

CHROM. 12,934

## A d.c. ELECTRON-CAPTURE DETECTOR WITH SEPARATED IONIZATION AND CAPTURE REGIONS\*

WALTER A. AUE\* and K. W. MICHAEL SIU  
*5637 Life Sciences Bldg., Dalhousie University, Halifax, N.S. (Canada)*

---

### SUMMARY

Further support for a recently proposed electron-capture detector (ECD) "space charge" mechanism was obtained from the successful operation of a d.c. ECD whose configuration effectively precluded cation/anion neutralization. This design also prevented chromatographic effluents from contacting the radioactive foil.

---

### INTRODUCTION

We have recently proposed an alternative mechanism for the response of d.c. electron-capture detectors (ECDs)<sup>1</sup>. This mechanism differentiates detector response from the electron-capture reaction proper, and suggests that the current drop during the passage of a peak is due to a space charge effect caused by migrating anions.

Furthermore, the ECD is viewed as largely unipolar, with charge recombination via cations and anions no longer a prerequisite of response. Accordingly, such an ECD should be able to function even if the neutralization of negative ions by positive ions were not permitted to occur. This, however, would clash with the classical ECD theory (a review of which is cited as ref. 2). If one wants deliberately to prevent neutralization of heavy ions, the best approach is perhaps to generate anions far away from cations and to keep the two species apart.

This paper, then, reports the construction and successful operation of an ECD in which positive and negative ions frequent separate regions. (The terms "negative ions" or "anions", for purpose of this manuscript, do not include free electrons. Electrons populate the whole detector volume.)

It must be mentioned, however, that this detector can only provide a low probability, not a complete impossibility, of anion/cation contact. Given the practical restraints of ECD design, the latter can be achieved only if cations are not present at all. This is the case in an elegant new detector construction by Sullivan<sup>3</sup>—a construction, incidentally, whose success we consider supporting evidence for our alternative ("space charge") mechanism<sup>1</sup>.

Sullivan's ECD, however, differs radically from established models, and could obviously not be used to investigate the relevance of cation/anion neutralization, in

---

\* Material taken from Ph.D. thesis work of K.W.M.S.

which we were interested. Our ECD, in contrast, is constructed well along classical lines and can be operated both in a conventional mode with overlapping cation and anion regions, and in a non-conventional mode where these regions are essentially separated.

## EXPERIMENTAL

Fig. 1 is a schematic diagram of the detector's construction. Its main body is made of borosilicate glass. The electrical connections to the adjustable electrodes are two platinum slide wires (platinum was our glassblower's choice). The 15 mCi  $^{63}\text{Ni}$  foil (New England Nuclear, Boston, MA, U.S.A.),  $0.5 \times 1.5$  in., is held inside a non-radio-active nickel cylinder used as cathode. The cylindrical anode is shaped from a plain nickel foil,  $0.5 \times 1.5$  in. The "space reducers", of borosilicate glass, serve mainly to limit the detector volume. Conventional Swagelock unions with PTFE ferrules connect gas in- and outlets with the glass detector body. The unit is kept at the chosen temperature by a heating cartridge (Watlow, St. Louis, MO, U.S.A.) sunk into the aluminum detector casing.

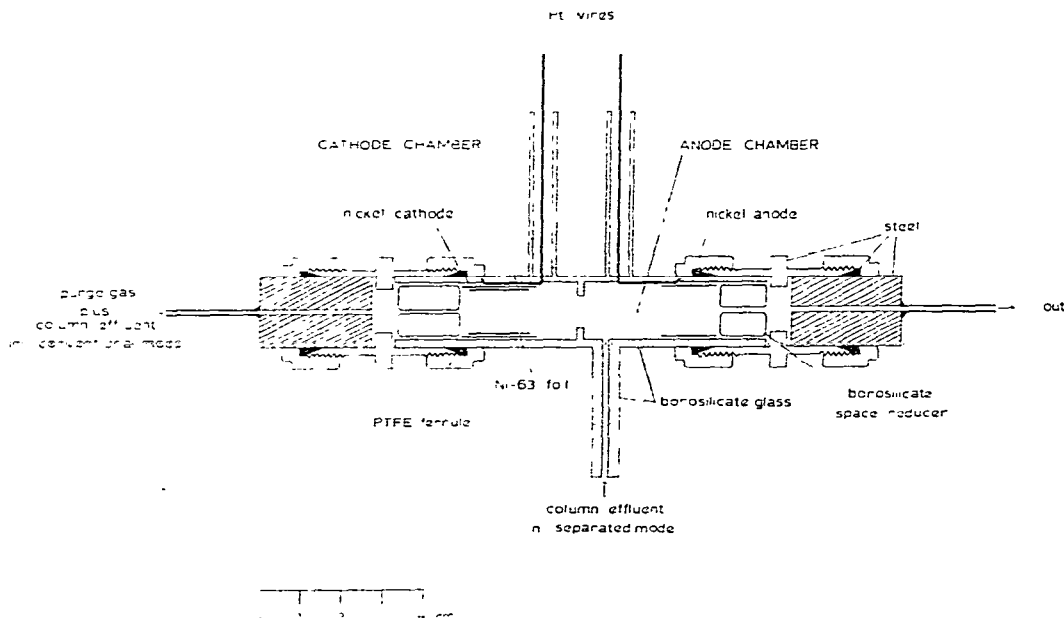


Fig. 1. Schematic diagram of the ECD.

For use as a carrier and purge gas, "high purity" grade nitrogen is doped with about 1 ppm hydrogen and further purified by passing through a cartridge containing charcoal, silica gel and molecular sieve 5A (Chemical Research Service, Addison, IL, U.S.A.). The gas chromatographic (GC) column is a  $1 \text{ m} \times 2 \text{ mm}$  I.D. borosilicate tube packed with silica gel grade 62, 60–80 mesh, modified with Surfynol 485 (Air Products, Allentown, PA, U.S.A.)<sup>4</sup>.

All runs on the ECD are carried out in d.c. mode. The cathode is polarized by

a Keithley 240A high-voltage power supply and the signal from the anode is processed by a Bendix SPED electrometer. (There is no significance to the use of these particular units; they simply happened to be at our disposal.)

## RESULTS AND DISCUSSION

### *Detector construction*

The basic geometry of the detector is far from being novel; in fact, a more or less conventional form has been deliberately used. Borosilicate glass, here chosen only for expediency, has served before in commercial ECD models. Its electrical conductivity prevents high-temperature operation, but that is not important for a mechanistic study. Furthermore, once the detector has been relegated to low-temperature operation, the use of PTFE parts becomes acceptable.

The two-chamber construction also has commercial precedents. Here it keeps anions away from the bipolar region. Construction-wise, this separation is not (can not be) complete, in terms of flow patterns and charge distributions, however, it is likely attained to a large extent.

That leaves a single, non-conventional feature: The column effluent can be routed through both cathode and anode chambers (the "conventional mode"), or through the anode chamber only (the "separated mode"). We shall discuss these two from different mechanistic viewpoints.

### *The conventional mode*

Column effluent and a regulated stream of purge gas enter the cathode chamber and exit through the anode chamber; *i.e.* in Fig. 1 the analyte molecules flow from left to right across the whole detector. What happens then, and how response is finally produced, is an open question.

That free electrons associate with electrophiles in the initial "electron capture" is still commonly accepted. However, the fate of the anion, *i.e.* a negative molecular ion or a fragment thereof like chloride, is less certain.

Since ECD response is a drop in current, it is reasonable to attribute it to a faster neutralization rate between cations and anions (as opposed to cations and electrons). As an often-quoted number from the classical theory, the former is considered  $10^5$ – $10^8$  times higher than the latter<sup>5</sup>. Estimates vary by orders of magnitude, not surprisingly so in this highly speculative matter. For instance, it has been suggested that the rate constants of the two types of reactions are comparable<sup>6</sup>. That alone would still allow one rate to be some  $10^3$  times faster than the other, considering the difference in drift speed, hence concentration at any particular time, of electrons and anions. A further complicating matter is the possibility of ambipolar diffusion, which would tend to equalize these speeds<sup>6</sup>. A measurement has shown no evidence for ambipolar diffusion<sup>7</sup>. However, considerations of this difficult matter are obviously dependent on how far one expects the bipolar plasma to extend into the detector cell. The fairly common assumption that it fills most or essentially all of it, may be incorrect for at least some circumstances<sup>1</sup>.

Be that as it may, accelerated *anion* neutralization is generally accepted as the mechanism responsible for ECD response. No other mechanism, to our knowledge, has been advanced in the literature.

The only suggestion of an alternative mechanism was made by our group in a recent study<sup>1</sup>—which was, as this paper is, experimentally restricted to d.c. operation. This “space charge” mechanism claims that response arises, at least in part, from accelerated *electron* neutralization.

How can this happen, given a fixed cation/electron neutralization rate constant? One must assume that the electrical field in the bipolar zone, hence the speed of charged particles there, decreases—which is equivalent to an increase in their concentration. Why does the field gradient decrease? Because the negative “space charge” (hence the name above) increases when fast electrons are converted into slow anions inside and especially outside the bipolar region.

For this study it is important to note that the classical mechanism requires anions to be neutralized by cations, while the “space charge” mechanism does not. When the detector shown in Fig. 1 was run in the “conventional mode” (with largely conventional results) either or both mechanisms could have been operative. In fact, the ECD was thus operated only to have an exact comparison with the much more interesting “separated mode”, in which the classical mechanism is precluded.

#### *The separated mode*

In this mode, the column effluent entered and left the anode chamber, *i.e.* in Fig. 1 it came from the bottom and flowed to the right. The cathode chamber, in contrast, was flushed with pure nitrogen only, using flows up to 300 ml/min. Hence, from the design, cations should frequent only the cathode chamber, anions only the anode chamber, and never the twain should meet. It remains to be shown that this is a reasonable proposition.

The undesirable meeting of cations and anions could occur in a variety of locations and ways: by  $\beta$ -rays reaching into the anode chamber where they would produce cations; by cations being swept by the purge gas into the anode chamber; by solute molecules diffusing or being swept by eddy currents into the cathode chamber where they would produce anions; or by diffusion and other means of transport like coulombic attraction of cations and anions across the relatively large aperture between the two chambers.

The question of  $\beta$ -ray range is perhaps the easiest to deal with. <sup>63</sup>Ni betas are generally assumed not to reach beyond 6–8 mm (ref. 2). Our own measurements suggest that the centre-of-charge of generated cation/electron pairs lies about 1 mm from the <sup>63</sup>Ni foil (in nitrogen at ambient temperature and pressure)<sup>1</sup>. A look at Fig. 1 shows that, unless these numbers are way too small,  $\beta$ -radiation should not enter the anode chamber.

Could a very fast purge gas flow sweep cations into the anode chamber? If so, then different flows should produce different voltage profiles (= plots of baseline current vs. voltage). This, however, has not been the case to any significant extent in a clean detector. Furthermore, one can compare, in a formal and very approximate manner, the flow velocity of the purge gas with the drift speed of the cations. Taking the detector as a cylinder of 7 mm radius, the average flow as 300 ml/min ambient, and the detector temperature as 115°C; the average speed is easily calculated as 4.2 cm/sec. The electric gradient in the cation region varies with the amount of anions produced, but is generally steeper there than in other parts of the detector<sup>1</sup>. Even if it were considered linear with, say, 40 V/3 cm, and if an average reduced

mobility of  $2.5 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$  (ref. 8) is assumed for the various cationic species, their drift speed computes as 36 cm/sec, almost an order of magnitude faster than the purge flow.

That leaves diffusion and eddy currents to worry about. The main danger here, in our opinion, is the possibility of analyte molecules straying into the cathode chamber and capturing electrons in the bipolar zone. Given the geometry of the detector, this possibility cannot be completely excluded. But if it transpires, slower purge flows should increase, faster ones decrease the effect. It is for this reason that the purge flow has been varied over such a wide range. As it turned out, its variation produced only small effects—exactly what had been hoped for. Furthermore, these small changes were opposite to what one would expect from a diffusion problem: high flows gave better, low flows worse performance.

We can therefore be reasonably confident that cations frequent only the cathode chamber—in fact, few should ever be found much beyond two or three mm from the radioactive foil—and that analyte molecules, hence anions, are essentially restricted to the anode chamber. If this virtual separation is indeed an acceptable premise, then the immediate question arises what constitutes response.

For every cation that is neutralized at the cathode, one electron enters the anode chamber and is collected by the anode. When analyte molecules capture these electrons, the resulting anions must also reach the anode. Any negative charge, in fact, will be collected once it has entered the anode chamber. Hence, from the classical theory, it should not matter whether or not intermediate electron attachment has taken place. Another way to derive the conclusion implicit in this case (namely that no response is expected) is to remember that the classical theory rests on (a faster) cation/anion neutralization. Since this neutralization has been prevented, no response should occur.

In our alternative mechanism, however, response should be strong. The anions, very slow in comparison with their precursor electrons, set up a sizable counterfield. In other words, the field gradient becomes steeper in the unipolar anode chamber, softer in the bipolar region of the cathode chamber (compared to baseline conditions). The anions and electrons in the anode chamber will therefore speed up, the cations and electrons in the ionization zone of the cathode chamber will slow down. If they slow down, the second order recombination rate increases and less electrons (and cations) will reach the electrodes: The system produces the current drop typical of ECDs.

### *Measurements in both modes*

The measurements, which were reproduced several times, needed a very clean system. It is easy to see why: had, for instance, the purge gas and the carrier gas been contaminated to different degrees (*e.g.* the latter by column bleed), the crucial experiment of varying the purge gas flow would have led to irrelevant observations and consequently incorrect conclusions. Leaks in, or contamination of, the detector could have proved similarly misleading.

When the system was clean—and this was fairly easy to ascertain from the voltage profiles—results as the one shown in Fig. 2 were obtained. There the conditions had been approximately optimized for each mode. The purge flow for the separated mode was kept relatively high (for demonstration purposes), while for the

conventional mode it was somewhat lower (for reasons of fairness: very high flows decrease conventional response). Both modes gave good linear range and detection limits. The separated mode, in fact, showed a slightly better sensitivity. Hence we have to conclude that the classical mechanism of cation/anion neutralization is *not a necessary condition* for observing electron capture response.

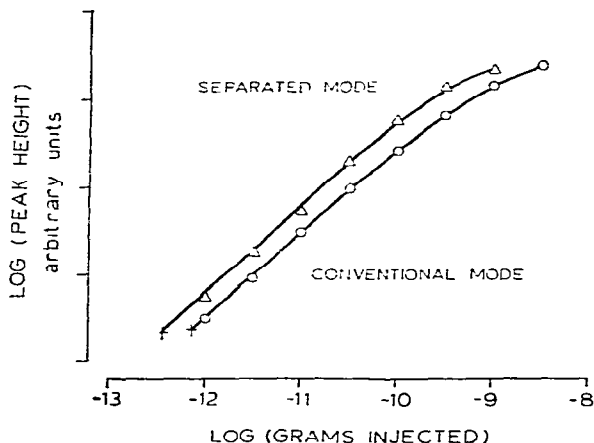


Fig. 2. Calibration plot of carbon tetrachloride. Temperatures: ECD 115°C, GC column 90°C, GC inlet 100°C. Flows in ml/min: column effluent 30, purge 170 for conventional and 270 for separated mode. Optimum d.c. voltage: 45 V for conventional, 40 V for separated mode. + = signal-to-noise ratio = 2:1.

To what extent the classical mechanism contributes to, or detracts from, common d.c.-ECD response, is at present a matter of pure speculation. How can one apportion the experimentally observed response of, for instance, the conventional mode, to the classical and the space charge mechanisms?

### *Some speculations*

It may be tempting to ascribe response in the conventional mode (in analogy to response in the separated mode, which is of similar magnitude) totally to the space charge mechanism. This would most likely be incorrect. For cation/anion neutralization must occur in the bipolar region of conventional ECDs; although the typical extent of neutralization, especially when compared to that of cation/electron recombination, is uncertain. We presume, however, that this matter is at present under world-wide investigation. (We should note here that the term "recombination" is formally not quite correct. The original cations quickly convert to cations of lower energy. Furthermore, the terminal cations of the baseline state are not to be equated with the terminal cations during passage of a peak.)

It is still interesting, however, to speculate what would happen if both classical and space charge processes were to be simultaneously operative (*i.e.* mixed mechanisms). Let us presume that the premise of a faster cation/anion reaction is valid. Then electrons captured in the bipolar zone will be neutralized, decreasing the electron current through the unipolar zone to the anode, but at the same time decreasing the

amount of electrons that can be captured there, *i.e.* the magnitude of the space charge (with its consequences on recombination in the bipolar zone). Loosely expressed (and from a rather theoretical viewpoint), one mechanism works against the other.

The fact that the separated mode showed a higher sensitivity than the conventional mode, could formally be considered an indication that opposing mechanisms were at work in the latter. However, this would overextend the data; a variety of other effects could have been responsible for the observed behaviour.

How much these mechanisms contribute remains open to question. It must be assumed, however, that their *relative* importance is strongly dependent on detector conditions. The fact that experiments have shown one analyte molecule "capturing" up to 50 electrons<sup>9</sup>—a phenomenon that is compatible with the space charge but incompatible with the classical mechanism—demonstrates that space charge effects (if this is what they are) can be very large indeed. How large depends on the detector geometry, radioactive source, and pressure, to name just a few variables<sup>1</sup>. Estimates from certain d.c.-operated detectors suggest that there the classical mechanism contributes little<sup>10</sup>. However, this is speculative and may furthermore change with changing conditions. One would assume, for instance, that pulsed operation with long, field-free intervals and a small, predominantly bipolar detector volume, should maximize contributions of the classical mechanism.

Aside from such theoretical speculations, which still await future data to confirm or deny them, a practical speculation may also be entertained. Deteriorating ECD response is often due to a dirty detector; and dirty electrodes are likely contributors to poor detector performance. As the separated mode has shown, it is possible to keep the radioactive foil in a chamber filled with pure carrier gas! In fact, one could imagine a detector with both electrodes purged by pure gas, wherein the only solute or bleed species reaching the electrodes would be charged ones (*i.e.* a minute fraction of those that can normally contact the electrodes). Such a detector, one would assume, should give satisfactory performance for longer periods of heavy use or abuse.

It is obvious, however, that such a detector would have to be constructed for high-temperature operation: first, to serve adequately in routine analysis; and second, to repeat some of the measurements and confirm the predictions made herein, under a different set of conditions.

#### ACKNOWLEDGEMENTS

This research was supported by NSERC grant A-9604, and a Killam Scholarship for one of us (K.W.M.S.). We appreciate the competent help of our master glass-blower Jürgen Müller, and the donation of Surfynol 485 by Noshir F. Chinoy of Air Products.

#### REFERENCES

- 1 W. A. Aue and S. Kapila, *J. Chromatogr.*, 188 (1980) 1.
- 2 E. D. Pellizzari, *J. Chromatogr.*, 98 (1974) 323.
- 3 J. J. Sullivan, *Hewlett-Packard Technical Paper No. 82; 30th Pittsburgh Conference, Cleveland, Ohio, March 1979, Paper No. 256.*

- 4 W. A. Aue and P. P. Wickramanayake, unpublished results.
- 5 J. E. Lovelock, *Anal. Chem.*, 33 (1961) 162.
- 6 M. W. Siegel and M. C. McKeown, *J. Chromatogr.*, 122 (1976) 397.
- 7 J. E. Lovelock and A. J. Watson, *J. Chromatogr.*, 158 (1978) 123.
- 8 F. W. Karasek, *Anal. Chem.*, 45 (1974) 710A.
- 9 S. Kapila and W. A. Aue, *J. Chromatogr.*, 118 (1976) 233.
- 10 S. Kapila, C. R. Vogt and W. A. Aue, *J. Chromatogr.*, 195 (1980) 17.