

Polarization, relaxation and unrestrictedly linear response in a bipolar, constant-frequency electron-capture detector[☆]

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Abstract

To investigate *bipolar* constant-frequency regimes in the electron-capture detector (ECD), a “tripulser” was built. The tripulser was able to generate unit sequences of up to three pulses, individually defined as to width, amplitude and relative position, with 600 ns to 1 s and 0 to 250 V definition ranges. On a commercial ⁶³Ni two-chamber ECD (Tracor), the high-frequency region of bipolar pulsing (ca. 10 to 100 kHz) was explored. The detector showed clear polarization–relaxation (PR) effects within time spans (on the order of 10⁻⁵ s) that were commensurate with the theoretical mobility of electrons. Speculative evidence was found to suggest that PR kinetics, as driven by particular bipolar pulse sequences, resulted in changes to the (heterogeneous) charged-particle distribution and effectively allowed higher than usual concentrations of electrons (and cations) to exist in the ECD. Based on this evidence, a bipolar, constant-frequency drive was developed that, when tested on the Tracor ECD, showed good analytical performance. Most important (and in contrast to the behavior of any other unipolar constant-frequency mode) the bipolar (Tracor) ECD yielded strictly *linear* calibration curves—starting from the detection limit (5 · 10⁻¹⁸ mol/s of α -1,2,3,4,5,6-hexachlorocyclohexane at $S/N_{p-p} = 2$), over three orders of magnitude, all the way to an amount of analyte that totally exhausted the baseline current.

1. Introduction

It seems obvious that “polarization” (electrical inhomogeneity, the development of space charges) must take place inside the electron-capture detector (ECD) when a constant or temporary external voltage is imposed across the cell. The grounds for assuming that internal polarization occurs on a significant scale are many; and they are both experimental and theoretical in nature.

One experimental example is provided by the

impedance to current flow in the two possible field directions. (In this study, “regular field” refers to the conventional situation in which the externally imposed voltage makes the radioactive foil the cathode, while “reversed field” makes the foil the anode—regardless of which electrode is at ground potential.) The current flows in the two possible field directions—given the same voltage drop, of course—differ greatly [1,2]. Thus the ECD can serve as a (not quite perfect) half-wave rectifier. If so, it must possess internal cell potentials (space charges) that preferentially hinder the flow of electrons in one, i.e. the reversed-field, direction.

One theoretical example is provided by the ab

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initio calculation of spatially and temporally resolved charged-particle concentrations and corresponding potential gradients in a simulated parallel-plate ECD driven by bipolar square waves [3]. This calculation clearly demonstrated that under reversed-field conditions electrons are trapped in a (positive) potential well. The well is situated close to the radioactive foil and its behaviour can be easily followed over the whole frequency range up to 50 kHz [3,4]. Regardless of the mechanism of impedance, however, it seems self-evident that the charged-particle distribution must become polarized when an external voltage is switched on, and that it must relax when that voltage is switched off.

Our interest in the process of polarization and relaxation ("PR") has several roots. The main one is this: because the ECD acts as a rectifier, it can be driven by directionally alternating (bipolar) voltages. In the simplest case, household current will do [5]. This mode of operation differs from the initial d.c. and all following, unipolar-pulsed ECD drives of the literature [6–16]. We call the detector, when driven by alternating voltages in sine or square-wave form, the a.c. ECD [17].

To our knowledge, the a.c. ECD has seen only minor, if indeed any, practical use in analytical laboratories. It is, however, a perceptually most interesting device. Indeed, based on the classical theory of electron capture one would argue that it should not work at all. In fact, it works quite well [4,5,17].

How does the polarization phenomenon tie in with sinusoidal or square-wave a.c. drives? Thus: When the imposed voltage switches direction, the polarization of the charged-particle distribution inside the ECD cell must follow suit. How much time does that take? Can the time necessary to achieve a sizable extent of polarization ever become comparable to the pulse repetition time of the drive? If it does, will the performance of the a.c. ECD become dependent on the kinetics of polarization?

Since the fastest reasonable type of polarization relates to electrons, and since the a.c. ECD uses drive regimes of up to ca. 10^6 Hz, the question appears justified. After all, at voltages and other conditions typical of the a.c. ECD,

unimpeded electrons' drift through nitrogen at about 10^5 cm/s [18]. That would suggest that somewhere in the 10^4 to 10^6 Hz range—the numbers depend on the construction of the detector, the nature of the radioisotope and the carrier gas, the imposed voltage and temperature, the existing contamination, etc., etc.—polarization kinetics could become dominant.

But what about relaxation? Under, say, a square-wave a.c. drive, the full regular-field voltage switches on immediately after the full reversed-field voltage switches off, and vice versa. The polarization adjusts accordingly: it finds no time for relaxation. To allow the ECD the time to dissipate the generated space charges requires pulse-free periods. (These intervals between pulses are conventionally characterized as being "field-free" in the ECD literature; however, the latter term will not be used here to avoid confusing the externally imposed voltage with the resulting but, in space and time, different and variable internal field.)

Thus, appropriately spaced pulses could be profitably employed to induce and test PR effects by time-integrated observation. In the simplest case that approach could answer some obvious questions. For instance: does a positive pulse preceding a negative pulse influence the current flow and response of the ECD? If so, does it make any difference how close the two pulses come? What about a negative pulse preceding a positive pulse? Aside from their potential analytical utility, the answers to these questions may also fill one of the several large gaps that still remain in our understanding of the ECD.

The only "practical" ECD use of bipolar pulsing has, to our knowledge, been proposed by Simon and Wells [19] for the *constant-current* mode. These authors describe their technical approach, mechanistic objectives, and practical results as follows: "The bipolar pulse consists of an initial extraction pulse, followed immediately by a reversed biased pulse. . . . The action of the bipolar pulser is to reverse the displacement of the ions due to the initial extraction pulse to their original position, thus minimizing the collection of anions. . . . The most notable effect of the bipolar pulser is to linearize the response of

the ECD at high sample concentrations . . .” [19].

Working under rather different conditions and toward a different goal, Warden et al. [20] found that “a bipolar pulse wave form [which] contains a positive-going pulse of amplitude and duration equal to the usual negative-going pulse which precedes it . . . had no measurable affect on the standing currents or on the responses at all pulse frequencies”.

Given the vagaries arising from different ECD constructions, operational modes and mechanistic theories, the reader may well question the wisdom of using *repetitive* pulse sequences. Could the PR process not be probed by monitoring the current flow during and after a *single* pulse? The literature experiment closest related to this question was carried out by Gobby et al. [21]. It used an atmospheric-pressure ionization source for mass spectrometry (API-MS), with the source resembling an ECD. The mass spectrometer monitored the flow of cations and anions through a pinhole.

The —to our knowledge— only single-pulse experiment with electrons in a (more or less) conventional ECD was carried out by Lovelock and Watson [22]. It was designed to answer the question whether electrons were drifting unimpeded through the cell or whether their drift speed was influenced by ambipolar diffusion (cf. [15]). The former was reported to be the case.

Lovelock and Watson’s report proved tantalizing to us, not the least because of its fairly obvious potential extension to, say, a probing of electron, cation and anion movements in the ECD under various drive modes. Apart from being of fundamental interest, such a probe could yield much-needed information on the chemical nature of peaks for, say, confirmation purposes; it could introduce selectivity among compounds of similar electron-capture cross-section for, say, more reliable analysis; and it could provide mechanistic details for, say, solving some of the design problems under which the ECD still labors. Being bereft of technical details, however, this lone report of singly-pulsed ECD operation could unfortunately not be reproduced by the modest means at our disposal.

To wit, our current was extremely low, the

required temporal resolution was very high, and the capacitance of the cell seriously interfered [3]. Although a ragged feature vaguely resembling Lovelock and Watson’s “electron pulse” [22] could finally be obtained; and although that feature was, very approximately, of the expected magnitude (charge), mobility, and also reactivity toward molecular oxygen (in other words, air injections wiped it out), our data were still of decidedly inferior quality. More importantly, an attempt to monitor the arrival of *positive* ions produced an equally ragged feature of exactly the same charge, mobility, shape and chemical reactivity as the “electron pulse” (an “image current”?) [3].

Single-pulse measurements of temporally resolved charged-particle flow were therefore discontinued and replaced by the —technique-wise more straightforward, though interpretation-wise more ambiguous— measurements of time-integrated currents resulting from multiple-pulse drives in a conventional ECD. For these measurements, the prototype of a microprocessor-controlled square-wave pulse generator [3] was constructed as a graduate course project.

Its use demonstrated that a positive (reversed-field) pulse, when it *preceded* a negative pulse by less than about 20 μ s, did reduce the detector current. The reduction in current was not (or at least was not predominantly) due to a reversed-field current. Rather, it was judged to be due to a polarization that, as long as it persisted, opposed the transport of electrons to the collecting electrode during the subsequent regular-field pulse [3].

For the objectives of the present paper, a more user-friendly, bipolar pulse generator of greater speed, power and versatility had to be developed. We boldly called it the “tripulser”.

2. Experimental

The tripulser¹ (Fig. 1 shows its block diagram) was a laboratory-built microprocessor-based square-wave pulse generator capable of repeat-

¹ Researchers interested in the tripulser are invited to contact B.M. for details.

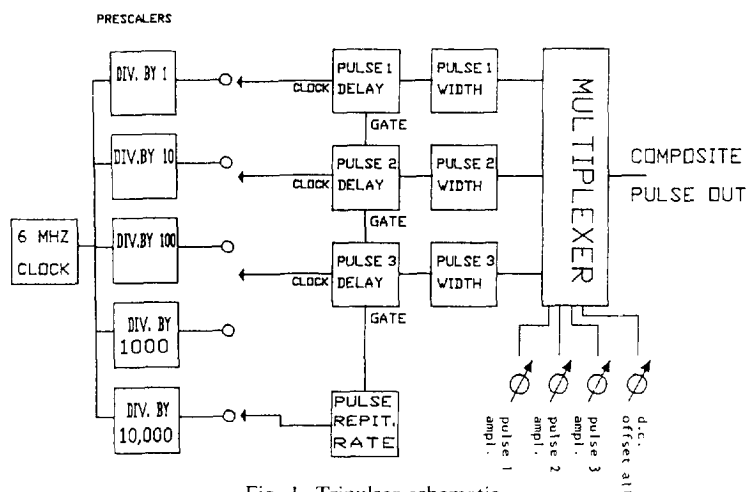


Fig. 1. Tripulser schematic.

ing a unit sequence comprised of up to three individually defineable pulses. The sequence repetition rate, as well as the delay time and width of each of the pulses within a given sequence, were entered on a key pad by the operator before each experiment. Time periods could vary from the upper limit of 1 s down to the (in practice achievable) resolution of 600 ns. All timing parameters were defined in response to prompts that appeared, prior to starting the experiment, on a terminal connected to the pulser through an RS-232 serial data link.

The polarity and amplitude of the individual pulses, as well as the d.c. offset, were controlled by potentiometers built into the tripulser. The overall attainable amplitude range was 250 V (e.g., up to $+/-125$ V for equal-sized bipolar pulses, or up to $+$ or -250 V for unipolar pulses), subject to a slew rate of 150 V/ μ s and the condition that pulses not overlap.

The tripulser circuit could be triggered by an external pulse generator that thus controlled, and was therefore able to vary, the pulse sequence's repetition rate during the experiment. (Note that, in contrast, the pulse widths, delays, polarities and amplitudes could be changed only if the experiment was interrupted; this precluded the use of any of the latter parameters as operationally active criteria in, say, a feedback circuit.)

The tripulser's output was always connected to

the ECD's foil: a "negative" pulse therefore imposed a "regular" field, a "positive" pulse a "reversed" field across the cell.

The gas chromatograph with ^{63}Ni ECD was a Tracor Model 550; it had been used in our laboratory for about two decades. The column was a 100×0.2 cm I.D. borosilicate tube packed with 5% OV-101 on Chromosorb W AW, 100–120 mesh (i.e. of particle diameters between 150 and $125 \mu\text{m}$, approximately); the 35 ml/min carrier gas and the 50 ml/min purge gas were "prepurified"-grade nitrogen, further freed of oxygen and water by passage through heated zirconium sponge (gas purifier; Supelco, Bellefonte, PA, USA).

For the frequently used test analyte α -1,2,3,4,5,6-hexachlorocyclohexane—an inactive isomer of the well-known insecticide lindane (which is the γ isomer)—the temperatures used were: injector 250, column 150, transfer line port 270 and detector 300°C. (Note that these altogether conventional GC–ECD conditions are mentioned here for the record only; similar results could have been obtained from a great variety of analytes under a wide range of conditions.)

α -1,2,3,4,5,6-Hexachlorocyclohexane was purchased from ICN Labs. (Irvine, CA, USA) and used without further purification. The solvent hexane was "distilled-in-glass, non-UV" grade from Caledon Labs. (Georgetown, Ontario,

Canada); it was distilled again from calcium hydride under a stream of nitrogen prior to each *high-sensitivity* experiment (cf. [23]).

The continued performance level of the ECD was tested from time to time in the —historically oldest, instrumentally simplest and diagnostically most revealing— d.c. mode. Scanning its current–voltage profile ascertained that the detector had not been contaminated —or that it had not otherwise suffered changes in its vital characteristics— by and during the experiments. (No significant changes were found during this study).

The ECD output current was amplified by the built-in Tracor electrometer and displayed on a Linear Instruments strip chart recorder and/or a Fluke 75 multimeter. The performance of the tripulser was monitored by a 60 MHz oscilloscope (Model 2215A; Tektronix, Beaverton, OR, USA) and/or a frequency meter (DFC 100 multifunction counter; JDR Instruments, 2233 Samaritan Drive, San Jose, CA 95124, USA).

3. Results and discussion

It may be well to start with two simple and general evaluations to set the stage and, in the process, define some parameters for the more specialized experiments to follow.

3.1. First general evaluation: what do the current profiles look like?

The most telling characteristics of pulsed ECDs are their current–frequency profiles. Fig. 2 shows three such profiles, presented for easier viewing in both semilog (left) and linear (right) form. Note that the specific shape of profiles can depend on the amplitude —and, if pulse-free intervals occur, the width— of the pulses. Each of the regular-field pulses used in this experiment (which exert at least -75 V for $6 \mu\text{s}$) would, by the tenets of the classical ECD theory (e.g. [14]), be strong enough to clear the cell of electrons.

The first profile uses a straightforward square-wave *a.c.* (no pulse-free intervals) [17]; the second a *unipolar* negative drive (identical with

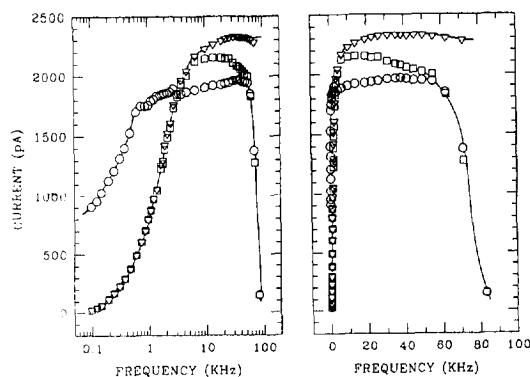


Fig. 2. Current profiles for comparison of a.c. (○), unipolar pulsed (▽) and bipolar pulsed (□) square-wave drives. Pulse width (unipolar and bipolar): $6 \mu\text{s}$. Pulse amplitude: a.c. and bipolar $+/-75$ V; unipolar -75 V. Bipolar pulses follow one another at equal intervals. Maximum d.c. current: 2.88 nA. Left plot: semilogarithmic; right plot: linear.

the secondmost popular ECD mode [6–11]); the third a *bipolar* (temporally symmetric) pulse sequence. Interestingly, but in hindsight predictably, there exist two separate locations in the plot where two (though not the same two) of the three profiles join.

At low frequencies, it is the two intermittently pulsing regimes whose profiles join. In other words, the positive pulse of the bipolar regime is ineffectual in this region. And this makes sense: its reversed-field current is only a minute fraction of the regular-field current, and the system has more than enough time to relax between pulses. At *very* low frequencies, both current profiles must obviously drop to zero.

The a.c. profile, in contrast, does not: a very heavy 75 V are *continually* imposed in one direction or the other. As the frequency reduces to extremely low values —i.e. as the alternating “d.c.” stretches of opposing polarity grow longer and longer, the instrument will show correspondingly alternating regular-field and reversed-field d.c. currents, provided the pulse width is significantly longer than the time constant of electrometer and recorder [24]. If the pulse width is significantly shorter, the instrument will show only the *difference* between the two currents. (The current shown in the 0.1–1 kHz range is of the latter type. Since the regular-field

current is still considerably larger than the reversed-field current even at a continuous 75 V, and since the two pulses have the same length, the profile straightens out at very low frequencies: it approaches a current level that is slightly lower than half the conventional d.c. current at -75 V.)

At medium frequencies, the bipolar regimes reach slightly different "plateau" regions. The left-side rise to the plateau is essentially governed by the recombination ($M^+ + e^-$) rate. The two pulsing regimes reach somewhat higher plateaus than the a.c. regime; a consequence of the heavier a.c. regime's higher reversed-field current. Further explanations on a.c. drive behaviour in this region have been given earlier [7,25] and, being of little importance to this study, need not be repeated here.

At high frequencies, it is the a.c. and the bipolar pulsed profiles that join and jointly drop to zero. (The unipolar pulsed profile, in contrast, must continue on to a level identical with the -75 V d.c. current [17].) This again makes sense: The bipolar pulses are starting to approach each other closely (at 83 kHz they would theoretically merge); thus they are beginning to resemble an a.c. regime. And the a.c. negative pulse becomes too short in that region to drive even perfectly unimpeded electrons across the cell to the collecting anode [17]. As a consequence, electrons may "oscillate" [4] under a high-frequency a.c. regime (until they recombine with positive ions, are captured by analyte molecules, or collide with some conductive structure). The two profiles join and start to drop from the plateau at about 15 μ s repetition time (a time that obviously depends on the chosen voltage).

It should be mentioned that the term "oscillation" is used here in a partly metaphoric sense—though physical oscillation of electrons is calculable for an idealized ECD system, it has never been experimentally observed in a real one. (The fact that the electrometer registers no current does not necessarily mean that no current flows: its time constant of about a tenth of a second renders the electrometer opaque to a.c. above ca. 10 Hz, and the instrument can thus register only the net (d.c.) flow of charges.)

Even the concepts of "oscillation" and "PR"

intertwine in that region. Whether one or the other is used at this stage depends mainly on the extent to which one sees electrons as being trapped in potential wells, or as being merely impeded, or as being allowed to travel freely back and forth; and whether one sees them as migrating to the collecting anode within one or within several pulse periods. Although there is a physical side to the difference between the two concepts and terms, there is also a semantic one—and the experiments, so far, permit description through either. (We consider such concepts to be more valuable for suggesting new than for explaining old research.)

3.2. Second general evaluation: where could polarization occur?

The second general evaluation we wish to include here was initially conducted to demonstrate the practical use of *three* pulses (the first experiment used only two) and also to check how large the integrated voltage would have to be in order to (apparently) sweep the cell free of electrons. Only as an afterthought did we pose the question what—if anything—should happen if two pulses were to change their *relative positions* within a given sequence. Several experiments were thus run at different combinations of voltage and pulse width. Fig. 3 shows two of these: there the pulses are 100 V high and 2 or 5 μ s wide.

The "stationary" part of the pulse sequence resembles bipolar pulsing at 5 kHz, i.e. at a repetition rate of 200 μ s. Positive and negative "stationary" pulses strike evenly every 100 μ s, while a "mobile" negative pulse strikes in the available intervals. In Fig. 3, the "delay" time of the mobile pulse, i.e. its position in the repeating sequence, is drawn as the abscissa. Fig. 3 also provides a largely self-explanatory schematic of the three pulses. As in the schematics of some later figures, the first pulse of the *subsequent* pulse packet is deliberately included, in order to better represent the *whole* duration of the unit sequence and more meaningfully portray *all* temporal relationships between pulses.

The "mobile" negative pulse ("2") is moved from a position closely following the starting

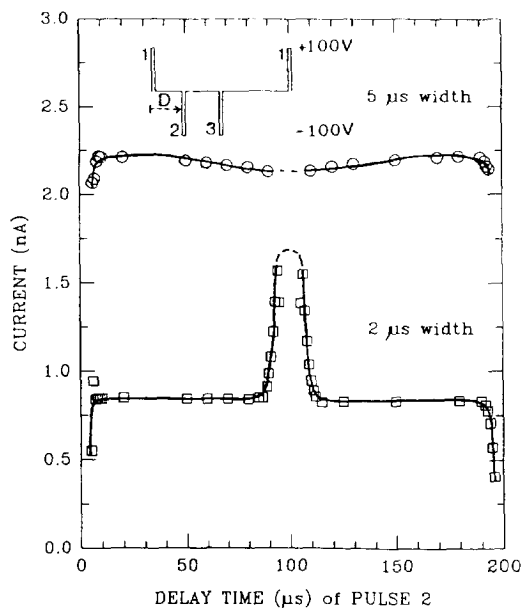


Fig. 3. Current profiles from a bipolar, triple-pulse drive, showing PR effects from $+/-$, $-/-$ and $-/+$ pulse approaches. Pulse width: 2 or 5 μ s. Pulse 1: +100 V, 1 μ s delay; pulse 2: -100 V, variable delay; pulse 3: -100 V, 100 μ s delay. Pulse sequence repeats every 200 μ s. D = Delay time.

positive pulse ("1") to a position closely preceding, then closely succeeding the center negative pulse ("3"), to a position closely approaching the starting positive pulse (again "1") of the next sequence. That means that the mobile negative pulse will, *inter alia*, strike just before and just after both positive and negative stationary pulses.

What makes Fig. 3 so interesting—and what we did not fully anticipate—are these four close encounters. Their interesting aspects are most clearly conveyed by the low-current 2- μ s profile—i.e. the profile of a system in which *both* recombination *and* collection of ionic species claim significant fractions of the available charge (or, using the conventional description, in which the pulses are too weak to clear the cell of electrons). In all four cases in which one pulse gets close to the next, the otherwise fairly constant current level is being severely disturbed. In each case the disturbance occurs within (very approximately) 8 μ s. (Again, this is roughly comparable to the time it would take

unimpeded electrons to traverse most of the ECD cell.)

This disturbance appears to be consistent, no matter whether the two pulses involved in the particular encounter are of the same or of the opposite polarity, and no matter which pulse leads and which follows. We first direct our attention to the center of the picture, where the mobile negative pulse gets close to the stationary negative pulse.

If two 2- μ s negative pulses get very close to each other, we can expect them to act like one 4- μ s pulse. (Although the pulser does not allow pulses to overlap or even touch, it can, of course, be used to produce an analogous 2-pulse bipolar series consisting of a 2- μ s positive starting pulse and a 4- μ s negative central pulse, in order to verify that the system behaves according to expectation.) But why does the mobile pulse, when it is *not* close to its centrally located companion—i.e. when it strikes somewhere else in the freely accessible regions from roughly 10 to 80 and 120 to 190 μ s delay time—have so much *less* effect on the current?

The only explanation for this is that the two negative pulses, when spaced far enough from one another, allow the system to relax in the intervening time. In physical terms, this could be envisioned as a process in which some of the electrons, having been pushed by the first negative pulse into the channel leading to the anode—but not far enough through to be immediately collected—are both pulled back (by the positive space charge they left behind) and pushed back (by their own negative space charge) before the second negative pulse strikes.

However, if the second negative pulse should strike *immediately* after the first, the electrons can not be pushed/pulled back but are rather given another push forward to the anode for collection. Since collection, when it occurs, is irreversible, closely spaced negative pulses (with no relaxation intervening) collect a larger current than widely spaced ones do.

If the result of closely spaced pulses of equal (negative) polarity is a relative increase in current, the experiment shows that the result of closely spaced pulses of opposite polarity is a relative decrease. Mechanistically, however, the

precipitous current decrease at the edges of Fig. 3 seems to make no sense—unless one were to invoke a substantial increase in reversed-field current, i.e. an a.c. contribution that the d.c. electrometer could not sense. But this is most unlikely to happen and we do not believe that it does. Rather, we believe that an increasing fraction of electrons simply fail to be collected under these circumstances.

But why should electrons fail to be collected just because a positive pulse struck very shortly before or after the negative pulse? The result seems particularly puzzling in the latter case: since it is the negative pulse that pushes electrons toward collection, and since collection is final, what conceivable difference could a subsequently occurring positive pulse make? It was this mechanistic question, plus the (in hindsight) potential analytical importance of the system, that enticed us to investigate the topic in greater experimental detail.

3.3. A closer look at PR regions

To define and explore the regions in which PR occurs, a simple bipolar regime was set up in which the two pulses were of equal width and amplitude. The (collecting) negative pulse was perceived as “stationary”, the (disturbing) positive pulse as “mobile”. The positive pulse could thus exert its influence on the negative pulse either by closely following or by closely leading it. The resulting current profiles from four such regimes, which differ only in their $+/-$ 10, 20, 50 and 100 V pulse amplitudes, can be found in Fig. 4. (Several more regimes were tested and behaved similar to the ones shown. The additional horizontal line in each graph indicates the corresponding unipolar (negative pulses only) current level. Maximum d.c. current: 2.88 nA. D = Delay time.)

At low voltages, the current drops dramatically when the “disturbing” positive pulse closely leads or follows the “collecting” negative pulse. Fig. 5 shows an estimate (using the first and last data points from Fig. 4) of the percent current remaining when the positive pulse follows (“-/+”, left side of Fig. 4) or leads (“+/-”, right side of Fig. 4) the negative pulse. In two of the

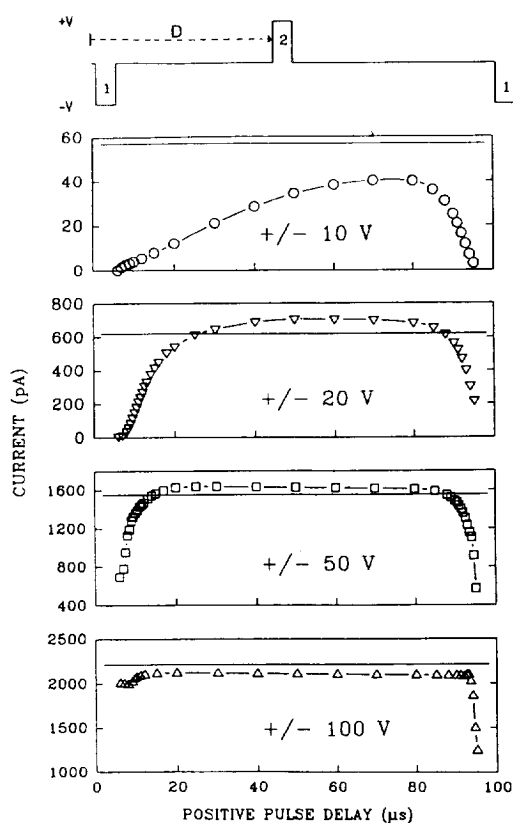


Fig. 4. Current profiles from a bipolar, dual-pulse drive, showing polarization/relaxation effects from close $-/+$ and $+/-$ pulse approaches. Pulse width: $5 \mu\text{s}$; pulse amplitude: $+/-$ 10, 20, 50 or 100 V. Negative pulse delay: $1 \mu\text{s}$; positive pulse delay: variable. Pulse sequence repeats every $100 \mu\text{s}$. The horizontal line indicates the corresponding unipolar (negative pulses only) current level. Maximum d.c. current: 2.88 nA. D = Delay time.

former cases, the current profile actually runs smack into zero: a surprisingly strong showing for a polarization effect.

3.4. First pulse configuration: negative leads positive

How can a complete or even a partial current reduction be rationalized? If we consider first the left side of the graphs shown in Fig. 4—i.e. where the negative pulse *leads* the positive pulse—the only reasonable explanation that we can think of is that the electrons were transported from the polarizing foil chamber into the

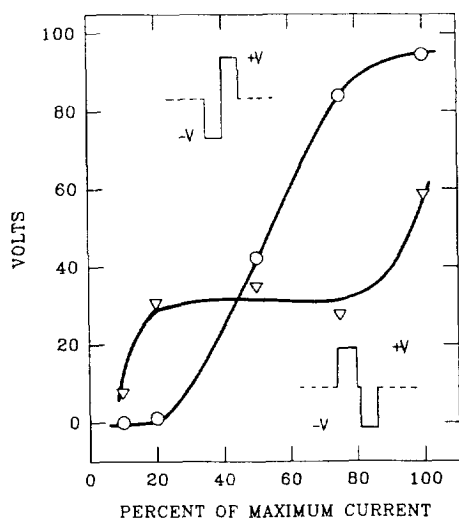


Fig. 5. Approximate current, expressed as percent of maximum, which remains during $-/+$ and $+/-$ pulse encounters. Data from Fig. 4 (plus one additional point).

central channel and on into the collecting-electrode chamber, but that they did not actually reach the anode during the negative pulse. (The fact that the Tracor ECD has a two-chamber construction with the anode, similar to the foil, being of relatively large and cylindrical shape [26], may have benefitted the experiment. It certainly supports the assumed scenario: the imposed-field gradient must be quite steep through the channel but quite gentle in its approach to the two electrodes.)

If no positive pulse were to follow, some of the electrons, driven by their own negative space charge in the essentially unipolar environment of the collection chamber, would migrate to the collecting electrode. Some might also return through the boron nitride channel to the foil chamber, being pushed this way by their own negative space charge in the collection chamber, and being pulled there by the net positive, much slower dissipating space charge of the plasma.

If, however, the positive pulse should hit before the system has had time to thus relax, *most* of the electrons would be forced to return to the foil chamber (to wait there for recombination or for the arrival of the next negative pulse). It seems obvious, however, that this process can

come into its own only if the pulses are so weak that they are barely able to force the electrons from the plasma into the channel: this should therefore occur at conditions of low voltage and correspondingly low overall current. Under these conditions, the concentrations of cations and electrons must be close to their steady-state maximum in the foil chamber.

If, on the other hand, the pulses are strong enough to drive most electrons right into the anode—where they are irreversibly collected—then the subsequent positive pulse can no longer reverse the electron flow. This should occur at conditions of high voltage and correspondingly high overall current. Figs. 4 and 5 are in essential agreement with this push/pull scenario.

3.5. Second pulse configuration: negative follows positive

We can now consider the “right side” of the graphs shown in Fig. 4, where the negative pulse *follows* the positive pulse. Here we can assume that the positive pulse merely polarizes the charge distribution in the foil chamber, since it is too weak to push larger numbers of cations into the collection chamber and electrons into the foil. (This assumption is strongly supported by the huge difference in impedance between reversed-field and regular-field operation in the Tracor ECD [1,2], as well as by response results to come.)

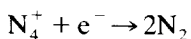
If the subsequent negative pulse then strikes before the system has had time to relax, it would need double strength to overcome the polarization *and* push the electrons through the channel into the collection chamber. Since the two pulses are of matched amplitude in each experiment, one would expect this effect to be less dependent on voltage. Figs. 4 and 5 bear this out.

3.6. Third pulse configuration: positive in the middle

The speculations above provide a reasonable answer to the riddle of the current that disappeared at the left and right sides of the Fig. 4 plots, but they still do not address the outright

paradox of the current in the middle. The paradox is this: in the cases of $+/-20$ and $+/-50$ V pulsing, the bipolar current is *larger* than the negative unipolar current. How can the latter, which is driven by negative pulses, *increase* when *oppositely* directed positive pulses are added? And, no, the effect is not an electronic artifact, and neither is it negligible: the bipolar regime, with the positive pulses striking right between the negative pulses, collects 13 and 5% more current at $+/-20$ and 50 V, respectively, than the corresponding unipolar regime of negative pulses only. But why?

The only “explanation” we can give here is, admittedly, speculative. It involves the highly concentration-sensitive *second-order* recombination reaction, e.g.



This reaction is fundamental to the ECD and, in conjunction with the activity of the radioactive foil, determines the maximum possible concentration of electrons in the (clean) ECD [25,27]. Although electron concentrations are often by custom (really: by necessity) calculated on the “stirred reactor” model, it is obvious that the distribution of ion pairs in the ECD is heterogeneous over long stretches (detector dimensions), owing to the short, roughly exponential distribution of ion pairs generated by ^{63}Ni β s. In other words, a relatively thin layer of relatively dense plasma lines the radioactive foil in the case of ^{63}Ni [28], and the situation is even more extreme in the case of ^3H [29].

Therefore, any process that polarizes (pulls opposite charges apart) and/or homogenizes (evens out charge concentrations across the cell) will result in a shorter- or longer-term decrease in the highly concentration-sensitive, overall rate of recombination, i.e. it will allow overall higher charged-particle concentrations to exist. And this is, of course, what the positive pulse does: it pulls electrons toward and pushes cations away from, the radioactive foil. The resulting increase in the overall electron concentration allows a larger current to be later collected. Note that the largest observed increase in current as a percentage of the total (about 13%), seems roughly

commensurate with the relaxation time as a percentage of the repetition time (the former being estimated from the left- and right-side descent of the $+/-20$ V profile in Fig. 4).

That the process is voltage dependent is experimentally obvious. But why in this manner? To answer we first need to consider the location, concentration and fate of charged particles under a unipolar pulse regime.

At a very *low* voltage, the current is also very low. That means that few charged particles (ion pairs) are collected; most simply recombine. The physical position of cations changes little, i.e. their time-averaged spatial distribution closely approximates the spatial distribution of ionization events. The concentration of charged particles is close to the maximum possible; i.e. it is close to that of the steady state of ion-pair generation vs. ion-pair recombination. In other words, recombination proceeds close to its highest attainable rate. (We recognize that some of the statements above and below are tautologous; however, we need to set the stage for discussions to follow.)

At a very *high* voltage, the current is close to its maximum. Most charged particles are collected; very few recombine. The average cation position lies between the place of generation and the place of collection (the foil). The cation sheath is thus contracted (compared to low- or no-voltage conditions). The concentration of charged particles is low, and so is the rate of recombination. (In this context, note that the repetition time is more than an order of magnitude shorter than the time the system needs to establish steady state [3].)

Let us now disturb these charged-particle distributions with a pulse: first at the very low, then at the very high voltage setting.

At the very *low* voltage setting—which is dominated by ion-pair generation and distribution—the effect of the disturbing pulse on the overall plasma distribution must be minimal. (The rate of ion-pair generation is far higher than the rate of ion-pair collection.) In contrast, the disturbing pulse affects the collection process much more strongly. Electrons that do not make it to the electrode while the negative pulse is on, have a high chance of recombining with the

greater number of wider distributed cations (all in comparison with the high-voltage regime). When the time allowed for relaxation is too short (left and right side of Fig. 4, $+/-10$ V), the number of collected electrons (the current) is thus severely curtailed. The effect is so strong and spreads so far in time that the bipolar current stays below the unipolar current even in the middle of the plot.

At the very *high* voltage setting—which is dominated by ion pair collection—the effect of the disturbing pulse on the charged-particle distribution could be strong and that should decrease the recombination rate. However, the recombination rate is already at a very low level (the rate of ion-pair collection is close to the rate of ion-pair generation). Thus the effect must remain small. Single negative pulses are, however, now strong enough to drive electrons right into the anode. This is an irreversible process that preempts any subsequent relaxation. The regions of close pulse approaches (left and right side of Fig. 4, $+/-100$ V) become therefore much less pronounced. Thus the bipolar current should be close to the unipolar current in the middle of the plot. However, because of its high voltage, the positive pulse also collects a small but significant *reverse* current that, monitored through the slow electrometer, makes the bipolar current appear smaller than the unipolar one.

At *intermediate* voltage settings, finally, the numbers of collected ion pairs is very roughly comparable to the number of recombined ion pairs. The system is not dominated by either a close-to-maximum recombination rate as in the low-voltage case, nor by a close-to-maximum collection rate as in the high-voltage case. This gives the positive pulse the chance to disturb the charged-particle distribution enough to depress the recombination rate, without exerting too much counterproductive influence on current collection from the (now higher) overall concentration of charged particles.

3.7. Current profiles under PR conditions

Similar information, accepting of similar explanations, is shown in the next three figures. These figures offer, however, a more complete

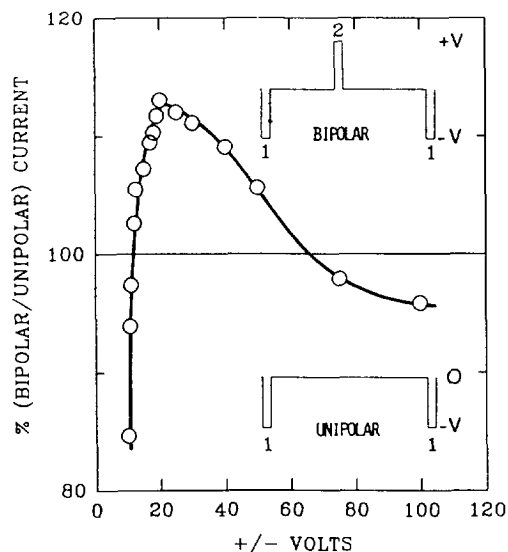


Fig. 6. Maximum current from a bipolar drive, expressed as percent of (negative) unipolar-drive current, as dependent on pulse amplitude. Pulse width: $5 \mu\text{s}$. Pulse sequence repeats every $100 \mu\text{s}$.

database and a more convenient picture for use in the later studies of response. Fig. 6 shows the percentage of maximum bipolar vs. unipolar current with other conditions as in Fig. 4. The region where the former exceeds the latter is rather prominent: it leaves little doubt about the existence of a current paradoxically strengthened by pulses that oppose it.

Figs. 7 and 8 show how the strength of the positive pulse influences the current under various circumstances: Fig. 7 in terms of positive-pulse *width* (with similar amplitudes for positive and negative pulses); Fig. 8 in terms of positive-pulse *amplitude* (for three different levels of negative-pulse strength). Note the relative position of the maxima in Fig. 7, which roughly conforms to expectations based on the value of the time-integrated positive voltage. Note also in Fig. 9 that the (negative) low-level current strengthens (thus showing the discussed paradoxon from a different angle), while the high-level current weakens, as the amplitude of the positive pulse increases. Figs. 6–8 are, of course, consistent with the data of, and explanations for, Figs. 4 and 5.

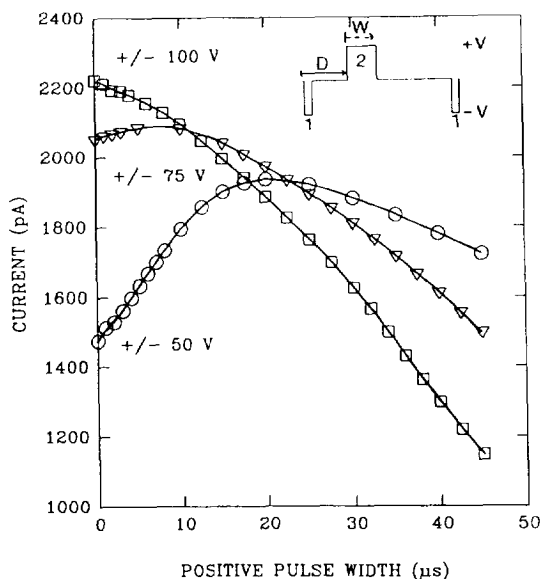


Fig. 7. Current profiles from a bipolar drive, showing the effect of increasing positive pulse width at three voltage levels. Pulse amplitudes ± 50 , 75 or 100 V. Pulse 1: negative, delay 1 μ s, width 5 μ s; pulse 2: positive, delay 30 μ s, width variable. Pulse sequence repeats every 100 μ s.

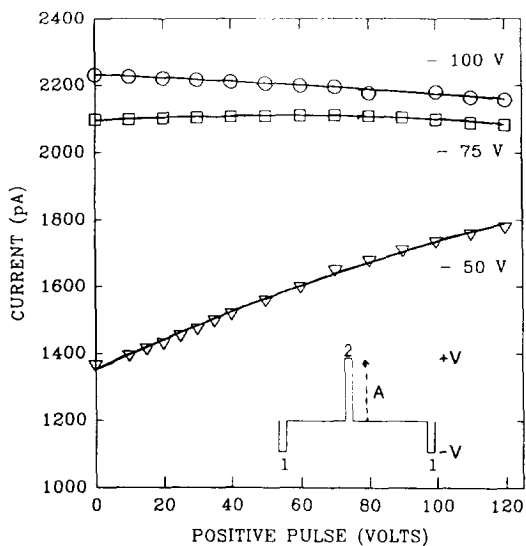


Fig. 8. Current profiles from a bipolar drive, showing the effect of increasing positive-pulse amplitude at three negative-pulse voltage levels. Pulse width 5 μ s. Pulse 1: amplitude -50, 75 or 100 V, delay 1 μ s; pulse 2: amplitude variable, delay 50 μ s. Pulse sequence repeats every 100 μ s.

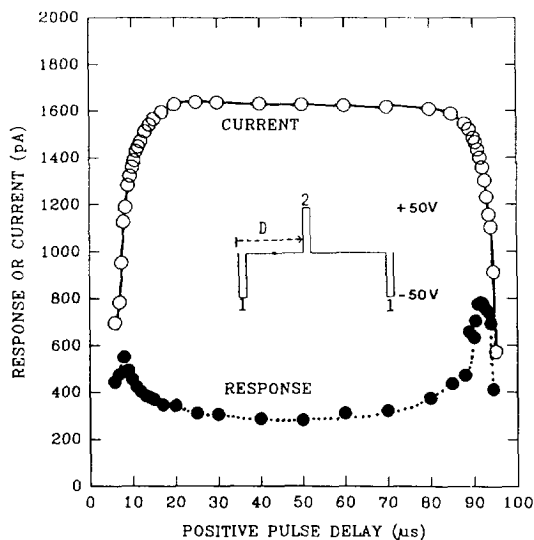


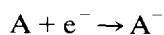
Fig. 9. Current and (inverted) response profiles from a bipolar drive, showing the effect of positive-pulse position (delay time). Pulse amplitude: ± 50 V, pulse width: 5 μ s. Pulse sequence repeats every 100 μ s, i.e. the repetition frequency is 10 kHz. Analyte: 5 μ g α -hexachlorocyclohexane.

3.8. Response profiles under PR conditions

We now have accumulated the necessary understanding of the system's behavior when analyte is absent: it allows us to proceed to the more difficult situation that arises when analyte is present. Two relevant circumstances come to mind.

First, since response to analyte in a constant-frequency regime represents the vertical distance between "baseline" and "peak" current profiles, it is usually strongest where the current profile shows the steepest slope. This would suggest that the best-responding regions should be those where the positive pulse moves close to the negative one (the extreme left and right sides in the graphs of Fig. 4).

Second, from what has been said before, it appears likely that a bipolar system could "store" a higher overall concentration of electrons in the cell than the conventional unipolar one. This is important in terms of linearity. If we formally assume that the rate of the analyte's electron-capture reaction, e.g.



is proportional to the response seen on the recorder, then an analyte depleting the electron concentration will cause the calibration curve to become non-linear.

Although this is readily apparent from first principles, it is difficult to formulate in a quantitative manner because of the periodic and—in its temporal consequences for ion concentrations and space charges inside the ECD—poorly understood mechanics of current collection. Operating within the first 5% of standing current is often thought to assure the analyst linear range. (This rule-of-thumb presumes, *inter alia*, that each single pulse is strong enough to collect all free electrons.) An earlier simulation of ours for such a case yielded indeed a value of about 3 to 4%. Using approximately 10^{1.2}% of the standing current thus lets the analyte stay below 10% deviation from linearity for “homogeneous” kinetics [27]; yet we believe this not to be applicable to the relatively large and heterogeneous two-chamber Tracor ECD. Some detectors like the Tracor ECD clearly do much better: linear ranges up to a third or a even a half of the standing current can be observed. Obviously, however, such excessive behavior has been difficult to reconcile with presumed ECD kinetics.

From an analytical viewpoint, if a bipolar ECD really allows the average electron concentration to rise above that of a comparable unipolar ECD, then the former may have the chance to produce a longer linear range. Or, from a mechanistic viewpoint, if the linear range of a particular calibration curve should indeed turn out to be longer than usual, then this may indicate a higher-than-expected electron concentration inside the ECD.

Fig. 9 shows the by now familiar current profile, together with the corresponding response profile as obtained by repeatedly injecting 5 pg of a strong electron capturer. Expectedly, the response profile shows maxima both on the left and on the right side of the plot (wherever the current profile steeply descends). The right-side response maximum, with the positive pulse preceding the negative one, is usually the stronger

of the two—not surprisingly so in light of the earlier discussions—and it is therefore used for all later figures.

The process of a positive (i.e. reversed-field) pulse striking just *before* the negative one, has, to our knowledge of the published literature, never before been investigated for mechanistic—never mind analytical—reasons. Investigating it would, indeed, seem to make little sense if the investigator happened to believe that electrons move unimpeded at all times and that negative pulses remove all electrons from the system: If the leading positive pulse skimmed electrons off the top before the following negative pulse has had a chance to herd them to the anode, the standing current would drop—and so would the response. Even if the positive pulse had no such effect, what good would it do to use it?

3.9. ECD diagnostics and performance characteristics in the PR realm

At the delay time of maximum response—i.e. with a pattern of bipolar pulses roughly optimized for the 10 kHz repetition frequency—current and response of the system were measured for different voltage levels. The strangely familiar looking result is shown in Fig. 10. What makes it look familiar is, of course, its resemblance to conventional current–voltage curves for d.c. and unipolar-pulsed ECD modes. The maximum of the response curve occurs at the “knee” position of the current curve; and we expect—though we have not ascertained—that it would move slightly to the right with larger amounts of analyte, in analogy to d.c. ECD behavior (e.g. [1], Fig. 8).

It seems reasonable to suspect that this response is *hypercoulometric*; meaning that e/m , the ratio of (apparently) captured electrons to analyte molecules, exceeds unity. To confirm this suspicion, the right-side ordinate offers a (hyper)coulometric ratio scale. Note that the hypercoulometric ratio, as defined here, is easily determined on a single peak from a single ECD, by dividing the peak’s area in faradays (moles of electrons) by the moles of analyte injected. (This “hypercoulometric ratio”, as we have been

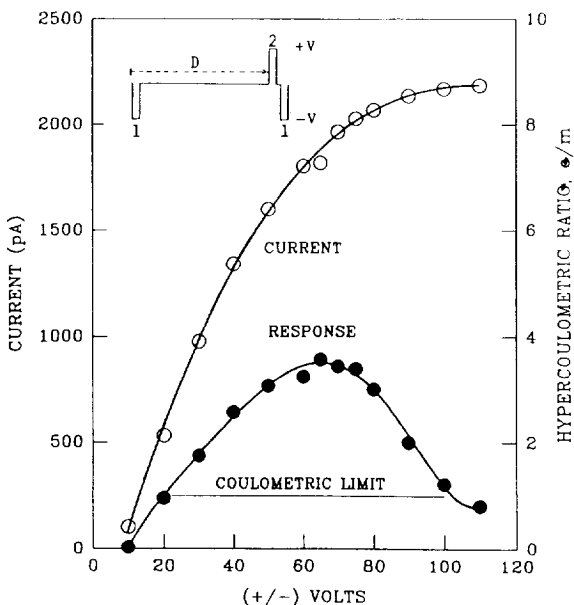


Fig. 10. Current and (inverted) response profiles from a bipolar drive at the $+/-$ (right side) response maximum, showing the effect of pulse amplitude. Pulse width: $5 \mu\text{s}$. Pulse 1: negative, delay $1 \mu\text{s}$; pulse 2: positive, delay $93 \mu\text{s}$. Pulse sequence repeats every $100 \mu\text{s}$, i.e. frequency = 10 kHz . Analyte: $5 \text{ pg } \alpha\text{-hexachlorocyclohexane}$.

[1,27,30] using the term, differs—in principle and in practice—from the “hypercoulometric ratio” or “hypercoulometry factor” used in the interesting work of Lasa et al. [31,32], which relates to the behavior of *two* ECDs connected in series.)

The hypercoulometric response of this study, i.e. $e/m \approx 3.5$ by our definition, is better than any *bipolar* result obtained so far [4,7]; although it is still dwarfed by the $e/m \approx 50$ of a d.c. system run under elevated pressure on the same detector [33].

The calibration curve prevailing at these hypercoulometric conditions is shown in Fig. 11. It is drawn at precisely unity slope; demonstrating thereby that the response remains linear over the *entire* standing-current range. The line starts at about 0.1% of standing current at the extrapolated $S/N_{p-p} = 2$ detection limit. [N_{p-p} is the peak-to-peak noise of the baseline with drift and spikes excluded, at an resistance–capacitance (RC) filter time constant of about 1 s.] The

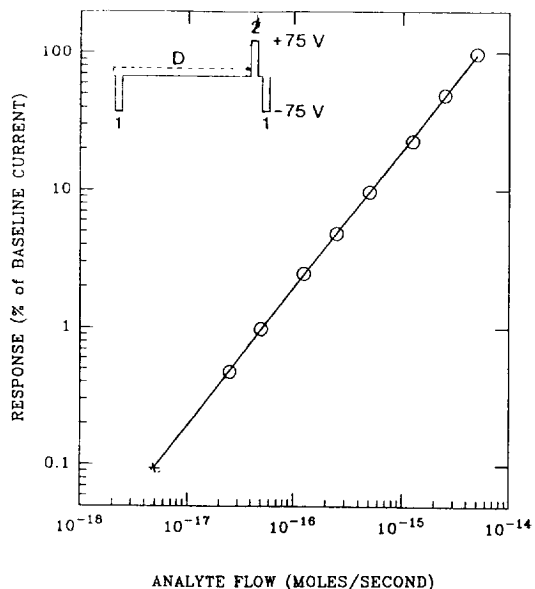


Fig. 11. Calibration curve of $\alpha\text{-1,2,3,4,5,6-hexachlorocyclohexane}$ from a constant-frequency (10 kHz) bipolar drive, at the $+/-$ (right side) response maximum. Pulse amplitude $+/-75 \text{ V}$, pulse width $5 \mu\text{s}$. Pulse 1: negative, delay $1 \mu\text{s}$; pulse 2: positive, delay $93 \mu\text{s}$. The lowest point is extrapolated; it marks the $S/N_{p-p} = 2$ detection limit. Extrapolate farther down to an ordinate value of ca. 0.03 for the $S/\sigma = 3$ detection limit.

detection limit for $\alpha\text{-1,2,3,4,5,6-hexachlorocyclohexane}$, at the $S/N_{p-p} = 2$ definition, is typically about $2 \cdot 10^{-14} \text{ g}$ or $5 \cdot 10^{-18} \text{ mol/s}$ (divide these numbers by about 3 [34] to obtain the $S/\sigma = 3$ detection limit).

The detection limits, while more than adequate, are however far less important and certainly much less surprising than the perfect linearity shown by Fig. 11. The actual peaks, some of which are reproduced in Fig. 12, look strangely cropped: the recorder pen rose straight to the zero-current line where it banked off as sharply as if it had hit the end of the recorder range (which, of course, it did not).

Even at less favorable pulsing conditions, a large degree of linearity is maintained. For instance, if a delay time of $7 \mu\text{s}$ is chosen (corresponding to the *left-side* maximum of Fig. 9, but otherwise conforming to the conditions of Fig. 11), the linearity extends to about 80% of

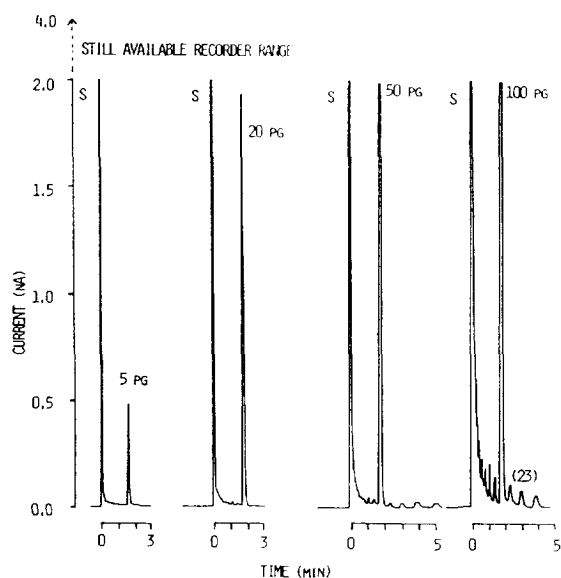


Fig. 12. Chromatograms obtained during measurement of the upper calibration range (Fig. 11) and beyond, of 5–100 pg of α -1,2,3,4,5,6-hexachlorocyclohexane as indicated, using a constant-frequency bipolar drive and showing the total consumption of the standing current in mid-recorder range. The additional peaks, which appear strongest in the right-side chromatograms, are oxidation products of the solvent (S) hexane (cf. [23]).

standing current; if a delay time of 50 μ s is chosen (corresponding to the middle of Fig. 9), the linearity still reaches about 70%.

3.10. Some further speculations

It is therefore reasonable to speculate—in view of earlier considerations dealing with the kinetic order of electron capture—that there must exist in the bipolar ECD a “storage facility” for, and hence an unexpectedly high concentration of, electrons (as always, of course, accompanied by cations). Only then can the overall second-order electron-capture reaction appear, as it does in Fig. 11, in the pseudo-first-order form of a calibration curve that is linear right up to the point where the electron current is completely exhausted. If our speculation is correct, then indeed the main role of the positive pulse is to help “store” electrons in the system.

It may be argued that this evidence of a vastly

extended linearity only appears so convincing because “linearity” traditionally refers to the *standing* (baseline) current—and standing currents vary greatly, of course, among the various (optimized) ECD modes. So, to buttress the evidence for extended linearity, we have calculated the linear ranges of three ECD modes not only as percentages of their individual standing currents, but also as percentages of the total number of electrical charges generated, i.e. of the “*maximum d.c. current*”. The results are shown in Table 1.

In Table 1, the d.c. and unipolar-pulse driven electron-capture linearities appear relatively similar when listed as fractions of the maximum d.c. current; the bipolar-pulsed electron-capture linearity, in contrast, extends over twice that range—in fact until it can no longer be physically measured. This suggests that the positive pulse does indeed allow the regime to “store” a higher than usual concentration of electrons. We speculate that it does so by inducing a temporary spatial distribution that protects some electrons from being collected and that, at the same time, protects some electrons from being neutralized by cations. Note that recombination is a second-order reaction, which is highly sensitive to (local) changes in concentration.

The numbers of Table 1 indicate also—that some “storage”-like effect occurs even in d.c. and pulsed unipolar systems. To pursue this argument further would, however, take us beyond the objectives of this study. It should also be pointed out in this context (as well as in the

Table 1
Current-related linear ranges in the tractor ECD

Polarisation mode ^a	Linearity as % of:	
	Maximum d.c. current	Baseline current
d.c.	28	34
Pulsed unipolar	34	47
Pulsed bipolar	(68) ^b	100

^a All constant voltage, constant frequency.

^b Baseline current limited.

general context of ECD characteristics and performance) that different commercial ECDs are of very different construction and that, therefore and so far, the described behavior patterns and trends *should be considered valid only for the two-chamber Tracor ^{63}Ni ECD*. Furthermore, we squeezed the analytical figures-of-merit from a squeaking clean (though two-decades old) ECD. If—for purpose of simulating ECD performance in, say, a typical pesticide residue laboratory—our detector had been given daily loads of dirty samples, it might have proved less obliging.

Whether and to what extent PR effects can be found and used in other detectors; and whether, perhaps, new detector constructions could maximize and capitalize on such PR, is at present an open question. The perfect linearity found in the Tracor ECD is, of course, very interesting—but its linear range, a full three orders of magnitude, may still be less than that of a good *constant-current* system. One particular constant-current system has, in fact, been coaxed to respond linearly over almost six (!) orders of magnitude [35]. On the other hand, most constant-current systems produce far shorter linear ranges (cf. [11]) and, in addition, are wont to cause a non-linearity problem with strong capturers (e.g. [22]). To our experience, and judging from explanations of the phenomenon advanced so far, this problem should not occur in the bipolar-pulsed, constant-frequency system of this study.

On strictly formal grounds, and over much of the calibration range, the unipolar *constant-current* system could be said to achieve linearity by rationing the supply of electrons to the capture reaction. The bipolar *constant-frequency* system, on the other hand, achieves the same purpose—or so we speculate—by supplying electrons in excess. Of course, to have available an excess of electrons also benefits response, as the clearly hypercoulometric performance and the related, quite respectable detection limit demonstrate.

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