

## Detector Cell for Measuring Picogram Quantities of Organophosphorus Insecticides, Pyrethrin Synergists, and Other Compounds by Gas Chromatography

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A detector cell was developed which shows unusual sensitivity to organophosphorus insecticides, pyrethrin synergists such as piperonyl

butoxide and MGK-264, and other compounds which are not easily detected by the electron-capture cells used in gas chromatography.

In our investigations of residues in foods, feeds, and water, special problems arose regarding the detection and measurement of very small quantities of organic phosphate insecticides and pyrethrin synergists. Gas chromatography with electron-capture detection lacked the desired sensitivity to some organophosphates and was insensitive to the pyrethrin synergists. Experiments were initiated to develop a detector capable of responding in a linear manner to less than 1 ng. of chemical.

Lovelock and Lipsky (5) first developed and recognized the infinite advantage of electron-capture detection in microanalysis by gas chromatography. Lovelock (4) described mechanisms of several detectors as well as an improved design for electron capture. The usefulness of gas chromatography with electron-capture detection has been demonstrated by Goodwin, Goulden, and Reynolds (3) and Watts and Klein (6) in the determination of residues of chlorinated hydrocarbons in foods. Egan, Hammond, and Thomson (7) used the detector for measuring 1- to 50-ng. quantities of organophosphorus pesticide residues. They pointed out some of the critical conditions associated with the use of gas chromatography for the analysis of organophosphorus insecticides.

The basic concept of the experimental detector herein described was quickly discovered, but the necessary improvements required several months of experimentation. The detector was designed to fit into a Parr bomb, which was 42 mm. long and 27 mm. in diameter (inside). Appropriate gastight connections were welded to the Parr bomb (Figure 1). The detector's parts are shown in Figures 2 and 3, as well as schematic diagrams of the electrical circuits. Electrodes of various shapes and dimensions were tested. Those shown in Figure 1 were found satisfactory, although a simple pair of pins 3 mm. long spaced 1 mm. apart have proved to be very good.

An innovation incorporated into the experimental cell was the use of a removable electrode rod which made it easy to select the most sensitive position for detection and to convert the experimental detector into a pin cup electron-capture detector by substituting a single electrode for the paired No. 28 Chromel electrodes. The 100-mc. tritium foil (Figures 2 and 3) was contained within a stainless steel jacket 13.0 mm. long and 12.8 mm. in diameter.

### Experimental Method

The same tritium source, structural cell parts, and gas chromatographic equipment were employed in all comparative tests involving the experimental detectors. Only the electrodes and the electrical circuits were changed. Stainless steel columns  $\frac{1}{8}$  inch in diameter were used for the various pesticides in this experiment. The packing material in the column consisted of 100- to 120-mesh Chromosorb W DMCS A/W containing 1.0% Epon 1001 and 0.5% QF-1. Another packing material, which performed equally well, used the same Chromosorb coated with 1.5% QF-1 and 0.5% Dow Corning 200 fluid. In current measurements applied voltages were varied between 0 and 270 volts across the paired electrodes and through the cell in the new detection circuits, as well as in the experimental electron-capture circuit. The current from the cell was amplified by a Keithley 600-A, electrometer coupled to a Sargent 1-mv. recorder by a 1000 to 1 voltage divider. Column temperatures ranged between 155° and 180° C. and nitrogen gas flow between 40 and 45 ml. per minute. The injection port temperature was maintained at a level about 20° C. higher than the column temperature. Voltage-response tests were made with the various pesticides to obtain the best operating voltages for the experimental detectors. For comparison several compounds were used to evaluate the sensitivity of the experimental detector, the experimental electron-capture pin cup detector, and a commercial gas chromatograph (Aerograph 204).

### Results

Current measurements were made with the electrometer to determine the electrical perimeters of the cell, as shown in Figure 4. There is a strong similarity between the standing current curve of the experimental electron-capture cell and the current curve through the new experimental detector cell. In addition to the standing current through the new detector cell there is a standing current between its electrodes. Figure 5, constructed to show the relationship between the volts supplied to the cell and to the paired electrodes, illustrates the operational voltages of the experimental detector when used for the detection of chlorinated hydrocarbons—e.g., 60 volts are applied to the paired electrodes and 10 volts are used to balance the current through the cell as indicated by the meter on the electrometer.

In operation, a decrease in the current through the

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**Chemicals Used in Comparing Detector Cells**

Piperonyl butoxide	$\alpha$ -[2-(2-Butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene
MGK-264	<i>N</i> -(2-Ethylhexyl)-bicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide
Ciodrin	$\alpha$ -Methylbenzyl 3-(dimethoxyphosphinyloxy)- <i>cis</i> -crotonate
Bidrin	$\alpha$ -Methylbenzyl 3-(dimethoxyphosphinyloxy)- <i>N,N</i> -dimethyl- <i>cis</i> -crotonamide
Azodrin	3-Hydroxy- <i>N</i> -methylcrotonamide dimethyl phosphate
Diazinon	<i>O,O</i> -Diethyl <i>O</i> -3-(2-propyl-6-methyl-4-pyrimidinyl)thiophosphate
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane
Malathion	<i>O,O</i> -Dimethyl dithiophosphate of diethyl mercaptosuccinate
Dieldrin	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4- <i>endo-exo</i> -5,8-dimethanonaphthalene
Carbaryl	1-Naphthyl <i>N</i> -methylcarbamate

paired electrodes results in a decrease in the current flowing through the cell. This response may account for some of the increase in sensitivity exhibited by the detector. The actual mechanism of operation is not well understood, but the author presumed that the nitrogen gas on entering the cell becomes ionized by the beta emission of the tritium and that the potential between the paired electrodes accelerates the electrons, which significantly increases the ionization. In some respects this resembles the electron-capture detector of the Beckman GC-4, where the initial gas ionization is produced by electrical discharge and further ionization by electron collision with other particles is accomplished by a potential difference between two elements within the cell. Details of the Beckman detector are de-

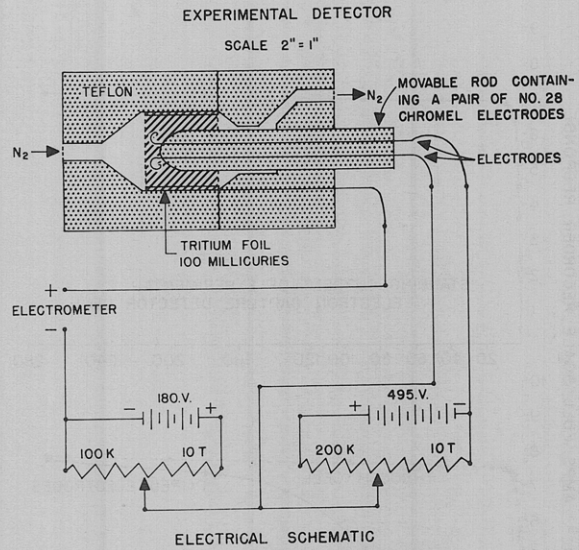


Figure 2. Cross-section diagram of experimental detector cell with schematic of electrical circuit

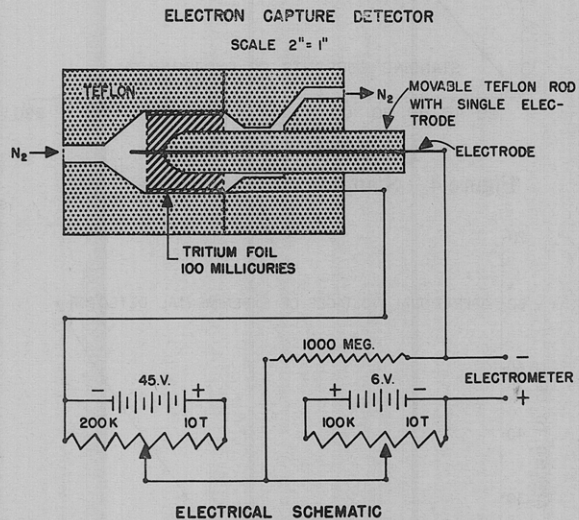


Figure 3. Cross-section diagram of electron-capture cell with schematic of electrical circuit

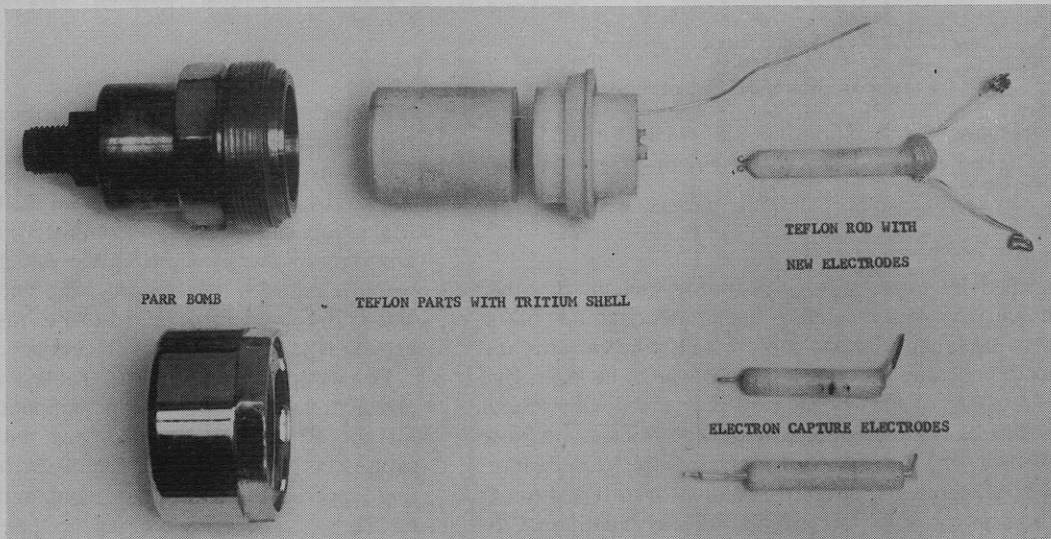


Figure 1. Separated detector cell parts

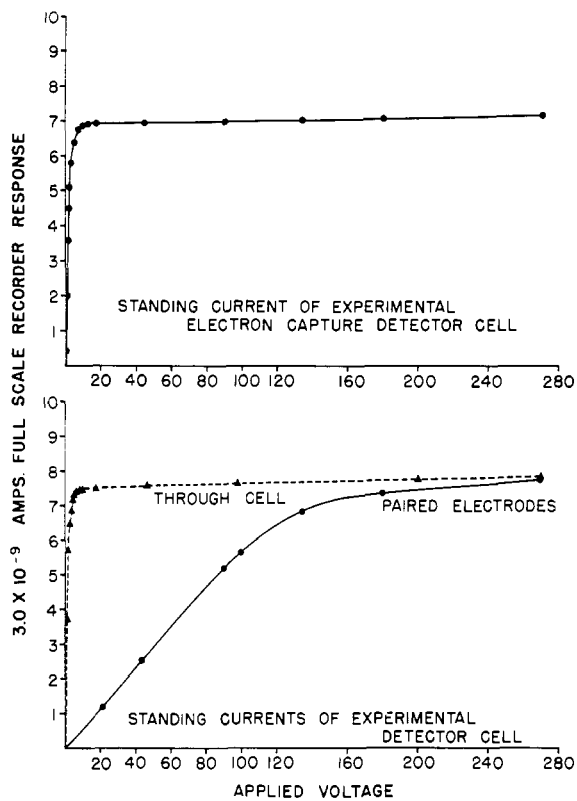


Figure 4. Standing current measurements

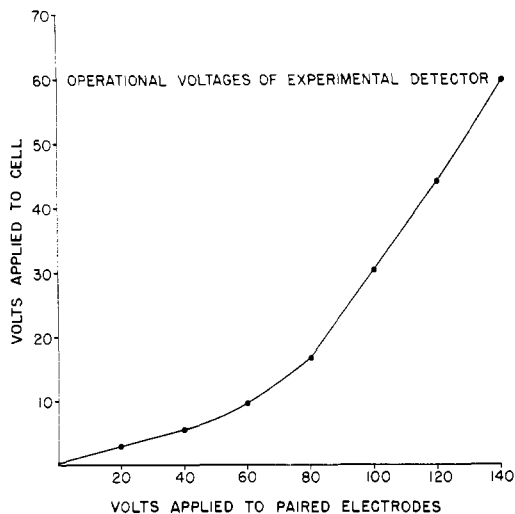


Figure 5. Relationship of volts applied to paired electrodes and to cell circuit  
 $3 \times 10^{-11}$  ampere flowing through electrometer

scribed by Foster (2). Apparently, helium or other noble gases must be used for the proper operation of the new Beckman electron-capture cell, whereas this detector operates efficiently in a stream of nitrogen gas.

A study of the voltage-response curves with several pesticides is shown in Figure 6. The voltages are those through the paired electrodes, and the recorded response represents the decrease of flow of current through the detector cell. Compounds such as malathion, Cio-

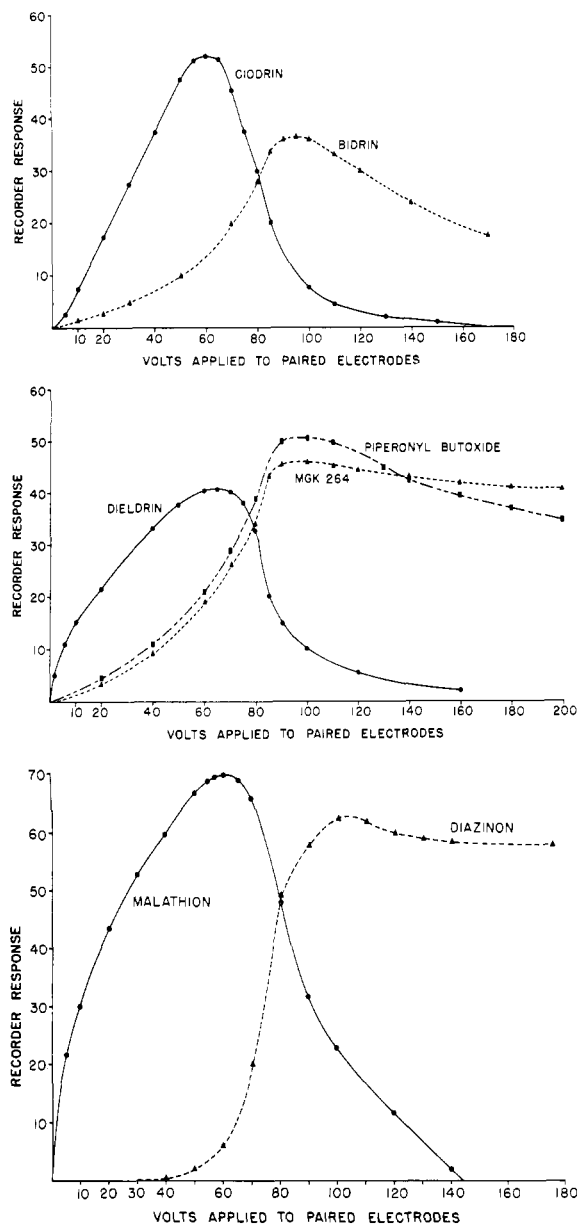


Figure 6. Voltage-response curves for MGK-264, piperonyl butoxide, dieldrin, malathion, Diazinon, Ciodrin, and Bidrin

drin, and the chlorinated hydrocarbons show greatest response at approximately 60 volts, whereas Azodrin, Diazinon, Bidrin, piperonyl butoxide, carbaryl, and MGK-264 are more easily detected at 100 to 150 volts. Malathion can be almost completely separated from Diazinon by merely changing the voltage applied to the paired electrodes. In Figure 7 are chromatograms of MGK-264 and piperonyl butoxide, measured by the experimental cell and electron-capture detector.

For comparative purposes, Table I reports the approximate minimal detectable amounts of pesticides for the Aerograph 204 equipped with an electron-capture detector, the experimental electron capture, and the experimental detector containing the paired electrodes. The voltage applied to the electron-capture

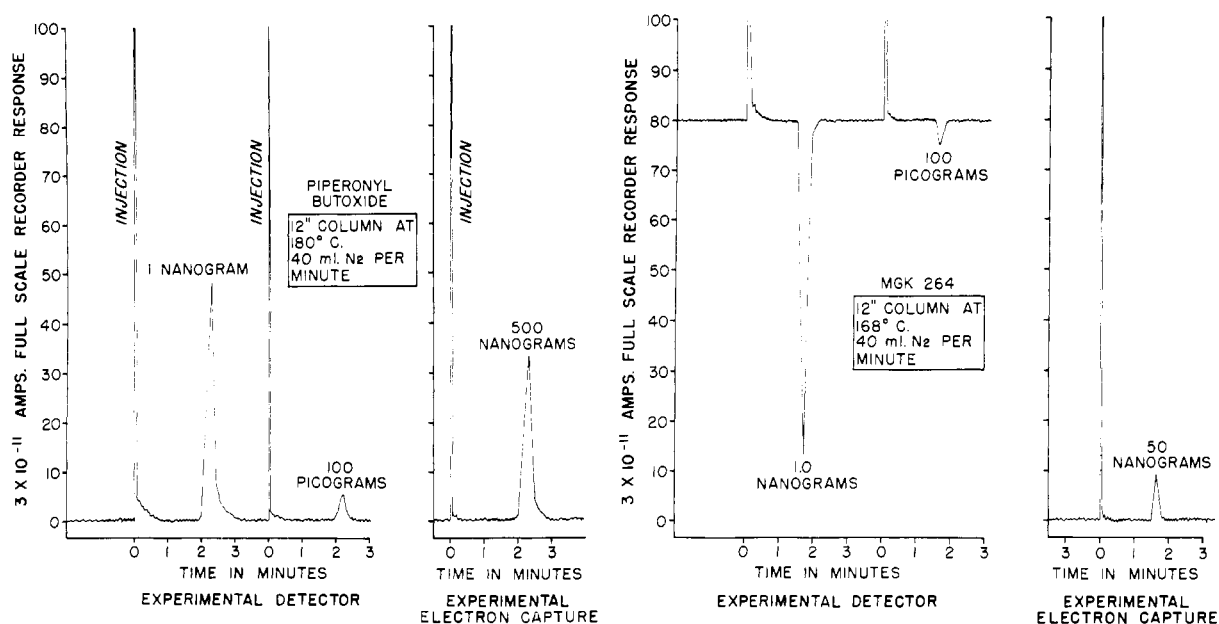


Figure 7. Comparative gas chromatograms for MGK-264 and piperonyl butoxide

Table I. Comparison of Three Detection Systems

Pesticide	Column Length, Inches	Column Temp., °C.	Approximate Minimal Detectable Amounts of Pesticides, Picograms		
			Aerograph 204 electron-capture with attenuation of 1	Exptl. electron-capture, $1 \times 10^{-11}$ amp. full scale	Exptl. detector, $1 \times 10^{-11}$ amp. full scale
Piperonyl butoxide	12	180	50,000.0 <sup>a</sup>	1650.00	22.00
MGK-264	12	168	6,500.0 <sup>a</sup>	6250.00	25.00 <sup>b</sup>
Ciodrin	12	168	3,000.0	112.00	45.00
Bidrin	12	168	25,000.0 <sup>a</sup>	2500.00	125.00 <sup>b</sup>
Malathion	24	168	175.0	25.00	16.00
Diazinon	24	155	500.0	100.00	25.00 <sup>b</sup>
Azodrin	12	168	Over 100,000.0 <sup>a</sup>	7500.00	250.00 <sup>b</sup>
Dieldrin	48	168	2.5	1.25	1.00
Lindane	48	168	0.2	0.15	0.10
Carbaryl	12	155	...	5000.00	250.00 <sup>b</sup>

<sup>a</sup> Sinusoidal shape elution curve. <sup>b</sup> Negative peak.

40 ml. N<sub>2</sub> per minute. Optimum operational voltages used with both experimental detectors.

detector of the Aerograph 204 was 90 volts, whereas the operational voltages of the experimental detectors were optimal. Six to 10 volts were used for the experimental electron-capture detector. These detector systems exhibited a linear range of response to concentration of between 3 and 5 decades, depending upon the stability of the pesticide. The new experimental detector possessed excellent sensitivity to piperonyl butoxide and MGK-264. Tests with organophosphorus pesticides were interesting, since the greatest advantage was realized for compounds detected with 100 to 150 volts applied to the paired electrodes. The chromatograms from the new detector system contain negative peaks for Bidrin, carbaryl, Diazinon, Azodrin, and MGK-264. By reversing the polarity, these appear as positive peaks and show a linear relationship with dosages.

#### Literature Cited

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