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Note

A Variac-driven electron-capture detector

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Electron-capture detectors are supposed to function by measuring free electrons. As a consequence, electron-capture detector designs always employ *unidirectional* electrical fields. This is true for all polarizing modes such as constant-voltage direct current (d.c.)¹, constant-current d.c.^{2,3}, constant-frequency pulse⁴, and constant-current pulse⁵ operation. Invariably, the radioactive foil is at a (constant or intermittent) negative potential and the signal-carrying current is taken off the anode.

The objective (and, indeed, the necessity) of collecting only electrons is repeatedly emphasized in the literature (for reviews, see refs. 6 and 7). That emphasis may account for the fact that there is no *bidirectional* [alternating current (a.c.)-powered] detector on the market. Yet such a device might have some unexpected advantages, say in the reduction of contact potentials, and for that reason alone it would be interesting to assemble a working model.

Given the literature emphasis on the exclusive collection of electrons, one may indeed ask whether the concept of an alternating polarization source for the electron-capture detector is even theoretically sound. The following paragraphs examine that question.

The classical kinetic theory of electron-capture detection^{6,7} describes the detector cell as a "stirred reactor"⁸ with essentially homogenous charge distribution. Taking the historically first and experimentally simplest constant-voltage d.c. mode¹ as an example, the entry of electron-capturing analytes produces a drop in current. This detector response is attributed by the theory to a much larger neutralization rate of cations and (heavy) anions as opposed to cations and electrons.

Since the analyte thus simply reduces the number of charged particles in a homogenous plasma, the conductivity of this assumedly isotropic medium should drop *whether monitored by d.c. or a.c. means*. In other words, proper response should be obtainable in either mode. There is, however, a technical problem to be considered. Conventional electron-capture detectors rely on d.c. electrometers for current amplification and these devices are, of course, opaque to a.c. Since typical currents are in the nanoampere range with signals being one to two decades lower, they would need to be amplified and rectified for display as conventional chromatograms. That need is, to say the least, technically cumbersome.

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A few years ago, our group developed a new scenario for explaining the response mechanism of electron-capture detectors⁹. The explanation is complex and need not be repeated here. For the purposes of this paper it suffices to mention that our alternative "space-charge" hypothesis regards the electron-capture detector in essence as a device with pronounced positive and negative space charge regions, whose impedance changes with the concentration of analyte. Due mainly to the restricted, exponential ion pair distribution generated by conventional β radiation sources¹⁰, the impedance change of efficient detectors is large when the radioactive foil is the cathode, small when it is the anode.

If so, an electron-capture detector should be able to function as a convenient a.c. rectifier in the nA-pA range. Thus one could use two detectors in series, the first serving as detector, the second as rectifier. It would be much simpler, however, to let the electron-capture detector serve as its own rectifier. In other words, a suitably dimensioned detector powered by a.c. and connected to a d.c. electrometer should be able to produce typical detector response, in spite of the fact that the d.c. electrometer does not transmit an a.c. signal.

This prediction proved easy to check by experiment. When an electron-capture detector was driven by a function generator with a $10\text{--}10^5$ Hz sinusoidal wave of alternating polarity, the detector output did indeed contain a usable d.c. component. The dependence of this component on frequency was complex but interesting in its own right, and will therefore be the subject of a separate report.

For the objective of this study, however, the simplest, most accessible a.c. source would obviously be the best choice for a demonstration experiment. If one just wants to polarize an electron-capture detector with an a.c. input and decide whether or not that produces reasonable analytical performance, the most accessible a.c. source is undoubtedly the wall receptacle, *i.e.* regular household current. The simplest means of adjusting it is the Variac. ("Variac" is the term commonly assigned to this ubiquitous laboratory item. Its rarely used generic name is "variable auto-transformer".)

A Variac was thus chosen to drive an electron-capture detector, with results to be compared to those from conventional constant-voltage d.c. and constant-frequency pulse polarization sources.

EXPERIMENTAL

The laboratory-made electron-capture detector had a large, dual-chamber design^{11,12}. Its ^{63}Ni radioactive foil was connected to the alternating outlet of a Variac (Powerstat type 116B, The Superior Electric Co., Bristol, CT, U.S.A.), whose other outlet was grounded. This simple arrangement sufficed for low-sensitivity measurements. For high sensitivity, the Variac was fed by an isolation transformer to smooth out the unusually high electric noise endemic to our laboratory. The other electrode of the detector was connected to the electron-capture detector electrometer supplied with the Tracor Model 550 gas chromatograph.

The detector was run in "separated" configuration¹¹⁻¹³ at 280°C with 60 ml/min purge gas. ("Separated configuration" means that the column effluent enters the anode chamber only, while the cathode chamber with the radioactive foil is flushed by pure purge gas.) The column, operated at 180°C and 20 ml/min carrier

flow-rate was a 1 m \times 2 mm I.D. borosilicate tube packed with 3% OV-101 on Carbowax 20M-modified Chromosorb W, 45-60 mesh. "High-purity" grade nitrogen, doped with *ca.* 1 ppm hydrogen, served as both carrier and purge gas. It was further purified by passing through a cartridge containing charcoal, silica gel and molecular sieve 5A, followed by a heated oxygen scavenger.

RESULTS AND DISCUSSIONS

Fig. 1 shows chromatograms of 3 μ g of lindane (γ -hexachlorocyclohexane) obtained with different means of polarization, each under its own optimum condition. All four modes provide a similar signal-to-noise ratio, hence detection limit, and a similar linear range. As it turns out, the Variac is just as efficient a polarization source as the two conventional ones. There is some theoretical interest in the fact that an electron-capture detector *can* be operated with alternating electric fields (in the absence of a separate rectifier). There is also some incentive now to explore any possible advantage a.c. polarization might have, by testing various designs of detectors and using them for various types of analysis.

It should be noted, however, that the rectifying properties of an electron-capture detector depend on its construction and condition: for instance, on the interelectrode distance in relation to the ionization range of the radioactive foil, and on the purity of the carrier gas. It would come as no surprise if different detector models, particularly those with very different geometry, were to differ in a.c. performance.

The Variac-driven electron-capture detector of this study could be described in systematic terms as a constant-frequency, constant-voltage (or more properly, sinusoidally alternating voltage with constant peak amplitude), variable-current de-

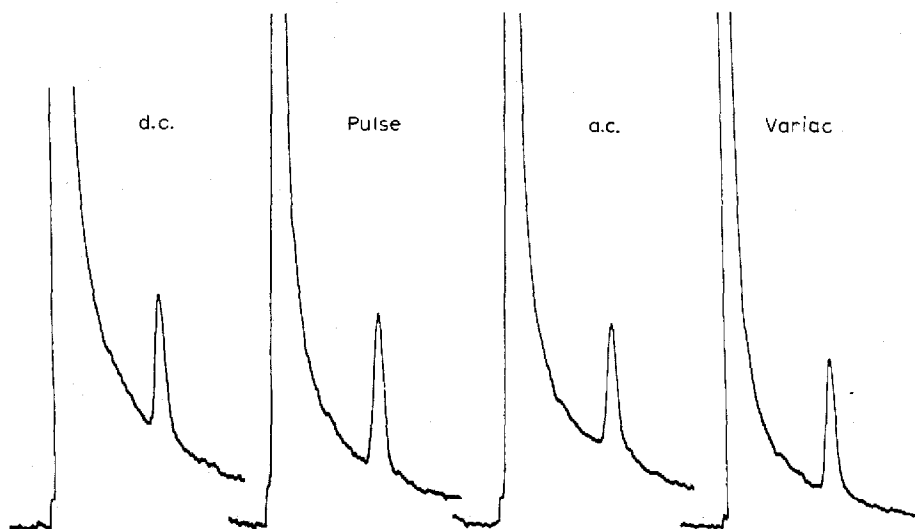


Fig. 1. Chromatograms of 3 μ g of lindane obtained with different polarization sources on the same electron-capture detector. Conditions: "d.c.", -12 V; "Pulse", height -12 V, width 7 μ sec, period 360 μ sec; "a.c.", amplitude 20 V (40 V peak to peak), frequency 10 kHz; "Variac", amplitude 7 V (14 V peak to peak), frequency 60 Hz.

vice. With somewhat more complex instrumentation, any two of the three parameters (frequency, voltage and current) could be kept constant and the third, variable, one could be monitored. For instance, constant-current systems could be devised that would either keep the voltage constant and let the frequency change in response to the passage of an analyte (the a.c. equivalent of ref. 5), or would keep the frequency constant and monitor the voltage (*cf.* refs. 2 and 3).

Constant-current operation is known to have brought about a significant improvement in linear range in any mode in which it has been tried. Whether constant-current operation (with either voltage or frequency as a variable) would also increase the linearity of an a.c.-driven electron-capture detector, and what other advantages or disadvantages would accrue to such a system, is an interesting question to ponder. However, to answer that question by experiment requires a primarily electronic effort that is beyond our present intentions.

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