second, hyper-coulometric response—can now be easily explained.

Under reversed-field conditions, the electron-capture reaction does proceed (as shown, for instance, by measurements of residual analyte). However, the negative ions now travel the much shorter path, adding very little to the overall impedance of

the detector (whose baseline impedance is, of course, determined by the positive ions travelling the long path and is therefore much higher than under regular field conditions). Comparing electron-capture response (impedance) under reversed and regular field conditions thus amounts to comparing a small change on top of a large value to a large change on top of a small one. Furthermore, the geometry that makes for a well-functioning d.c. ECD is exactly the one that would provide minimal response with the electrical field reversed. Hence it is not surprising that, in our experience, response under those conditions was hardly if ever noticed.

The second disturbing effect, hypercoulometric response, is now well explained by a mechanism based on migrating negative ions. Beyond the main desirables listed (low V , high p , and a pronounced unipolar region) there may have been other circumstances contributing to the experimental observations^{5,6}. High pressure not only slows down the migration of negative ions, it also restricts thermal diffusion, narrows the ionization region, and provides, in general, a considerably larger baseline current⁶. Furthermore, a peak (at constant column retention) passes through the detector slow and compressed. These effects may well have further improved response.

Having been confronted by the experimental finding of hypercoulometric response in the past, our primary aim in this study has been to provide a reasonable picture of what might be happening. We shall attempt to prove or disprove this developed concept by experimental means in the future. This will involve the use of suitably constructed ECDs used under conditions closer to actual practice than the arrangement shown in Fig. 2.

There may be other, very direct ways of getting at the mechanism. For instance, the "unipolar" region of a suitably constructed d.c. ECD, operating under or close to d.c. conditions, could be sampled by mass spectrometry. This may not only provide an answer to the questions raised, but also (given that the answer is in the affirmative) yield interesting results on, say, ion lifetimes and chemistry. However, this particular arrangement is beyond our means and so we hope that other researchers might find this an interesting question to pursue.

If the proposed response mechanism can be proven, it should be interesting to investigate whether and, if yes, to what extent, it influences measurements conducted under other than d.c. conditions.

APPENDIX

Parts of this paper have been written some time ago and, in the meantime, attempts to separate the initial electron capture process from that responsible for response, have been largely successful. Details of these experiments will be provided in subsequent papers.

Support for the proposed mechanism of response has also come, we believe, from a rather unexpected direction, namely from the recent, very impressive development of a non-radioactive ECD by Sullivan of Hewlett-Packard²⁶. In this device, electrons are generated by thermionic emission, thus there are no cations, ionization zones or recombination reactions. Anions, furthermore, "must flow to the collector along with the electrons".

Thus, from a classical point of view, no response should occur. But the device

provides, in fact, excellent response. (The paper does not indicate whether or not it is hypercoulometric; we would not be surprised if it were.)

Sullivan's study²⁶ does not include an explanation of how response comes about. Thus left free to speculate, we assume that his ECD, in fact, operates by a mechanism similar to the one developed in this study: when electrons are captured in the "collector" region, the gradient there becomes steeper. Consequently, since the device is operated in d.c. mode, the gradient in the "electron source" becomes softer and more electrons are diverted to ground.

In other words, the ground in this non-radioactive detector plays the same role as the recombination reaction in the radioactive one, a sink for electrons that is responsive to changes in gradient. When peaks pass through either device, impedances rise as fast electrons are converted to slow anions and, as a consequence, more electrons are removed by conductive surfaces or by recombination, respectively.

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