

CHROMSYMP. 1161

a.c. ELECTRON-CAPTURE DETECTION*

WALTER A. AUE

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia (Canada)

and

K. W. MICHAEL SIU* and SHIER S. BERMAN

Division of Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Ontario (Canada)

SUMMARY

Theoretical arguments notwithstanding, it is possible to drive electron capture detectors with alternating current (a.c.). This study examines the basic features of such detectors, in particular their current and response profiles. It does so over a 10–10⁶ Hz range of sinusoidal and rectangular a.c. polarization, and compares the results with corresponding data from conventional, unipolar regimes.

In contrast to the authors' own expectations, the a.c. driven detector is capable of collecting nearly all, and not just half, of the generated electrons on the counter-electrode. On the lower and higher frequency slopes of this current level (called the "plateau") are situated two response maxima. According to speculations advanced in this study, the position of the former maximum is determined primarily by the cation–electron recombination rate, but the precise nature of its mechanism cannot be further defined without knowledge on recombination and neutralization rate constants. The position of the latter maximum is governed by the onset of electron oscillation, and its mechanism relies, predominantly if not exclusively, on a migrating negative space charge. A self-consistent interpretation is advanced for the various features of the current and response profiles, and experimental evidence is provided from corresponding unipolar pulsing regimes in support of this interpretation.

Four ⁶³Ni detectors, two commercial and two lab-made, were used in this study. All four showed similar behaviour but, depending on their construction, the relative sizes of the two response maxima (hence, speculatively, the relative contributions of the two response mechanisms) varied widely.

The a.c. mode produced approximately the same calibration curves and detection limits as optimized unipolar regimes, and there are reasons to expect that it might work particularly well with analytes that have relatively low electron-capture cross sections. It is also suggested that "constant current" operation should be possible in the a.c. mode.

* NRCC 27 343.

INTRODUCTION

Sometimes it is helpful to ask not what a detector can do but what it cannot do. A question of this sort invariably prompts further ones. For instance: What are the real reasons for a detector's inability to perform a certain task or to work under certain conditions? Is this inability imaginary, *i.e.* predicted by theory; or is it real, *i.e.* demonstrated by experiment? And, most importantly: Can the detector be made to change its mind about what it can and cannot do?

This is a study prompted by just such a question: "Why can an electron-capture detector (ECD) not run on alternating current (a.c.)?"

That it cannot would appear obvious to any practitioner of the art. ECDs are always driven by unipolar sources, be it direct-current (d.c.) or negative-pulse power supplies^{1,2}. This seems to make sense since it is only electrons one wishes to sample.

Furthermore, most of the current literature considers the ECD, implicitly by the kinetic treatment^{1,2} or explicitly in that many words (*e.g.* ref. 3), to be a "stirred-reactor", *i.e.* an ionization cell with close to isotropic distribution of all relevant particles. If such a system were to exist and if it were to be powered by a.c., equal numbers of positive and negative ions would arrive at each of the electrodes.

That could still lead to response provided that (a) an electron-capturing substance introduced into the detector brings about a decrease in the number of charged particles, *i.e.* an increase in neutralization; and (b) an a.c. amplifier is used. Condition a is generally (though not unanimously) considered to be fulfilled by the literature on that point. Condition b would be difficult to meet. The current from an ECD is very low, a few nanoamperes, and amplification of an alternating current that low is, to say the least, inconvenient. If one would want to use an existing ECD system, *i.e.* by just replacing a d.c. or pulsed-power source by an a.c. generator, no current could be expected to register: conventional ECD amplifiers are opaque to a.c., with time constants perhaps in the 0.1–1 s range.

Thus it is unlikely that any analyst should try to use a.c. and, to our knowledge, none has. (We should point out, however, that combinations of direct and alternating fields have been used for different purposes in at least two devices. One employed a rapidly alternating electrical field to probe capture cross sections at electron energies considerably in excess of the thermal level, in an attempt at electron attachment spectroscopy^{4,5}. The other device, based on the very different mobility of electrons and anions and called the Loeb electron filter⁶, was used in the early days of gas chromatography by Smith and Merritt⁷ in what they called "negative ion gas analysis technique". This technique was designed to separate anions from electrons by means of combined a.c. and d.c. fields. Not surprisingly, their device did respond to organohalides.)

Aside from Smith and Merritt's a.c./d.c. device, of which we were fortunately not aware when this study was started, there are some further reasons why a purely a.c.-driven detector might work. For one, we do not consider modern ECD designs to represent a "stirred-reactor" system. In contrast to, say, the Smith and Merritt construction, which used the much more energetic beta radiation from a ⁹⁰Sr source, modern ECDs are based on either ⁶³Ni or ³H foils. ⁶³Ni and, particularly, ³H emit electrons of much lower energy, so the plasma they generate is unlikely to fill the whole detector volume. (The initial ion-pair distribution produced by a typical ⁶³Ni ECD foil has, in fact, been recently measured⁸.)

Hence, if the gas phase of an ECD is electrically asymmetric, and given the over three orders of magnitude difference in mobility between electrons and cations, the detector is likely to impede charge transport in one direction more than in the other. That means it can act as a (more or less efficient) high-impedance half-wave rectifier. Whether a particular ECD can do so can be checked out easily by changing the electrical bias of the conventionally used d.c. or pulse power supply, *i.e.* by changing from a “regular” to a “reversed” electrical field direction. (From here on, the field or potential will be termed “regular” when the radioactive foil is the cathode and “reversed” when it is the anode, regardless of which electrode is connected to the power supply, which to the amplifier). As it turns out, conventional ECDs display a much higher impedance in reversed than in regular field configuration. They do not function well, if at all, in reversed configuration, regardless of whether the cathode or the anode is connected to the electrometer⁹ (although the electron-capture reaction itself proceeds very efficiently). Thus it would be reasonable to drive detectors with a.c. while still using d.c. amplification. Parenthetically, one may note that the ECD can function not only as a highly sensitive detector but also as an electronic gadget for processing extremely low currents: besides its present use as a rectifier, we have also employed it in the past as a constant-current source¹⁰.

This, then, was the pretext that allowed us to try driving an ECD with sinusoidal or rectangular alternating power. The first such experiment was as easily done as connecting a laboratory Variac to an ECD. The response was immediate and unequivocal: the detector worked just fine on household current. (This experiment was actually run some time ago and it turned out that any of the conventional power sources would provide, in terms of sensitivity, about the same performance as the 60-Hz common a.c. sine or a 40-kHz a.c. square wave¹¹).

While being then reported as a curiosity (and, perhaps, a first indication of things to come), the fact that a.c. can be used to drive an ECD obviously prompted further questions: What does an ECD's current profile, what does its response profile look like over a range of frequencies? Are there any unusual, *i.e.* not easily predictable, effects occurring? Would a.c. have any advantages over existing unipolar modes of operation, either in an electronic or a mechanistic context?

One advantage it may possibly have is to allow, under certain circumstances, an increased electron-capture rate. The reason for this is complex, rests on a number of assumptions, and may not be all that important in a real system. However, we shall discuss it here because, first, some of the experiments were done in that particular context and, second, the basic idea was the very same one that triggered the question: “Why can an ECD not run on a.c.?” in the first place. It was the idea of storing electrons, of keeping them around until they could be captured. There are various ways of doing that but, to keep matters simple, it meant forcing electrons to oscillate in an a.c. field in order to increase their effective concentration.

Electron oscillation

Why would one want to increase the electron concentration? The easy and somewhat simplistic answer is, of course, that one would like to obtain as high a rate of electron capture as possible, *i.e.* one would like to provide the highest electron concentration still commensurate with maximum response. Where and under what conditions can that be done in a typical ECD?

The concentration of electrons in the plasma region (in the absence of analyte) is primarily determined by the activity of the radioactive foil on one hand and the recombination constant on the other. If no charge is withdrawn for some time from the system, the recombination rate reaches a steady state (after about a millisecond or two) and the electron concentration can go no higher. This, of course, has all been well known and understood for quite some time.

If no charge is withdrawn from the system, and if the steady-state plasma does not fill the whole detector volume, the regions of dilute or no plasma contain few, if any, electrons. These regions would therefore be useless as far as the capture of electrons by analyte molecules is concerned. This scenario (if we are allowed to adopt for a moment the tenets of the classical kinetic theory^{1,2}) should for instance be the case in a unipolar pulsed system where short pulses of high amplitude remove all free electrons; where such pulses are followed by long intervals during which the system moves to, or close to, steady state; and where electron capture occurs under essentially field-free conditions. It is presumed that the plasma does not significantly extend during field-free periods, as would appear likely from experimental evidence¹². Thus, one would seek to populate primarily the plasma-free region of the detector with electrons for capture.

In contrast, electrons in the d.c. system are being continuously withdrawn to the anode. Doing this they must traverse the empty (no plasma) regions of the detector, and they can be captured there.

However, there is a catch to that. In order to save a large enough number of electrons from recombination in the plasma region and obtain a substantial background current, which, after all, must carry the signal, a voltage has to be used in the d.c. system that makes electrons travel faster through the plasma-free region than is desirable for maximizing their chance of being captured there. That this is so has been demonstrated by experiment. To wit, the capture rate of electrons in a d.c.-ECD, as measured by the consumption of analyte, is constant in the low voltage region and, as voltage is increased, drop off. At the same time, the baseline current rises. The observed *response* maximum occurs at the "knee" position of the current *vs.* voltage ($I-V$) profile, *i.e.* at a voltage at which the electron *capture* rate has already been significantly reduced¹³.

Logically, one would thus want to devise a system where electrons are withdrawn very fast from the plasma, but are then slowed down as much as possible for capture by analyte molecules. Actually, some detectors, *e.g.* the Tracor ECD, do possess a geometry (hence electric field) that works toward that end. Historically, however, the Tracor's dual chamber construction was designed with a very different purpose in mind, and it was assumed at that time that its excellent performance was due to this purpose having been achieved. Thus, a further change of field gradient by optimizing the dimensions may not result in a drastic improvement. Besides, any large increase in response would likely necessitate an increase in detector volume or pressure⁷, changes an analyst would rather avoid.

So, what other means could be employed to keep a sizeable concentration of electrons around? The answer, while logically not without its faults, is nevertheless interesting enough to be allowed an experimental try-out: Keep (some) electrons oscillating in the plasma-free region of the detector. Immediately, however, two counter-arguments spring to mind: the questionable compatibility of this approach with

the prevalent ECD theory, and the side-effects of the required electrical regime on the plasma. We shall discuss these two predicaments in turn.

First, the prevalent ECD theory relies on the neutralization of analyte-derived anions as its only response mechanism. If anions are not neutralized but collected by the anode, they do not contribute to response. Thus, no additional response should be observed if electrons are made to oscillate outside of the plasma, simply because anions generated there would not find any cations for neutralization. Still, there is hope: the classical response mechanism is not the only one available to the ECD. At least two, very different types of detectors^{14,15} have been constructed in which essentially all anions lacked the chance to react with cations but still gave excellent response. This rather interesting behavior was in both cases ascribed to space charge effects^{9,16}. Such effects were also believed to occur in more conventional ECDs—in fact, they were considered responsible for their frequently observed “hypercoulometric” behaviour⁹—but it is not clear under *all* circumstances how much of a particular detector’s response is attributable to a space charge and how much to a more classical mechanism. Different detectors are expected to differ in this regard. Our best estimate on “typical” ECDs is that response is in essence decided by the space charge and that the competing neutralization mechanism contributes only a small amount¹⁷. If so, it may be quite worthwhile to test a variety of commercial detectors for their behaviour under a.c. conditions, besides using two-chamber constructions¹⁵ in which the anions have no chance of gas-phase neutralization.

The second argument against expecting increased response from the oscillation of electrons is perhaps more serious. Any change in the driving fields, designed to benefit electron capture in the non-plasma region, will influence the plasma as well. Further, oscillation, so to speak, is a two-way street: Electrons also return to the plasma which they earlier escaped. As well, not only will electrons have to oscillate but electrons will also have to be collected: The response signal needs a sizeable current to “carry” it.

Fortunately, however, plasma borders are fuzzy, electrons are created during all phases of the alternating field, and it is probably good enough to have some electrons oscillate while others reach the electrode in one pulse. In other words, one need not really construct a complicated ECD with different, externally imposed field gradients in different regions. Rather, one can get away with optimizing response in a simple, conventional design.

In this context one ought to remember that the task of maximizing the electron-capture reaction must remain subservient to the goal of maximizing electron-capture response (under certain conditions the former can be maximum while the latter can be nil—*e.g.*, in the most drastic case, in an ECD with no polarization).

Thus, on one hand, one needs to get electrons out of the plasma, *i.e.* out of the reach of recombination, as quickly as possible. On the other hand, one needs to have the same electrons stay around in the plasma-free region as long as possible.

Fortunately, to optimize response is easier done than said. Besides, the main impetus for conducting these experiments has not been the belief that existing ECD performance could be improved. Rather, we have to admit to a certain curiosity how the ECD would fare under an a.c. regime. In hindsight, our decision to satisfy this curiosity appears to have been amply rewarded.

EXPERIMENTAL

Four ECD models, two constructed and two purchased, were used in this study. Fig. 1 presents comparative, and very simple, schematics of their basic geometry. All four use ^{63}Ni foils.

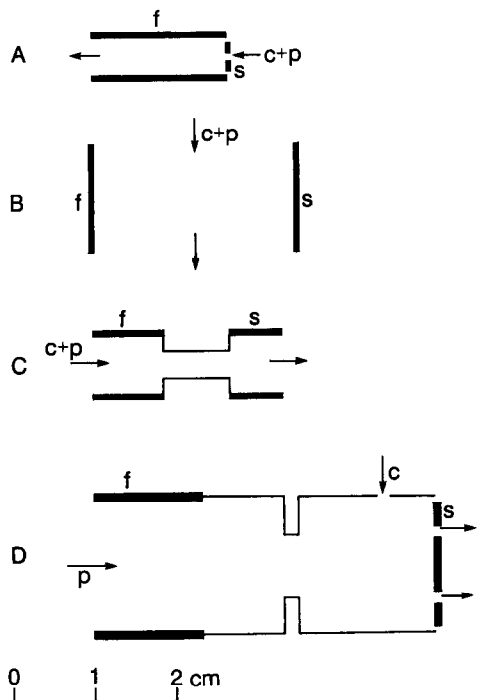


Fig. 1. Schematic detector diagrams. A = Varian, B = parallel plate, C = Tracor, D = dual chamber, f = ^{63}Ni foil, s = collector electrode, c = column effluent (arrow indicates flow), p = pure carrier gas (arrow indicates flow).

Detector A, a commercial Varian model¹⁸, is a small-volume design with cylindrical foil and coaxially displaced anode.

Detector B, a larger, lab-made model, has parallel-plate geometry. Its inter-electrode distance, hence volume, is adjustable. Column effluent enters at a point midway between the electrodes from one side and leaves at the other. For the a.c. experiments described in this paper, the interelectrode distance was kept constant at 2.5 cm.

Detector C, a commercial Tracor model¹⁹ (see also Ref. 9 for a short description), consists of two cylindrical chambers connected by a fairly narrow channel.

Detector D, another lab-made model, is the high-temperature, two-chamber unit described earlier¹⁵. It uses a cylindrical foil and a coaxially displaced, flat collecting electrode. Its most important characteristic is, however, that the cathode (foil) chamber is swept only by pure carrier gas while column effluents are essentially restricted to the anode chamber.

It must be noted that the choice of the four ECDs was not done particularly with a.c. detection in mind: These detectors simply happened to be available in the Halifax and Ottawa laboratories where the experiments were carried out.

The term "a.c.", as used in this paper, describes two types of alternating electrical bias: rectangular pulses and sine waves. Function generators were used as available in the two laboratories including an Interstate high-voltage Model F 41 and Wavetek Models 130 and 162. Current was monitored by the electrometers supplied with the various gas chromatographs, *i.e.* Tracor 550 and Bendix 3500, as well as by stand-alone Keithley electrometers 610 C and 417. When deemed necessary, waveforms were monitored by Philips Model PM 3231 or PM 3110 as well as other oscilloscopes. Gas chromatographs and their conditions were equally conventional.

PREDICTIONS AND RESULTS, DISCUSSION AND SPECULATION

The one curve most characteristic of an ECD is its current profile. In the simplest case, an I - V plot from a d.c. system will tell the analyst how clean the detector is, at what voltage it would work best, etc. In our case, the primary plot is obviously one of current *vs.* frequency (I - f).

Before measuring such a plot, however, it may be worthwhile to predict, from general principles (and with, admittedly, just a trace of hindsight), what it should look like.

The current profile: the prediction

An a.c. regime, whether sine or rectangular shaped, provides the ECD half of the time with a "regular", half of the time with a "reversed" potential. If the ECD functions as a perfect half-wave rectifier, the maximum number of electrons that can be collected on the counterelectrode (counter to the foil, that is) must be half the number generated. The other half, during the time the reversed potential is on, is lost either by recombination in the gas phase or by collection on the (then) anodic foil.

On one hand, one might suspect that it should be much easier for the electrons to be collected on the anodic foil during reversed field, than on the counterelectrode during the subsequent regular-field half cycle. After all, the electrons are being created and are situated⁸ much closer to the foil than to the counterelectrode.

On the other hand, given enough time to develop a steady-state charge distribution, the reversed-field condition will have less electrons collected by the foil. This is so because the ECD, like any other element of an electrical circuit, must maintain overall electrical neutrality. The currents flowing in and out must be equal. (This principle is so simple and self-evident that it is occasionally forgotten when conceptual attention is focussed almost exclusively on the role of electrons.) As we have pointed out before, the current of a d.c.-ECD (unless operated with extremely high voltages) is very low under reversed field. A similar situation must exist during the reversed-field a.c. half wave. (If it did not, then considerable numbers of cations would have to reach the counterelectrode and, since the electrometer connected to it recognizes only the net excess of one or the other charge, they would noticeably decrease the current.) Thus, with the ECD working (let us assume) as a perfect rectifier and the maximum number of electrons being collected during the 50% of the

time the regular field drives them to the counterelectrode, one would expect to measure a current close to one half of the maximum d.c. current that the detector is capable of.

To the question of frequency range, at the lower end, around 1–10 Hz, an electrometer with a time constant of 1–0.1 s should register the on-and-off of regular-field half cycles. Clearly this is a frequency region too low for useful work. The minimum practical frequency is therefore the one at which the electrometer response becomes integrated (smooth).

The upper end of the workable frequency range is obviously reached when the electrons are no longer capable of reaching the counterelectrode during a regular field phase, but simply oscillate near their point of generation. It is fairly easy to estimate at what frequency this should occur, simply by assuming that electrons travel freely and through a linear gradient from the foil to the counterelectrode. (For this rough estimate we need not be concerned with the time and location of electron generation nor with the actual gradient and its time dependence.)

If, to take an illustrative case, an electron should travel 1 cm through 10 V in nitrogen at 1 atm and 280°C, it would need (using the drift velocity data of Pack and Phelps²⁰) about 10 μ s to do so. Oscillation requires twice that time and hence corresponds to an approximate frequency of 50 kHz. Thus, if the electrons migrate unimpededly, the detector current should begin to drop with increasing frequency in this region and eventually reach zero.

Crude estimates have been made for the four detectors used in this study, under the same conditions as given for the experimental I - f profiles shown in Fig. 2. The calculated estimates are listed in Table I.

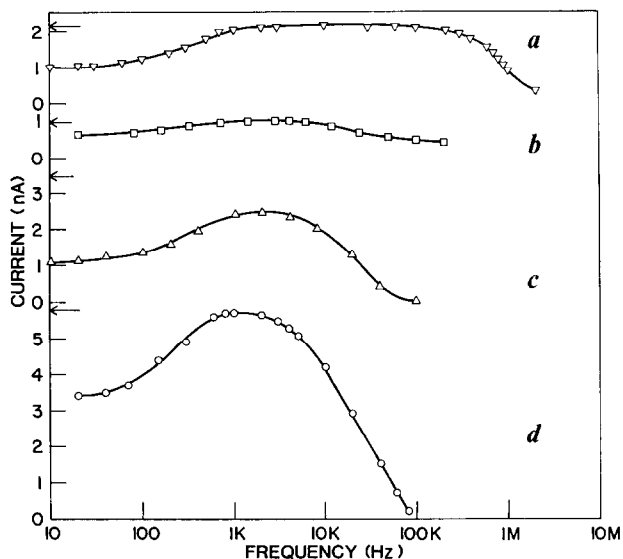


Fig. 2. Current profiles under a.c. polarization. (∇) Varian, \pm 10 V rectangular wave, (\square) parallel plate, \pm 20 V sine wave, (\triangle) Tracor, \pm 10.6 V sine wave, (\circ) dual chamber, \pm 10 V sine wave. The arrow indicates the d.c. current limit of each detector.

TABLE I

DETECTOR TEMPERATURES, DIMENSIONS AND ELECTRON OSCILLATION FREQUENCIES

<i>Detector</i>	<i>Temperature (°C)</i>	<i>Estimated average interelectrode distance (cm)</i>	<i>Observed onset of electron oscillation (kHz)</i>	<i>Calculated onset of electron oscillation (kHz)</i>
A Varian	300	0.9	50	61
B Parallel plate	225	2.5	5	12
C Tracor	320	1.9	4	11
D Dual chamber	280	4.0	2	2.5

The current profile: the experiment

The estimated onset of electron oscillation is compared in Table I with the frequencies at which the current really begins to drop. It is evident from the numbers that, despite the many assumptions and approximations, the basic perception of what happens in this region is essentially correct.

The same, however, cannot be said of our earlier expressed expectation that the a.c. current can at best reach one half of the maximum d.c. current. (We apologize to our readers for having led them down the same garden path we followed: We simply wanted to make use of this excursion for focussing attention on an important and scendipitous find).

We found, much to our surprise, that the maximum a.c. current reached a level clearly more than half, and sometimes even close to the full, d.c. maximum. Fig. 2 demonstrates this with four detectors. (As will be discussed later, higher amplitudes increase the maximum a.c. current and extend its "plateau" region. One of the detectors, the Tracor ECD, should have been run for this picture at a higher power level but, unfortunately, a suitably rated a.c. power supply was no longer available at the time of the experiment.)

Although the four detectors differ in geometry, foil activity, etc., and operating conditions are likewise different, the general pattern is four times repeated. Particularly striking in this regard are two features that will be described below.

First, the current at the low frequency side, *i.e.* at about 10 Hz, is close to one half the maximum d.c. current (the Tracor, again, is low). This, in a way, is as it should be. It simply reflects the fact, mentioned earlier on, that little current passes during the reversed-field half cycle. Electrons generated during this cycle are largely lost to recombination with cations. (If they were collected by the foil, a corresponding amount of cations would have to reach the counterelectrode, depressing the integrated current way below 50% of the d.c. maximum.)

Second, all currents rise (starting with the lowest frequency measured) and reach the plateau at about 1000 Hz. At first sight this may seem a strange coincidence. If it is not coincidence, however, then it must relate to some property common to all four detectors and that is likely the fact that all four have ^{63}Ni foils. Disregarding for the moment their different shape (cylindrical or flat) and size, as well as the

detector cell geometry—all of which influence the density distribution of the plasma, hence the rate of recombination—it stands to reason that the time in which the ion densities reach steady state (under field-free conditions) should be about the same for the four foils. But how does this field-free condition relate to what is being observed under the a.c. regime?

Two paragraphs up, the point was made that very little current flows during the reversed-phase at low frequencies and that electrons and cations simply recombine in the plasma region. Under these conditions, the concentrations of electrons and cations should be close to those that prevail in a truly field-free steady state.

When the reversed-field phase ends and the regular-field phase starts, the electrons that have accumulated can join the newly generated electrons in migrating to the counterelectrode. Most revealing in this context is the following question: What length of time does it take for the plasma to reach a steady state of electrons? This time obviously depends on a variety of conditions; however, as is well known from the literature^{1,2}, it is generally of the order of a couple of milliseconds. Thus, very approximately, the time in which the electron concentration rises linearly with time and in accord with input from the radioactive foil (starting from zero) is about half a millisecond. During this time recombination is still small.

Therefore, if the reversed-field phase is less than half a millisecond long, electron-cation recombination is negligible and essentially all the electrons generated during this phase can be swept over to the counterelectrode during the ensuing regular-field phase. Under these conditions, all electrons generated, regardless during which phase, can potentially be collected and the magnitude of the a.c. current can therefore approach that of the maximum d.c. current. This should occur roughly when the reversed-field phase is shorter than $0.5 \mu\text{s}$, *i.e.* at frequencies higher than 1 kHz. And that, as shown in Fig. 2, is indeed the observed behaviour of all four detectors.

Before progressing to higher frequencies, a short paragraph may more closely examine the rise of the current profile from the low frequency end to about 1 kHz. This rise should include two regions, one from the lowest frequency to around 100 or 200 Hz (an estimate), the other from there to 1000 Hz. In the first region, the rise in current is due to f (frequency) equivalents of steady-state electron populations, which have accumulated during the reversed-field phase and are being added to the subsequent regular-field phase. (The rest of the reversed-field electrons is lost to recombination.) This is the region where the rise in current should be linear with frequency. In the second region, steady state is not reached. Less current is collected per cycle from reversed field but the overall current, owing to the increasing collection rate, still rises. (Fewer and fewer of the reversed-field electrons are being lost to recombination.)

Progressing to higher frequencies, the current reaches a maximum or plateau. The higher the a.c. amplitude, the higher this maximum and the more pronounced its "plateau" quality as it gets closer to the limiting value of the d.c. maximum. At higher frequencies still, the plateau must finally come to an end when the pulses become too short to transport all electrons out of the plasma and to the counterelectrode, *i.e.* when electron "oscillation" starts. The frequency at which this occurs is different for different detectors, quite understandably so in the light of the earlier discussion.

While there should be little doubt about that, our interpretation of the low-frequency region and the rise to the plateau may be in need of some experimental support. In particular, our contention that a reversed-field phase is really close to a no-field phase in terms of electron concentrations, may be subject to doubts. Fortunately such doubts can easily be dispelled by experiment: One merely has to use a unipolar pulse train of the same frequency. That is, the regular-field phases would be exactly the same, but instead of the reversed-field phase in a.c. there would be a field-free interval in the negative pulse regime.

The results of this experiment are shown in Fig. 3, with excellent agreement between the bipolar and unipolar curves in the low-frequency and plateau regions. This clearly confirms the explanation given above. Beyond the plateau region, the two curves must deviate: electrons oscillate with the bipolar pulses but move, in a series of smaller steps, to the counterelectrode with the unipolar ones. For the latter, this means that electrons continue to be collected at plateau level. That this must be so becomes also apparent when approaching the plateau from the other side, *i.e.* from infinite frequency. Infinite frequency in this waveform simply means d.c. at half the pulse amplitude, and if the latter corresponds to a voltage located in the plateau region of a d.c. I - V curve, it further means that the current level is the same in both cases. As can be gleaned from Fig. 3, this is very nearly the case.

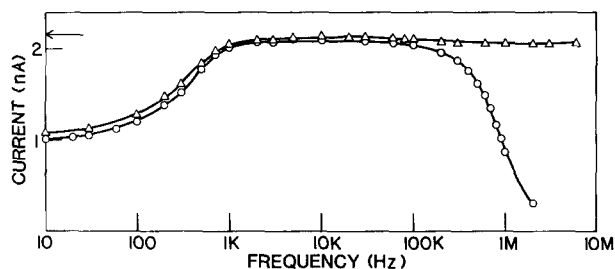


Fig. 3. Current profiles under unipolar and bipolar drives. Varian ECD; (Δ) - 10 V rectangular wave, (\circ) \pm 10 V rectangular wave. Arrow indicates d.c. current limit.

A short comment should be made here about the fact that the unipolar current profile is a trace higher than the bipolar one, particularly so in the low frequency region. While the discrepancy is small and probably close to experimental error, it makes sense that some difference should exist. The reason for this is that the reversed-field half cycle (if d.c. under reversed field can be taken as an example) produces a small but still noticeable current. Also, one can run through the frequency range with a reversed-field unipolar pulse train and measure this very small current. From the measurement it appears that the difference between the two plots may indeed represent the reversed-field current.

So far we have considered only the baseline current profile, without introducing electron-capturing substances. Clearly, any conclusion drawn about the baseline current must be reflected in a discussion of response as well.

The response profile: the prediction

There is quite a bit that one can predict about what response will be like, judging from the baseline profile alone. It is obvious, of course, that when there is no current, there can be no response. In other words, at the high frequency end the response profile must vanish when the current profile reaches zero. Before that point, though, lies the interesting region of electron oscillation. If oscillation helps capture in some way, and if a large number of anions are created in the plasma-free regions of the detector, a sizeable space charge should develop there and response should be high.

It is also apparent that, when almost all electrons are collected, there can be little or no response. Thus, response in the plateau region of the current profile should be very low. (The argument here is the same one would make about the plateau region of a d.c. detector. The residence times of the electrons under the steep gradient are very short, hence the electron-capture rate is low.)

Moving to the low frequency region between about 10 and 100 Hz for the moment (the final rise to the plateau region will be discussed later) it is fairly easy to predict from what has been said before that response should be low. First, the voltage has been set at a relatively high level (in order to produce a sizeable current plateau). This means that, if the same voltage were used in a d.c. drive, this voltage would correspond to a position above the "knee" in the $I-V$ plot, *i.e.* to a situation where almost all the electrons are withdrawn and their short residence time allows only reduced electron capture to occur. The same effect should prevail in a.c. during the regular-field phase. In fact, an a.c.-ECD in the very low frequency region can simply be considered equivalent to an arrangement of two d.c.-driven detectors, one under regular, the other one under reversed field, which switch on and off, respectively, with a.c. frequency and thus contribute, on a 50/50 basis, their well known baseline and response behaviour.

Thus, while the regular-field phase accounts for only reduced response because there is reduced electron capture, the reversed-field phase produces little response because there is very little baseline current to carry the signal (electron capture *per se*, however, is high). When the two are put together, only a small response can result. It should be noted, however, that this conclusion is based on a pulse amplitude above the voltage used for maximum d.c. response: If the pulse amplitude had been chosen to equal the voltage of the knee region in the d.c. $I-V$ plot, *i.e.* the setting that produces the highest d.c. response, a similar response would have been obtained for the regular-field phase of a.c. In other words, its contribution to response would have been about half that of a comparable d.c. set-up.

For the last region, that of the rise to the current plateau from the low frequency side, the point was made before that electron capture *per se*, *i.e.* the actual reaction, is strong during the reversed-field but weak during the regular-field phase. As long as the frequency is very low, nothing comes of that in terms of response. However, as the frequency increases and the current rises to the plateau, the situation changes. It is easy to see why.

As was demonstrated earlier, it is the electrons of the reversed-field phase that are responsible for this rise. But many of these electrons have been captured and are no longer available for fast transport to the counterelectrode. Hence, some response must be observed in this frequency region.

The total scenario thus predicts response in the two areas of major change in the $I-f$ profile: where the current rises from the low-frequency level up to the plateau and where the plateau descends down to zero.

It may be noted in this context that an earlier study²¹ of (unipolar) pulsing regimes in a dual-chamber detector found that the maxima in response occurred approximately at the frequency where the $I-f$ profile showed inflection points (steepest slope). A similar situation may prevail under a.c. conditions.

The response profile: the experiment

A very clear response profile, superimposed on the $I-f$ profile, is shown in Fig. 4 for the determination of 10 pg lindane in the Varian ECD. The two response maxima occur at or close to the inflection points of the current profile and are of approximately the same magnitude. The Varian is the smallest one of the four detectors studied; it is therefore likely the one with the largest relative contribution of the neutralization mechanism.

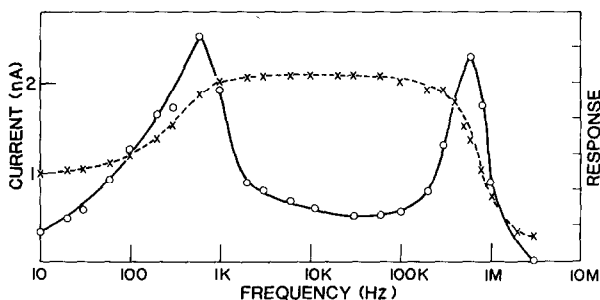


Fig. 4. Current and response profiles of 10 pg lindane under bipolar drive. Varian ECD, ± 10 V rectangular wave. (\times) Current, (\circ) response (arbitrary units).

While the above scenario of two response maxima was developed with at least partial encouragement from hindsight, it was also done from general principles only and without reference to the different response theories, neutralization^{1,2} and space charge⁹ mechanisms, available from the literature. Since attempts have been made to distinguish between the two under suitable circumstances²², it may be appropriate here to speculate how these would relate to the two response maxima observed under a.c. conditions.

Speculations about mechanisms: the high-frequency maximum

The response maximum at high frequency relies on electron capture occurring throughout the whole detector volume (electrons begin to oscillate). Therefore anions should be formed also in non-plasma regions, where they cannot find cations for neutralization. Hence a negative space charge develops there, changing the potential gradient across the cell and thereby causing increased electron-cation recombination in the plasma region. The high-frequency response maximum can thus be attributed to the space charge mechanism. (Note that this does not exclude the neutralization of cations and anions in the plasma; but the latter does occur at all frequencies. At most it could be as high as the valley between the two response maxima.)

An equivalent way of describing this situation is that, as electrons are being increasingly converted to anions in the non-plasma parts of the detector and the potential gradient changes accordingly, migration of the electrons left over does slow down. The distance of their oscillation shortens, hence fewer of them reach the counterelectrode. The drop in current thus produced we call response.

Still another way of expressing the same thought is that with increased numbers of anions being formed along the electron path, the impedance for electrons increases and the I - f curve in this region shifts to the left, with the shift, as usual, seen as response. Or, if one considers a fast enough equilibrium involving the electron and the analyte-derived anion, it is the resultant speed of the negative charge that decreases with decreasing electron/anion ratio.

More speculations: the low-frequency maximum

While the high-frequency response maximum is thus clearly attributable to a space charge mechanism, the low-frequency response is not as easy to characterize. We shall discuss reversed-field and regular-field half cycles in turn, before combining them for the overall effect.

As was mentioned earlier, the electron-capture reaction takes place preferentially in the reversed-field phase, particularly when the $+/-$ a.c. amplitude is larger than the voltage characteristic of the knee position in a corresponding d.c. system. Under reversed-field conditions, charged particles have little movement. Consequently, the electron concentration in the plasma can be expected to be close to the field-free condition, *i.e.* close to that of steady state or a pseudo steady state maximum. This should certainly be the case at lower frequencies. Electron concentrations will decline, however, as the frequency increases and the reversed-field phase is no longer able to reach highest possible electron concentrations. Thus, cation-anion neutralization can occur easily during the reversed-field phase in the plasma, and the neutralization mechanism should be considered.

In the a.c. system under reversed-field conditions, electrons are not collected by the foil to any significant extent and the heavier anions and cations hardly move at all. Thus, neutralization is not favored over recombination on account of residence times alone. Rather, the relevant criterion is whether the neutralization rate *constant* or the recombination rate *constant* is the larger and by how much. Aside from the fact that the particular nature of the cations and anions may play a certain role here, both one and the other constant have been regarded in the literature as being the larger. Most authors nowadays consider them to be "comparable".

We may therefore characterize the situation as follows: If recombination is faster than neutralization, then the end of the reversed-field half cycle finds a plasma with a somewhat larger concentration of negative (and positive) particles, a considerable fraction of the former being anions. If, on the other hand, neutralization is faster than recombination, then the opposite occurs: The concentration of negative (and positive) particles has decreased and few anions are present.

The latter is a clear case of the neutralization mechanism at work. The former is somewhat ambiguous: When the reversed field switches off and the regular field switches on, electrons are removed from the plasma, leaving the slow anions more or less in place. (Furthermore, with the electrons having been "stored" during reversed field close to the foil, this is where most of the anions should have been created,

increasing their chance of reacting with cations on their longer way out of the plasma when the field switches.) If the two rate constants were not too far apart, then the neutralization *rates* should still be larger than the recombination *rates* because of the low electron concentration (short residence time) during regular field. This, again, would favor the neutralization mechanism. If, however, the recombination rate constant is very much larger than the neutralization rate constant, then a neutralization mechanism would not be favoured and, given the fact that significant response is observed, one would have to look at other mechanistic possibilities. Thus, a primary objective, but one which is beyond the scope of this study, would be to establish some typical neutralization and recombination rate constants by measurements under a.c. conditions.

It is, of course, conceivable that some anions are able to leave the plasma and do set up a negative space charge. This is the more likely because the a.c. amplitude is relatively high, and the potential under which anions can effectively move is on half of the time (as compared to a unipolar pulse regime, where the width of the pulse is short compared to the field-free interval). Whether the space charge becomes effective in terms of response, depends of course on the dimensions of the detector and the particular conditions under which it is run.

During the regular-field phase (disregarding the reversed-field contribution just discussed) the detector functions essentially like a d.c.-ECD. It is easy to achieve hypercoulometry in a d.c.-ECD; in fact, the same Tracor detector as used in this study, running at 5 atm, showed the apparent capture of about 50 electrons by one molecule of analyte²³. Such numbers make it most likely that the predominant response mechanism is based on a space-charge effect⁹.

However, in the a.c.-driven mode of this study, it is unlikely for hypercoulometry to occur during the regular-field phase. This is because the a.c. amplitude is chosen at a level as high as possible, in order to produce a clear plateau in the I - f profile and two sharp response (R) maxima in the R - f profile. This amplitude corresponds to a voltage beyond the "knee" region in the I - V profile of the same detector run in d.c., hence response during the regular-field phase of a.c. is far from optimum. Thus, all things considered, it is not likely that the regular phase would produce hypercoulometric response, and if it does occur it would most likely mean that the reversed phase had a significant part in producing it.

It would be possible to draw inferences on the nature of the response mechanism by operating the detector in two clearly distinct configurations representing heterogeneous and homogeneous plasma distributions²². However, the work involved in such an experiment (it would call for rebuilding three of the detectors with adjustable interelectrode distances, etc.) was not considered worthwhile in the present context. Here, the question of mechanism did not influence the choice of experiments and, overall, plays only a very minor role. Consequently, one has to look at other indicators.

One indication of mechanism comes from an experiment in which a space-charge effect was used to produce an ECD with positive response (*i.e.* an increase rather than the conventional decrease in current upon introduction of the analyte). This experiment was also run under a.c. conditions and it did show a clear low-frequency maximum, suggesting a contribution of the space charge mechanism²⁴. Further circumstantial evidence comes from the response profiles of detector D (a

lab-made, two-chamber construction in which the neutralization mechanism is precluded). As will be shown in Fig. 8, a small low-frequency maximum does appear in the response profile. It therefore seems safe to assume that the space-charge mechanism does operate during the regular-field a.c. phase; however, it is not clear how much it contributes to response on a quantitative basis. Obviously, its relative contribution would also depend strongly on the particular detector construction and conditions.

Since the reversed-phase contribution to response depends on the subsequent regular phase in order to be expressed as observable response, it will be very small at low frequencies. Given that fact, the lowest measured level of response can be taken to reflect, approximately, the roughly constant contribution of the regular phase. Any rise above that level would therefore be attributable to electron capture and its associated response mechanisms during reversed field.

A rough estimate made using the response curves given in this study (if we exclude the special case of the dual-chamber lab design which produces response but, as expected, only a vanishingly small first maximum) shows that the presumed contribution of the reversed-field phase to total response is about 80–85% at the low-frequency maximum. As stated earlier, one needs to know the recombination and neutralization constants to further define the response mechanism during this phase. If neutralization constants are larger than recombination constants, then any hypercoulometric response would have to be attributed to a migration of anion out of the plasma since without such a space charge effect, the system could not exceed the coulometric limit. If, however, the neutralization constants were to be much smaller than the recombination constants, the effects of much higher charged-particle concentrations could lead to hypercoulometric effects inside the plasma. In the moment, no clear judgement is possible.

To summarize the mechanistic speculations, it appears that the low-frequency maxima observed under the conditions of this study arise predominantly from a contribution of the reversed phase and involve primarily processes in the plasma region, while the high-frequency maxima are essentially caused by the space-charge mechanism based on electron capture outside the plasma.

Bipolar vs. unipolar regime

Returning to the experiments, it is fairly obvious from earlier discussion what must happen if a.c. is replaced by pulse, *i.e.* when the detector is run in a unipolar rather than a bipolar mode, with negative pulses of the same amplitude and with a field-free interval replacing the reversed-field a.c. half-phase. Electrons can no longer oscillate and the plateau region will stretch more or less undisturbed to infinity (Fig. 3): The high-frequency response maximum must therefore vanish. The low-frequency maximum, however, must stay: The two currents behave the same way in this region.

Fig. 5 shows this experiment, with results as expected. Beyond the apparent agreement, the response peak in the unipolar regime appears a trace larger than in the bipolar one (Fig. 4). This may be accidental but, more likely, the slightly higher availability of electrons and cations and/or the somewhat higher chance of space charge effects in the unipolar mode may have led to the observed result. In this regard, the response profiles of Fig. 4 and 5 agree with the current profiles of Fig. 3 discussed earlier.

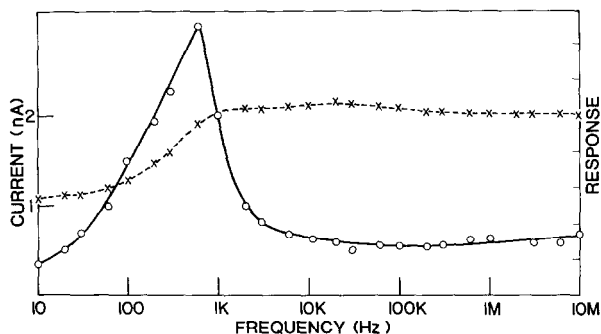


Fig. 5. Current and response profiles of 10 pg lindane under unipolar drive. Varian ECD, -10 V rectangular wave. (\times) Current, (\circ) response (arbitrary units).

One may note that the best response shown in Fig. 5 is below the coulometric limit (at about 0.45 F/mol). This condition is by far not the best at which this detector can be run, but it was called for to allow comparison with the a.c. regime. The amount of electron capture may close to double if field-free conditions were to prevail most of the time. This would, however, still only reach and not surpass the coulometric limit. It seems fairly obvious, therefore, that this detector needs some additional response from another mechanism, such as the space charge, in order to reach the clearly hypercoulometric values (up to at least 8 F/mol) of which it is capable²⁵. However, given the fact that the detector conditions are set for reasons other than those to show the largest possible response, there is a good chance that hypercoulometry, if sought, could be found in the first a.c. response maximum.

The weak electron capturer

Returning to a.c. conditions, another speculation needs to be examined. It was mentioned earlier on that weak electron capturers should benefit more than strong ones from an increased availability of electrons, as occurs in the otherwise sparsely populated detector region through which electrons begin to oscillate only at relatively high frequencies. This speculation is based on the respective rate equations. The strong electron capturer, because of its large capture rate, has most of its molecules converted to anions. The same is clearly not the case for the weak capturer. Its concentration remains approximately constant, since it has to enter the detector in much larger amounts to produce a comparable response. Therefore, it stands to profit more from a higher electron concentration. (Note that the argument concerning the strong electron capturer presumes a coulometric limit of sorts; however, it does so on the molecular level, not on the level of response. Hypercoulometry is based on *observed* response, it does not necessarily imply that the electron-capture reaction exceeds one electron/molecule or even approaches that value.)

Fig. 6 presents the case of a weak electron capturer, 1,4-dichlorobenzene. It is injected under the same conditions as lindane in Fig. 4, but, in order to produce approximately the same response, in an amount one hundred-fold higher. As speculated, its response in the second response maximum region (*i.e.* the one where some electrons begin to oscillate) is about twice as large as response at the first (low fre-

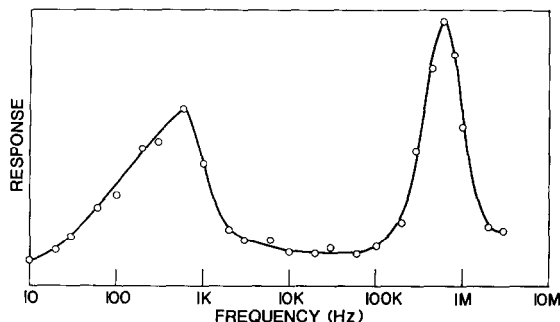


Fig. 6. a.c. response profile of 1 ng 1,4-dichlorobenzene. Varian ECD, ± 10 V rectangular wave.

quency) maximum in contrast to lindane, whose two response maxima are of about the same magnitude.

However, no systematic study of weak electron-capturing molecules has been conducted and, until such time, the observed effect should be taken only as indication and not as proof of the suggested mechanism.

The space-charge effect

It is, of course, quite easy to increase the second response maximum in comparison to the first, even with strong electron capturers. All that is necessary is to choose a detector configuration favouring the space-charge mechanism. For instance, the point has been made before that the Tracor ECD happens to be of such a design. Indeed, lindane in that detector shows a very prominent second response maximum. The situation is documented in Fig. 7 for another interesting and well capturing analyte, piäzselenol (which behaves, in this regard, like any strong electron capturer, including our favourite analyte lindane).

The reason why the Tracor ECD favours a space-charge mechanism is its two-chamber construction. The anode chamber is outside of the plasma, hence without cations and without the possibility of neutralization for anions created there. (Anions created in the plasma, however, can be neutralized.) Consequently, a detector

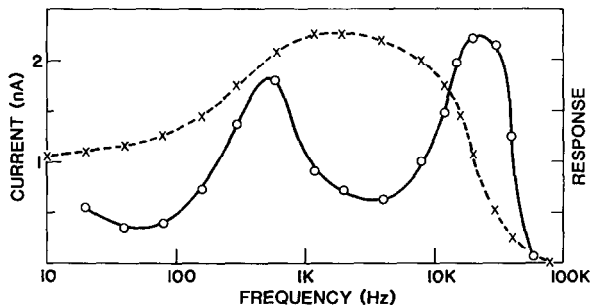


Fig. 7. a.c. current and response profiles of 10 pg piäzselenol. Tracor ECD, ± 10.6 V sine wave. (x) Current, (o) response (arbitrary units).

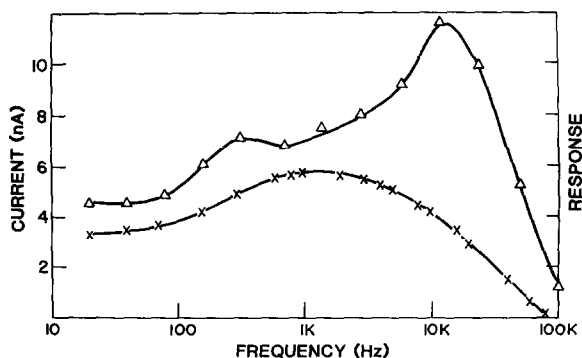


Fig. 8. a.c. current and response profiles of 10 pg lindane. Dual chamber ECD, ± 10 V sine wave. (x) Current, (Δ) response (arbitrary units).

where the possibility of cation-anion neutralization is precluded even for the plasma, *i.e.* our own dual-chamber design run in the “separated” mode, should produce a very large second but a very small first response maximum. As shown in Fig. 8 for 10 pg lindane, this is indeed the case.

The position of the response maxima

We now return for a moment to the baseline (*i.e.* the current *vs.* frequency) profiles. The basic shape of all these profiles from the four detectors is the same, as shown in Fig. 2. Also, variation of parameters affects these profiles in similar ways.

One of the parameters that can be easily changed is the a.c. amplitude. This is shown, as an example, for the Tracor ECD run with sine waves of ± 10.6 , 10.2 and 9.9 V in Fig. 9. With higher amplitudes, electrons travel longer paths, so the cut-off due to complete electron oscillation is shifted to higher frequencies. Below, the currents increase due to the fact that the one-half and the full values of the d.c. maximum have not yet been attained in the low-frequency and plateau regions, respectively. Visually, the current (and also the response) profiles become sharper, *i.e.* show more pronounced features as the a.c. amplitude is increased. (The low voltages shown here for the Tracor ECD may appear to have been chosen for the purpose of obtaining well-spaced profiles. However, necessity played a part as well: This study

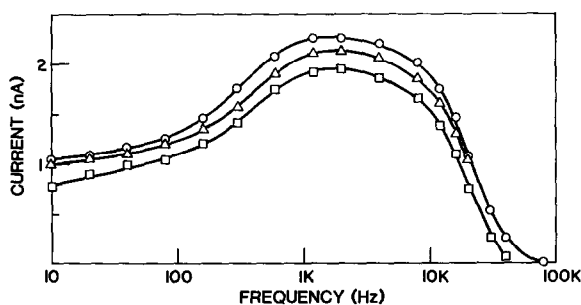


Fig. 9. Variation of current profile with a.c. amplitude. Tracor ECD. (O) ± 10.6 V sine wave, (Δ) ± 10.2 V sine wave, (\square) ± 9.9 V sine wave.

was conducted in two locations and the power supply available at the time in one of them had a ± 10.6 V maximum. With a better power supply we could have produced a higher and wider plateau region and sharper response maxima, though not as well-spaced plots as in Fig. 9.)

Current profiles of this sort suggest an empirical but interesting form of data manipulation. In the space-charge mechanism, at least, the effective voltage across the plasma (and some other) regions of the detector volume can be viewed as the externally imposed voltage minus the counterfield internally generated by the migrating anions. Thus, a current profile run at lower voltage might, to some degree, simulate one run under the load of a small amount of electron-capturing substance. The comparison, obviously, is not perfect: Capture rates do vary with frequency and anions are created in different parts of the detector, not to mention the possibility of response due to a mechanism based inside rather than outside the plasma. However, it is still an exercise worth doing.

Fig. 10 shows the differences between two current profiles of the Tracor ECD (from Fig. 9) together with a response profile from this detector (from Fig. 7). The resulting subtraction profiles are not *equal* to the response profile, but they do show maxima at approximately the same frequencies. A similar point could be made about plotting the slope of a current profile, dI/df , against frequency. This, of course, is identical with the earlier statement that the response maxima coincide more or less with the inflection points of the current profile.

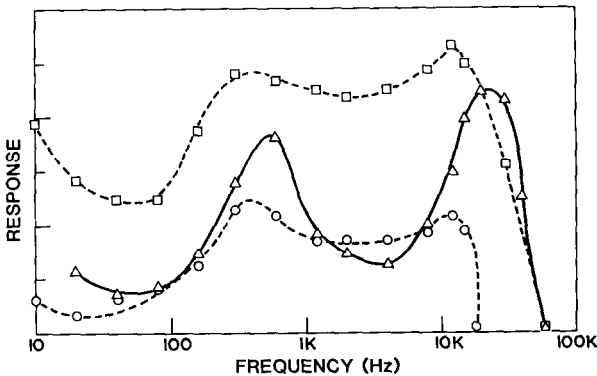


Fig. 10. Difference plots of a.c. currents compared with a.c. response profile. Tracor ECD. (O) (± 10.6 V) minus (± 10.2 V) sine wave current profiles, (□) (± 10.6 V) minus (± 9.9 V) sine wave current profiles, (Δ) response profile from Fig. 7 (arbitrary units).

This holds for any pulse amplitude. Fig. 11 shows as an example three current profiles measured on the Varian ECD with amplitudes of ± 2 , 5 and 10 V. As discussed earlier, the rise to the plateau occurs at about the same frequency regardless of amplitude since it is determined primarily not by the pulse parameters but by the recombination rate during reversed field. The descent from the plateau occurs at different frequencies, signalling the onset of electron oscillation. The plateau itself becomes higher, wider, and more pronounced with increasing amplitude.

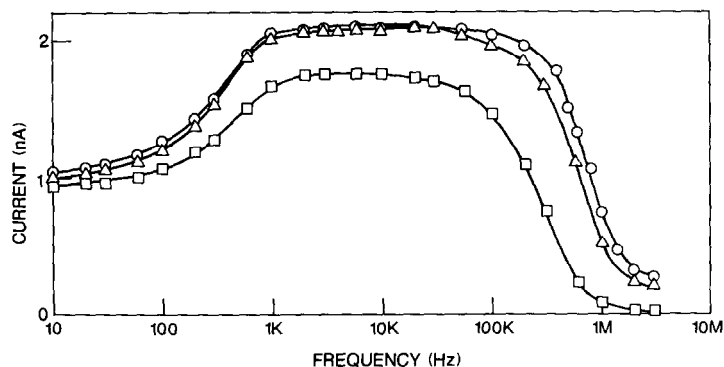


Fig. 11. Current profiles under bipolar, rectangular wave of varying amplitude. Varian ECD. (O) ± 10 V, (Δ) ± 5 V, (\square) ± 2 V.

The response maxima must behave accordingly, and this (with vertical offsets for clarity) is shown in Fig. 12. The left maximum remains at approximately the same frequency but becomes sharper as the amplitude increases. The maximum on the right shifts to higher frequencies as the amplitude increases and it becomes sharper as well. The response valley between the two maxima corresponds to the current plateau: the higher and wider the plateau, the lower and wider the valley.

In fact, it should be possible to approach a state in which the plateau is almost at the current level of the d.c. maximum (more precisely: at the current level of the d.c. maximum minus the current level under reversed field) and the response in this

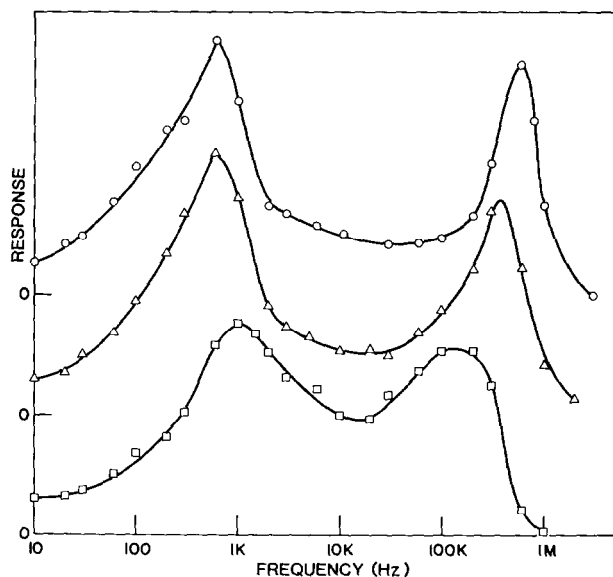


Fig. 12. Response profiles of 10 pg lindane under bipolar, rectangular wave of varying amplitude. Varian ECD. Curves offset for clarity. (O) ± 10 V, (Δ) ± 5 V, (\square) ± 2 V.

region, accordingly, becomes very low. By comparison with a d.c. system, in which response can be shut off by a high enough voltage, one might have suspected that here, too, response might approach zero. However, the reversed-field phase under the a.c. regime, unless it is so strong that it does remove the electrons to the foil, still allows some capture and subsequent effects on response to proceed. The effect decreases with increasing frequency—the pulse becomes shorter and both electron and cation concentrations cannot build up as high—and it would seem reasonable to assume that the descent from the first maximum into the valley in Fig. 12 reflects this influence.

Practical performance

For practical purposes, a.c.-powered detectors appear to respond just as well as their more conventional counterparts driven by d.c. or various unipolar pulse trains. This point was made earlier in a study using a simple Variac¹¹ and it is repeated here in a short experiment comparing calibration curves for lindane under unipolar and bipolar drives. The detector is the lab-made dual-chamber unit¹⁵ and the analyte lindane enters only the chamber housing the collecting electrode. Thus neutralization is excluded and the response plotted is considered due only to the space-charge mechanism.

The three drive modes produce very similar results, as documented in Fig. 13. The minimum detectable limit of 0.3 pg is respectable in light of the fact that the high-boiling analyte was separated on a packed column.

Some more predictions and speculations

It is apparent that the lower detectable limit most likely to be obtained by using, say, a stronger electron capturer eluting at a lower temperature from a capillary column, would apply equally well to the bipolar as to the more conventional unipolar drives modes. It is also quite likely, judging from other evidence presented in this

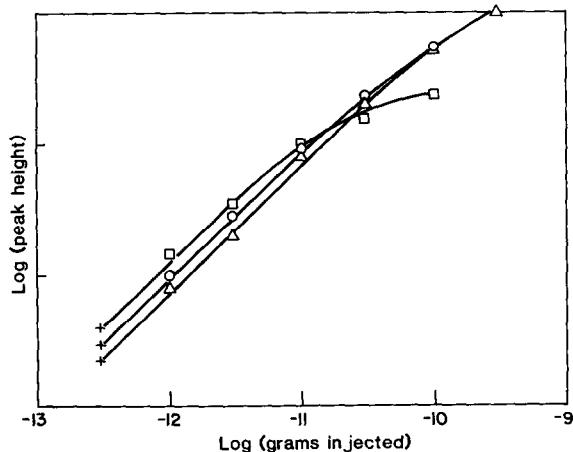


Fig. 13. Calibration plots of lindane. Dual chamber ECD. (O) d.c., -12 V, (Δ) ± 20 V sine wave at 10 kHz, (\square) unipolar, rectangular pulse train: Amplitude -60 V, width $7 \mu\text{s}$, period $360 \mu\text{s}$, (+) minimum detectable amount at signal-to-noise-ratio = 2.

study, that the two commercial detectors, the Varian and the Tracor, would show presentable calibration curves when run by an a.c. regime. It would be quite interesting, furthermore, to compare the performance of various commercial detectors under a.c. regimes, both against each other and against their behavior under unipolar drive conditions. As long as these detectors have high enough impedance ratios, *i.e.* as long as their charge densities are sufficiently heterogeneous (for the second response maximum, in particular), the a.c. drive should provide adequate results.

However, such a study is expensive, lengthy and really beyond the scope of this introductory one. Besides, we expect (and hope) that other groups would see fit to give the a.c. mode a try-out on their own equipment.

It may also be possible to extend the benefits of constant-current operation²⁶ to the a.c. regime. In unipolar operation, the highly successful constant-current mode relies on the common variation of frequency²⁶ or the less common one of voltage^{27,28}. In an a.c. driven detector, the descent from the current plateau on the high-frequency side, *i.e.* the region of limited electron oscillation, shifts on the frequency scale with both pulse amplitude and addition of analyte. Hence we expect that, when operated at frequencies corresponding to the second response maximum, the detector would accept a current constraint. Given suitable electronics, it would respond to analyte by a *decrease* in frequency when driven with constant amplitude, and by an increase in amplitude when driven with constant frequency.

It may be noted that this is opposite to the reaction of a unipolar detector when operated under constant current constraint: The conventional ECD reacts to analyte with an *increase* in frequency when driven with constant amplitude. It would be possible to request similar behaviour of an a.c.-powered ECD, but its conditions would then have to be adjusted to those of the first response maximum. We consider those conditions, perhaps unfairly, to be less interesting at the moment. Of course, the very idea of a.c.c. (alternating constant current) remains pure speculation without proper experiments to demonstrate its validity and viability.

Experimental evidence would also be needed to establish the particular advantages and disadvantages of an a.c.-driven system under routine analytical use, not to mention the analysis of comparative costs involved in building it. One of the reasons we chose a space-charge design for determining the calibration curves shown in Fig. 13 was that we wanted to demonstrate that the a.c. mode could be well combined with a foil chamber that was swept only by pure carrier gas, thus preventing any contamination and premature deterioration of the radioactive foil.

It would not appear totally impossible that the a.c. drives could provide a viable alternative to the currently used unipolar power supplies. Certainly the fact that the a.c. current and response profiles appear quite amenable to interpretation and manipulation should prove helpful. In this context we ought to admit, however, that we have circumvented one particular question by simply accepting the experimental evidence without providing a cogent explanation for the observed fact.

This question is why electrons can easily be collected by the counterelectrode, which is farther away from the plasma, during the regular-field, while they cannot be collected by the foil, which produces and embraces the plasma, during the equally strong reversed-field half-phase. (The answer suggested in the manuscript, *i.e.* the reference to the low current of unipolar reversed field configurations, is certainly valid for longer time spans but begins to look questionable in the milli- to microse-

cond range in the plateau region.) However, the real answer to this question is a complex one and beyond the scope of the present manuscript. It will be dealt with in a future report.

As is evident from the paragraph above, the a.c. mode has proven useful so far in probing (if not in solving) certain mechanistic aspects of electron-capture detection. It is some of these aspects that have been used here to provide a speculative interpretation of why the detector behaves in the way it does. Also, such aspects have allowed a moderate amount of prediction as to how other detectors and similar modes of operation might perform. Mechanistic aspects, furthermore, appear to have somehow become further diversified and magnified under the bipolar drive conditions of this study and, for this reason alone, the a.c. mode of electron-capture detection invites future development.

ACKNOWLEDGEMENT

Work done at Dalhousie University was supported by NSERC operating grant A-9604.

REFERENCES

- 1 E. D. Pellizzari, *J. Chromatogr.*, 98 (1974) 323.
- 2 A. Zlatkis and C. F. Poole (Editors), *Electron Capture, Journal of Chromatography Library*, Vol. 20, Elsevier, Amsterdam, 1981.
- 3 E. Broś and F. M. Page, *J. Chromatogr.*, 126 (1976) 271.
- 4 J. E. Lovelock, D. C. Fenimore and A. Zlatkis, *J. Gas Chromatogr.*, 8 (1967) 392.
- 5 P. Popp, J. Leonhardt and G. Oppermann, *J. Chromatogr.*, 147 (1978) 127.
- 6 L. B. Loeb, *Phys. Rev.*, 48 (1955) 684.
- 7 V. N. Smith and E. J. Merritt, *Anal. Chem.*, 34 (1962) 1476.
- 8 K. W. M. Siu and W. A. Aue, *Can. J. Chem.*, (1987) in press.
- 9 W. A. Aue and S. Kapila, *J. Chromatogr.*, 188 (1980) 1.
- 10 W. A. Aue and K. W. M. Siu, *Anal. Chem.*, 52 (1980) 1544.
- 11 K. W. M. Siu and W. A. Aue, *J. Chromatogr.*, 268 (1983) 273.
- 12 K. W. M. Siu and W. A. Aue, *J. Chromatogr.*, 392 (1987) 143.
- 13 S. Kapila and W. A. Aue, *J. Chromatogr.*, 108 (1975) 13.
- 14 J. J. Sullivan, *30th Pittsburgh Conference, Cleveland, OH, March 1979*, paper 256.
- 15 K. W. M. Siu and W. A. Aue, *Mikrochimica Acta*, 1 (1983) 419.
- 16 W. A. Aue and K. W. M. Siu, *J. Chromatogr.*, 203 (1981) 237.
- 17 S. Kapila, C. R. Vogt and W. A. Aue, *J. Chromatogr.*, 195 (1980) 17.
- 18 R. Simon and G. Wells, *J. Chromatogr.*, 302 (1984) 221.
- 19 *Manual, Electron Capture Detector*, Tracor Inc., Austin, Texas, 1972.
- 20 J. L. Pack and A. V. Phelps, *Physical Rev.*, 121 (1961) 798.
- 21 W. A. Aue and K. W. M. Siu, *J. Chromatogr.*, 239 (1982) 127.
- 22 W. A. Aue, *18th International Symposium on Advances in Chromatography, Tokyo, April, 1982*, paper L 30.
- 23 S. Kapila and W. A. Aue, *J. Chromatogr.*, 118 (1976) 233.
- 24 A. McMahon and W. A. Aue, *J. Chromatogr.*, in press
- 25 K. W. M. Siu, G. J. Gardner and S. S. Berman, *J. Chromatogr.*, 330 (1985) 87.
- 26 R. J. Maggs, P. L. Joynes, A. J. Davies and J. E. Lovelock, *Anal. Chem.*, 52 (1971) 1966.
- 27 K. W. M. Siu, C. M. Roper, L. Ramaley and W. A. Aue, *J. Chromatogr.*, 210 (1981) 401.
- 28 Y. Nagayanagi, S. Matsumoto and T. Fukushima, *15th International Symposium on Chromatography, Nuremberg, October, 1984*, paper 4PF-42