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EFFECTS OF DIMENSION AND DENSITY IN ELECTRON CAPTURE DETECTORS*

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SUMMARY

The response of different electron capture detectors with ^{63}Ni and ^{3}H sources has been measured in relation to interelectrode distance and cell pressure. Results for d.c. operation are in agreement with the suggested dependence of response on the difference between reversed-field and regular-field voltage profiles[1].

INTRODUCTION

In a recent study[1] we suggested an alternative mechanism for d.c. electron capture detector (ECD) response. In contrast to the classical view (for a review of it, see ref. 2) of accelerated neutralization, the proposed *modus operandi* was the impedance offered by migrating (heavy) negative ions. Since their mobilities are comparable to those of typical positive ions, we suggested that the ECD voltage profile ("voltage profile" is a common term for the current *vs.* potential plot of a detector in the absence of peaks) under reversed-field conditions should correlate with the magnitude of response. More precisely, the difference between the voltage needed to collect $I\%$ of the maximum current under reversed-field condition, V_I^+, and the voltage needed to do the same under regular-field conditions, V_I^-, should be roughly proportional to the d.c. response of this detector to a standard amount of analyte, R,

$$(V^+ - V^-)_I \propto R.$$

This should hold true for various settings of density (cell pressure) or dimension (interelectrode spacing), provided experiments are done within linear range and other conditions remain the same within a test series. Ideally, it would be the same as that

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used for analysis (in most well-functioning detectors around 90%). To measure V^+ values at $I = 90\%$, however, is experimentally difficult under certain conditions such as high cell pressure. Ergo the values of $I\%$ had to be chosen within the accessible range for each set of experiments. It is reasonable to expect that an approximate proportionality as indicated by the equation above should still prevail. Voltage profiles are subject to many conditions, primarily the choice of carrier gas, the nature of the radioisotope, the interelectrode distance, the cell pressure, and, generally, the cleanliness of the detector. For this study, nitrogen served as carrier gas and ^{63}Ni and ^{3}H foils in cylindrical and planar form as radioactive sources. These were used in cells that could be pressurized and whose electrode position could be altered.

Direct current was the predominant detection mode; however, pulsed (constant-frequency) operation was run alongside d.c. for reasons of general interest. In our opinion it would not be appropriate to compare (such as: Which has the greater response?) the d.c. and pulsed modes even where they are shown in the same graph. The reason for this cautionary attitude is simply that optimization of d.c. response is easy and involves one parameter: voltage; while the same for pulsed operation is difficult and involves three parameters: width, interval and amplitude of the pulses. Only the first two were optimized while full pulse height, 60 V, had to be used throughout. Up to certain interelectrode distances (*ca.* 4 mm for ^{3}H and *ca.* 10 mm for ^{63}Ni under our conditions), optimization was possible. Beyond that, "reasonable" pulse conditions had to be chosen, since conditions as close to d.c. as the pulser would permit were clearly better than any other pulse conditions that the equipment (Tracor electron capture pulse power supply) could generate.

EXPERIMENTAL

Fig. 1 shows in schematic form the ECD configurations A, B and C used in this study. "Regular-field" refers to the radioactive foil being the cathode; "reversed-

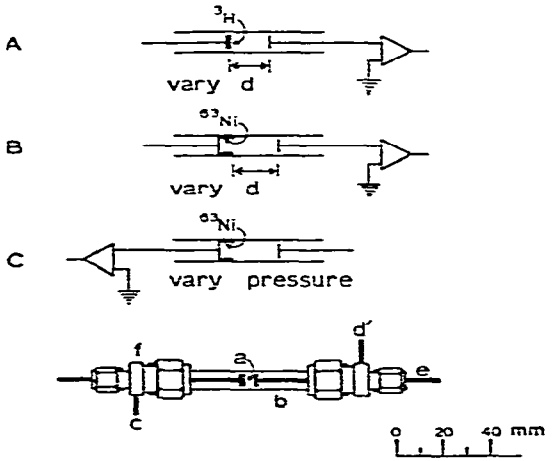

Fig. 1. Schematic of ECD configurations and detector construction: a = electrode with radioactive foil; b = quartz tube; c, d' = inlet and outlet for carrier gas; f = modified Swagelok; e = adjustable electrode.

field" to it being the anode (regardless of which is the "polarizing" and which is the "collecting" electrode).

At the bottom of Fig. 1 is shown a typical ECD drawn to scale. It is made from a 9 mm O.D. quartz tube with modified stainless-steel Swagelok fittings. The electrodes enter through Vespel (polymide) reducing ferrules. The carrier gas, nitrogen, enters and leaves through 1/16 in. stainless-steel tubing silver-soldered to the suitably drilled 3/8–1/4 in. Swagelok reducing unions. The tritium foil is carried flat on one of the parallel plate electrodes; the ^{63}Ni foil is a cylinder in contact with the electrode.

The ECD is kept at the proper temperature by an enclosing aluminum block with cartridge heaters. Other details conform to conventional ECD practice. The standard test compound is a popular fungicide, 2,3,5,6-tetrachloronitrobenzene, (TCNB), usually at the 100 pg level.

RESULTS AND DISCUSSION

The aim of this study was to prove or disprove our earlier prediction[1] that ECD response should correlate with the difference between the reversed-field and the regular-field impedances, defined as the difference in voltage necessary to produce the same current (of some experimentally convenient magnitude) in either field direction.

There are, in essence, only two experimental parameters that can be conveniently varied to influence response. According to our alternative mechanism for d.c. ECDs[1], one needs to maximize the counterfield created by migrating negative ions in order to maximize peak size (response). This can be done by having the center-of-ionization situated as close as possible to the cathode and as far away as possible from the anode. Hence one can either move the anode further away from the radioactive foil, or increase the pressure in the detetor cell.

Obviously, one could also use different β emitters with varied β range, however, only the two conventional ones, ^{3}H and ^{63}Ni, were available to us during the experiments. We used both in order to demonstrate that the predicted effect could be found with either type of foil.

Tritium, because of its shorter β range, was used only for experiments in which the interelectrode distance was varied (configuration A in Fig. 1). Typical response and voltage profiles from these are shown in Fig. 2. As expected, and as is well known, response increases as the electrode distance increases.

Fig. 3 shows that this increase in response does correlate with the difference between the reversed- and regular-field voltage profiles (here measured at 25% of maximum current).

It must be noted, however, for this as well as for the following experiments, that the fact of finding the predicted correlation does not necessarily establish beyond doubt the proposed alternative d.c. ECD mechanism. (One could, for instance, argue that the increased response may be due to an increased number of electrons being captured in the larger active cell volume.)

Variations both in interelectrode distance and in cell pressure were used in conjunction with the ^{63}Ni foil. The general trends, not surprisingly, were similar to those measured with the ^{3}H foil.

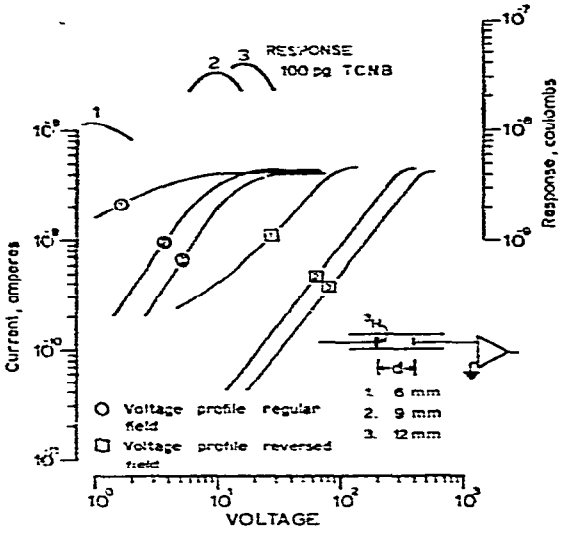

Fig. 2. Variation of interelectrode distance. Response profiles (charge *vs.* potential curves, top maxima) in coulombs for peak areas of 100 pg tetrachloronitrobenzene; and voltage profiles (current *vs.* potential curves in lower part) in amperes baseline current. Numbers refer to interelectrode distances as indicated. Configuration A (Fig. 1) with scandium tritide as radioactive source.

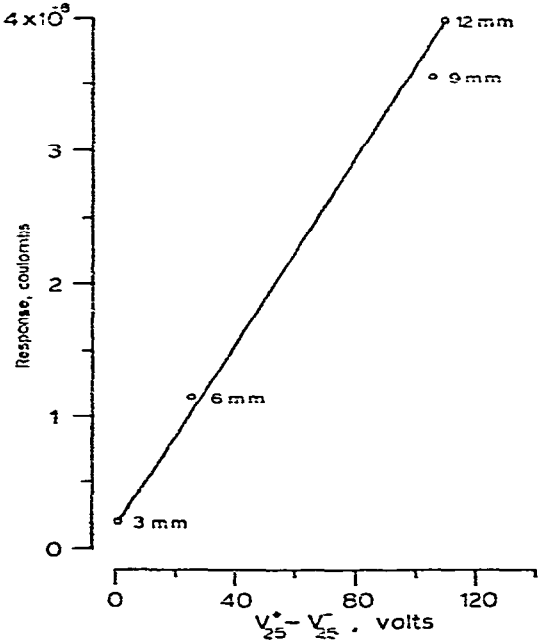

Fig. 3. Correlation plot. Variation of response in coulombs peak area *vs.* difference between voltage profiles (in reversed- and regular-field direction) measured at 25% of maximum current. Configuration A; data correspond to Fig. 2.

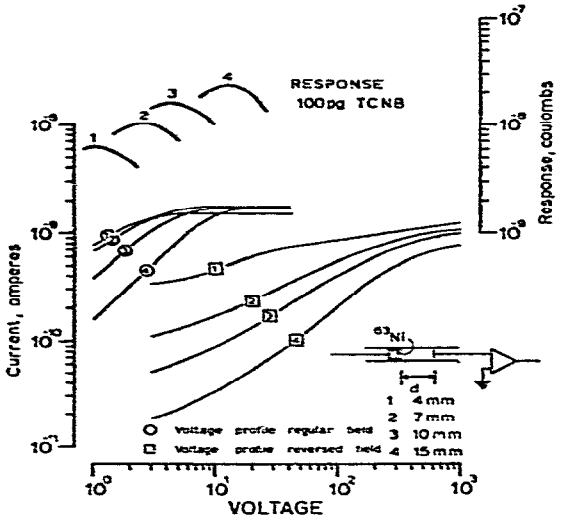

Fig. 4. Variation of interelectrode distance. Similar to Fig. 2, but configuration B with ^{63}Ni cylinder as radioactive source.

Fig. 4 shows a series of response and voltage profiles for different interelectrode distances; Fig. 5 shows the correlation between response (that is, the maximum response at each given distance) and reversed- and regular-field voltage.

Changing pressure produces another set of curves, shown in Fig. 6. The increases in response and maximum current with pressure have been reported earlier[3]. Fig. 7 depicts these increases. It also lists, in percent, portion of total available current at each setting where best response was obtained. Here as in other experi-

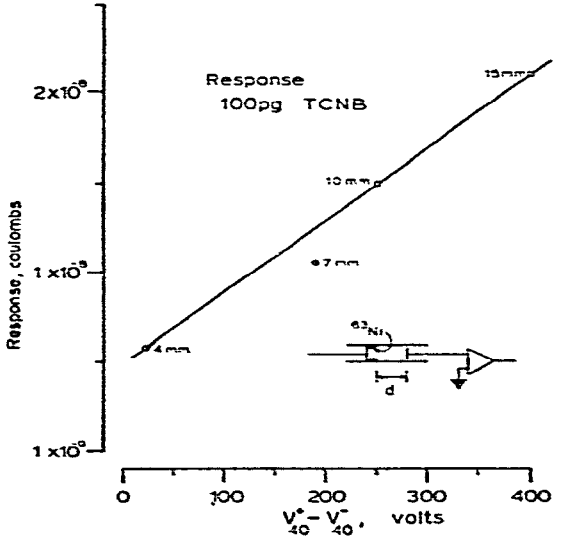

Fig. 5. Correlation plot. Data from Fig. 4. Values in mm refer to interelectrode distance d. Similar to Fig. 3, but ^{63}Ni is used and voltage difference is measured at 40% of maximum current.

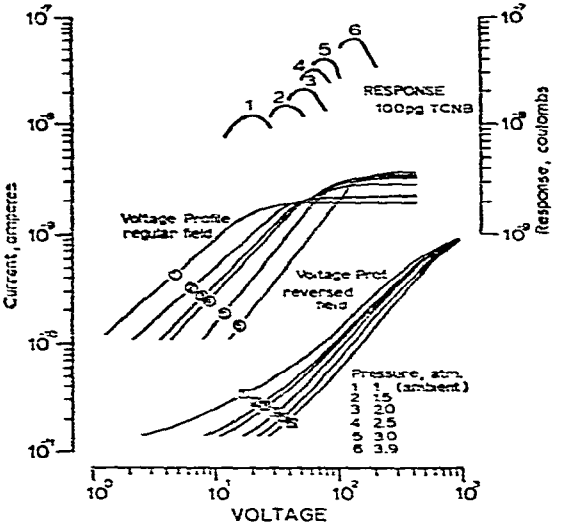

Fig. 6. Variation of cell pressure. Response profiles (upper part) in coulombs peak area and voltage profiles (lower part) in amperes baseline current. Numbers refer to pressure settings as indicated. Configuration C, ^{63}Ni cylinder, interelectrode spacing 15 mm.

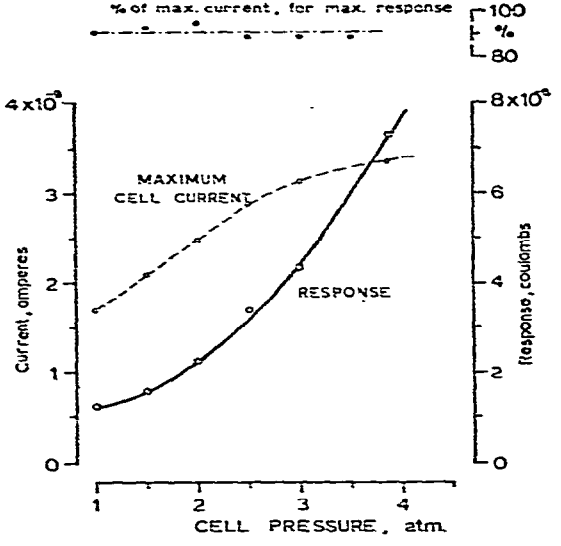

Fig. 7. Pressure effects on maximum cell current (in amperes), % of maximum cell current necessary for maximum response, and maximum response (in coulombs). Data from Fig. 6.

ments, "response" means "maximum response"; *i.e.* the value measured at the top of the response profile (peak area *vs.* voltage curve). Even though the maximum cell current increases considerably with pressure, the "percent of maximum current required for maximum response" stays practically the same. As in most well-functioning ECDs this value lies around 90%. (Lower values can be found at short electrode distances.)

Fig. 8 again shows the predicted correlation between response and voltage difference. (It was unfortunately necessary to measure the difference in voltage profiles at 5% of maximum current in order to cover the whole range.)

Thus, both variation of electrode gap and of pressure appear to confirm the predicted correlation. At this point, a short speculation involving the relevant plots (Figs. 3, 5 and 8) is in order.

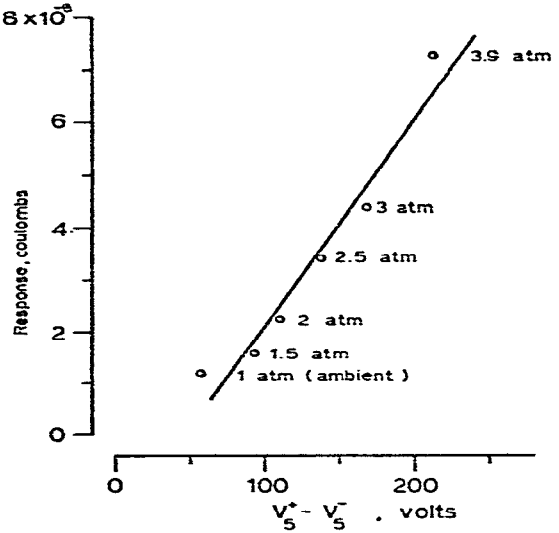

Fig. 8. Correlation plot. Data from Fig. 6.

If response were based on the classical mechanism (accelerated neutralization of heavy anions compared to electrons) then *some* response should always be present, regardless of electrode spacing or pressure. If, on the other hand, the alternative mechanism proposed by us is the *only one* operative, then situations where $V^+ - V^- = 0$ (*i.e.* the ECD impedance is the same for either field direction) should result in hardly any response at all.

Thus it is interesting to extrapolate the curves of Figs. 3, 5 and 8 to the point where $V^+ - V^- = 0$. Response at this point should indicate whether or not (and if yes to what extent) the classical mechanism is operative. A rough overall estimate on that basis would lead to the surprising conclusion that the classical mechanism contributes at best a rather small amount to the typical d.c. ECD response.

However, the data from the low response region are neither precise or numerous enough to allow anything but outright speculation on this point.

To the same point, it is interesting to measure response not just under d.c. but also under pulse conditions. Pulse conditions with their long, field-free intervals have been considered in the literature as being much closer to portraying the "true" electron capture reaction than the d.c. mode.

Unfortunately, there are technical and conceptual difficulties involved in this endeavor, as shortly alluded to in our preceding paper[1] and reiterated in the introduction to this one. At electrode distance beyond *ca.* 4 mm for ^{3}H and *ca.* 10 mm for ^{63}Ni, no optimum in pulse conditions could be found (other than

operating as close to d.c. as the pulse power supply would allow) and arbitrary pulse conditions had to be substituted. Even with this fact in mind, however, it is interesting to consider a comparison of d.c. and pulse mode response as it depends on interelectrode distance. Such a comparison is shown in Figs. 9 and 10 for ^{3}H and ^{63}Ni, respectively.

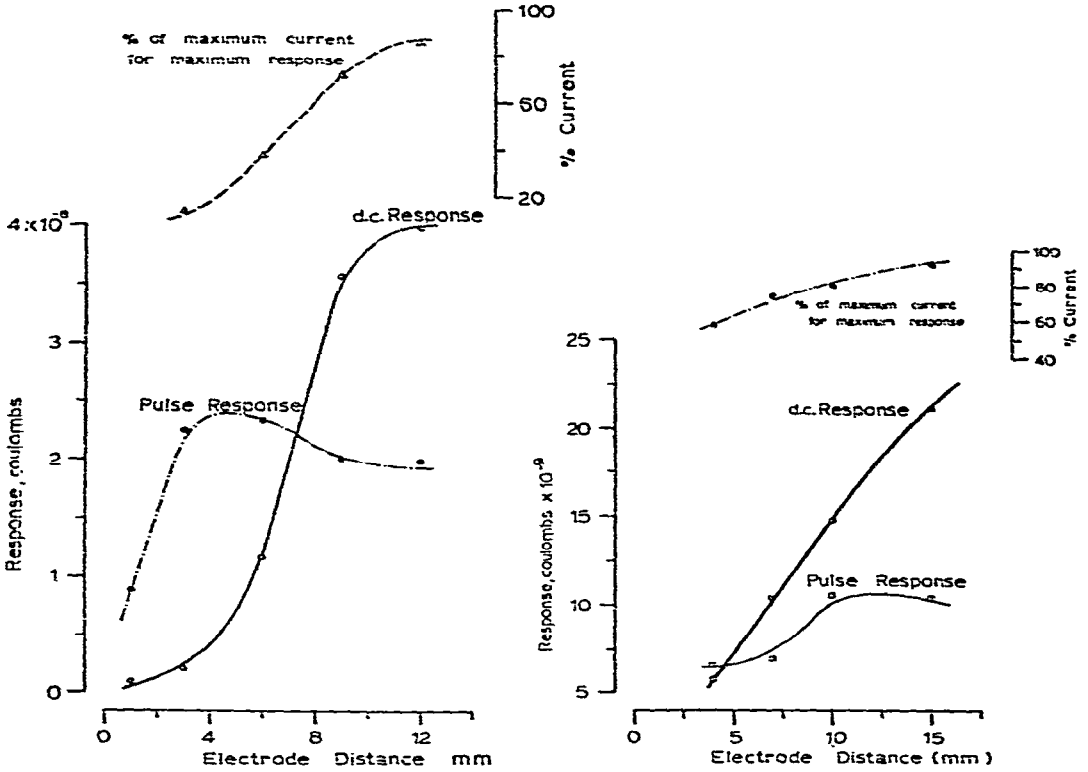

Fig. 9. Variation of response with interelectrode distance for d.c. and pulse conditions (see text for explanation). Percent current graph on top refers to d.c. mode. Configuration A, scandium tritide, ambient pressure.

Fig. 10. Similar to Fig. 9, but configuration B, ^{63}Ni.

Pulse response levels off at greater distances when it can no longer be optimized, but at shorter distances it follows, very approximately, the same trend as the d.c. response. This could conceivably indicate that pulse response, too, is subject to space charge effects.

Before such conclusions are drawn, however, one would need to establish that the electron capture reaction proper is not similarly affected by the changes in detector geometry. A study with this aim is now under way.

REFERENCES

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2 E. D. Pellizzari, *J. Chromatogr.*, 98 (1974) 323.
3 S. Kapila and W. A. Aue, *J. Chromatogr.*, 118 (1976) 233.