Improvement of Identification in the Gas - Liquid Chromatographic Analysis of Agricultural Samples for Residues of some Chlorinated Pesticides*

Part II. A Halogen-sensitive Detector in Complementary or Alternative Use to an Electron-capture Ionisation Detector

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Gas - liquid chromatography with detection by electron-capture ionisation has found considerable use in the analysis of crops, soils and animal tissues for residues of the chlorinated pesticides. The chief limitation of the method, however, lies in incomplete certainty of identification of a pesticide based on retention time alone on a single column of the resolving power at present available.

Two methods of increasing certainty of identification, the use of single columns of higher resolving power and the application of the multi-column "spectrochromatogram," were described in Part I of this paper.

In Part II, a third method based on simultaneous detection by two highly sensitive and selective detectors with dissimilar response characteristics to individual chlorinated pesticides is described. One of these sensors is the electron-capture ionisation detector, and the other is a halogen-sensitive cell of the type used in refrigeration leak detection. The last-mentioned detector has great potential value in residue analysis for the chlorinated pesticides. It is sensitive to the nanogram range, is more selective than the electron-capture ionisation type and has greater linearity of response. Moreover, it is relatively cheap and can be operated with simple circuitry.

Gas - liquid chromatography with detection by electron-capture ionisation has rapidly proved itself[1,2,3,4] to be a technique of particular value for detecting and determining residues of chlorinated pesticides in crops, soils and animal tissues. Its main advantages over alternative methods are greater sensitivity, greater selectivity and its ability to analyse for more than one component at the same time. These advantages result in a method in which extracts of small samples can be analysed rapidly for nanogram amounts of several pesticides without a concentration step, and with the minimum of prior clean-up.

Although care is necessary in the proper operation[5] of the detector itself, the main limitation of the method lies in the degree of certainty of identifying the individual pesticides, when this identification is based only on retention times obtained on a single column of the resolving power at present available. This factor is most relevant in screening analyses on samples of unknown history, when valid control material is not usually available.

In Part I of this paper,[6] two methods intended to overcome or reduce this problem were described: the use of single columns of higher resolving power than that of earlier versions, and the production of multi-column "spectrochromatograms" having an appearance and showing retention times highly characteristic of the individual pesticides being analysed.

A third approach, using highly sensitive detectors whose responses to the halogenated pesticides differ, is described in Part II. A detector is needed that has the unusual properties of exceptional sensitivity and high selectivity to the halogenated pesticide, but significantly different response characteristics from the electron-capture ionisation detector with which it could be used in tandem. Such a device is the halogen-sensitive element used in the Type HA leak-detector made by Associated Electrical Industries Ltd.

The idea of applying a halogen-sensitive device of this type to the analysis of pesticide residues is not new, for in 1952. C. A. Reilly, working in the Laboratories of the Shell Development Company at Emeryville, California, reported on a determined effort to use the General Electric Type H leak-detector of similar design to the Type HA for this purpose. This

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work, however, was not altogether successful, partly because the use of the detector was not preceded by a gas - liquid chromatographic step, and partly because of the electrical or electronic instability of the systems examined.

Much more recently the successful use of this type of halogen-sensitive element as a detector in the gas - liquid chromatography of volatile chlorinated hydrocarbons was briefly reported by Cremer, Kraus and Bechtold[7] in Germany. In this detailed study, high selectivity to chlorinated compounds was recorded, and such a sensitivity was developed that 0·3 nanograms of chlorine could be detected under favourable conditions.

This lead was followed in the Tunstall Laboratory of "Shell" Research Ltd. by A. Richardson, who showed that the A.E.I. halogen-sensitive element already referred to would function as a gas - liquid chromatographic detector, and could provide a relatively high sensitivity with the aid of only simple circuitry.

We therefore undertook a detailed evaluation of two versions of this halogen-sensitive device with the object of using it for determining residues of the chlorinated pesticides on the nanogram scale, and of operating it in tandem with an electron-capture ionisation detector as a method for increasing the certainty of identifying these compounds.

Experimental and results

Description and operation of the halogen-sensitive element—

The A.E.I. Ozotron Type H halogen-sensitive element,[8] shown diagrammatically in Fig. 1, consists of a pair of concentric platinum cylinders mounted within a protective borosilicate glass envelope through which, in normal operation, the air to be tested for traces of halogenated compounds is drawn at a rate of about 150 ml per minute. The inner platinum

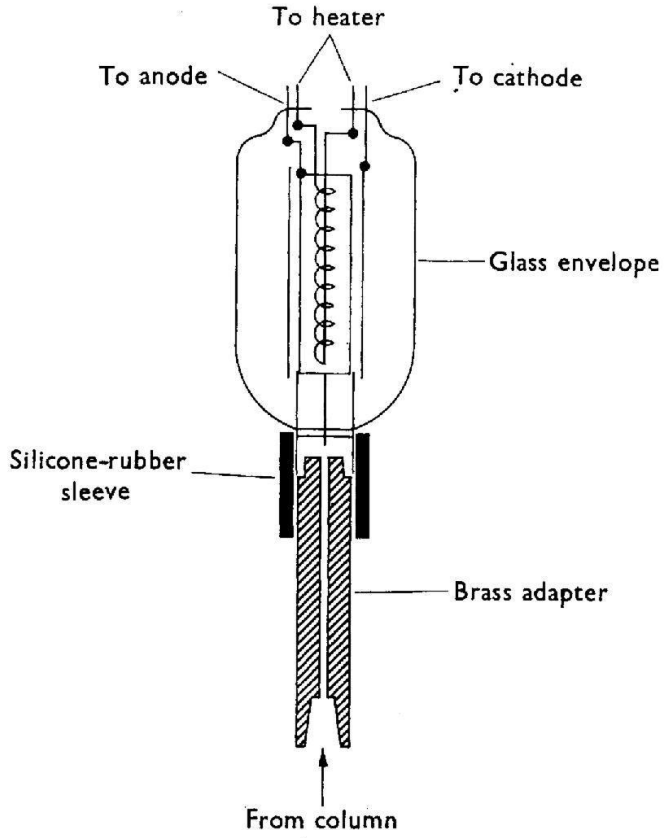


Fig. 1. Halogen-sensitive detector (A.E.I. type H)

cylinder, or anode, which has been sensitised by an alkali treatment, is indirectly heated by an internal platinum filament taking a current of 7·4 amps at 6 volts a.c., and operates at a temperature of about 800° C. An anode-to-cathode potential of 250 volts d.c. is normally used, resulting in the production of a positive-ion standing current that can be suitably amplified and presented. When air, containing halogen vapour, is drawn through the cell there is an apparent increase in the positive-ion current, whose magnitude is indicative of the concentration of halogen vapour present.

A newer version of the above detector has recently become available. This model, the Ozotron Type J, is basically the same as the Type H except that the element is mounted more rigidly in a two-piece ceramic envelope from which the platinum heater filament and electrodes are easily removed.

DESIGN OF CIRCUITS AND PERFORMANCE OF HALOGEN-SENSITIVE DETECTORS—

An Ozotron Type H halogen-sensitive element was connected up as detector to a 4 feet long × 0·125-inch bore silicone - Epikote column of the type described in Part I of this paper. The detector circuitry used is shown diagrammatically in Fig. 2(*a*). Power or the

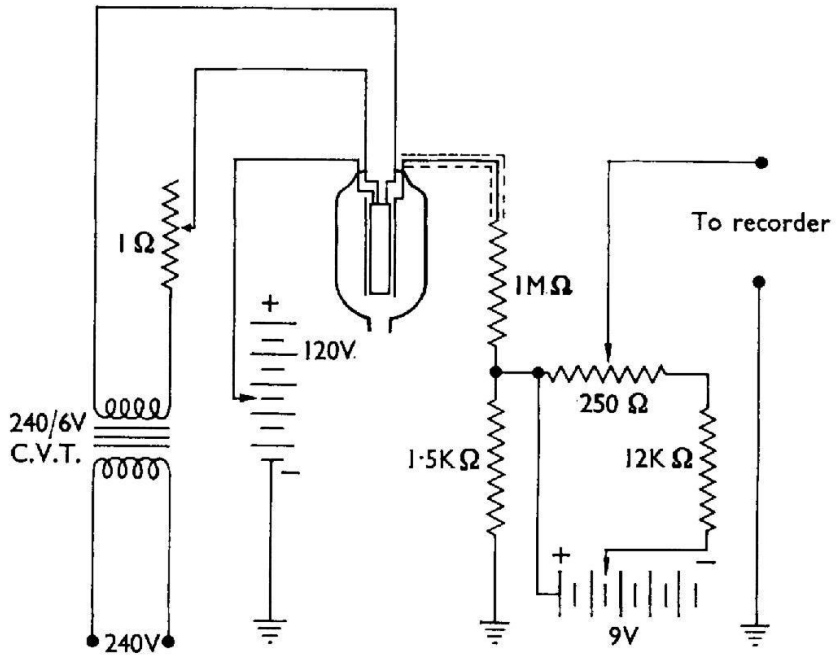


Fig. 2 (*a*). Simple circuit for halogen-sensitive detector

heater filament was supplied from a 240 to 6V step-down transformer connected in series with a 1-ohm sliding resistance, and the potential required for the anode was taken from 0 to 120 V high tension batteries. The signal from the cathode was led, via a 1-megohm load in series with a 1500-ohm input resistor (backed off by a 0 to 9 V grid-bias battery controlled by a wire-wound variable resistor), before being led directly into a 1-mV full-scale deflection chart recorder having a maximum input impedance of 1000 ohms and a pen-response time of 2 seconds.

An evaluation of detector performance was made under these conditions by injecting 1 to 10 μl volumes of dilute solutions of chlorinated pesticides in light petroleum (boiling-range 62° to 68° C) into the gas - liquid chromatographic apparatus at a column temperature of 163° C, while varying the operational parameters. Nitrogen was used as carrier gas at various flow-rates in the range 100 to 200 ml per minute, with and without the admission of air at the inlet of the detector.

It was found preferable to use separate leads to the anode and inner heater terminal instead of a common one as indicated by the manufacturer, as the latter procedure resulted in a higher electrical noise level.

Sensitivity, both to chlorinated pesticides and to light-petroleum solvent, increased with increase in heater voltage, but in favour of the solvent. In consequence it was impracticable to work at the highest heater voltage (6 volts), as the large solvent response obtained masked the early part of the chromatogram. Below about 4 volts, however, sensitivity rapidly decreased.

Similarly, increase in the potential applied to the anode of the cell resulted in an increase in both sensitivity and electrical noise level. Disproportionate increase of the latter made it desirable to operate at comparatively low potentials, although below about 36 volts d.c. a marked increase in peak tailing seriously affected the chromatograms obtained.

The time-constant of the cell was observed to be rather longer than that for the electron-capture ionisation type of detector, and in consequence, higher nitrogen flow-rates (greater

than 100 ml per minute) resulted in improved chromatogram peak shape, but at the expense of some sensitivity. Admission of air to the inlet of the detector to effect oxidative combustion of the pesticides rather than pyrolysis, produced a marked increase in the standing current of the cell and a reduction of sensitivity that became significant at air flow-rates in excess of about 5 ml per minute.

The level of sensitivity obtainable by using the above-mentioned simple circuitry and with a power input to the heater filament of 4·6 volts a.c. at 6·7 amps, an anode potential of +36 volts d.c. and a nitrogen carrier-gas flow-rate of 100 ml per minute at 163°C, corresponded to a limit of detection of about 2 nanograms for aldrin (approximately twice the noise level). Response of the detector *versus* pesticide load was observed to be linear up to recorder full-scale deflection, which for aldrin occurred with 100 nanograms.

This sensitivity, while encouraging, was not quite sufficient for our purpose, and a more sensitive version of the circuit, shown diagrammatically in Fig. 2(*b*), was therefore developed.

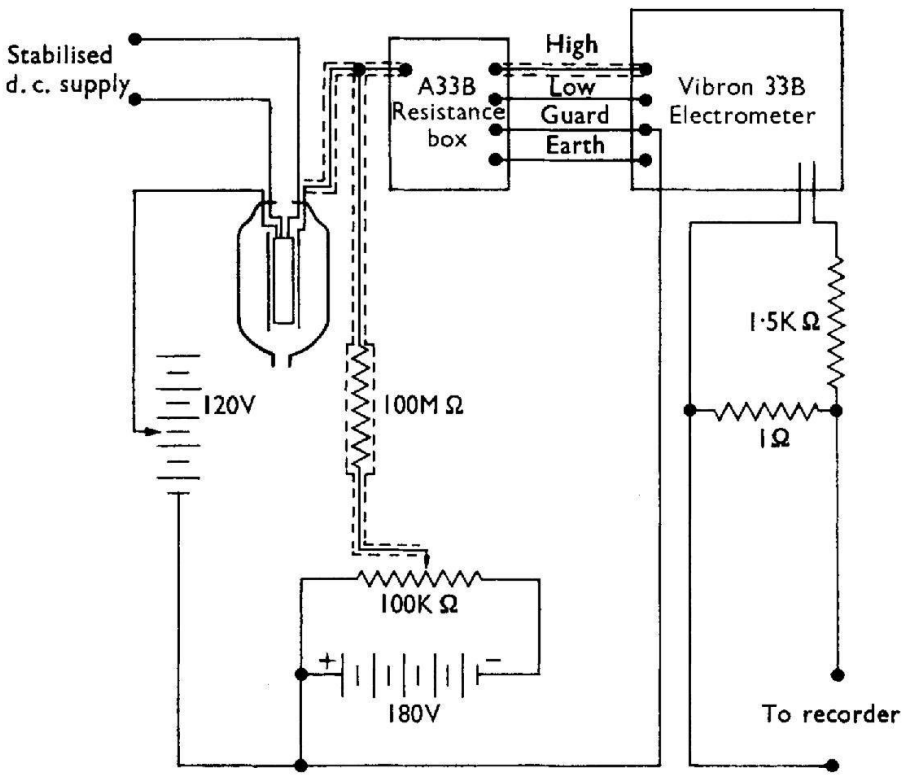


Fig. 2 (*b*). More sensitive circuit for halogen-sensitive detector

With this arrangement it was found essential to provide the heater filament with a more stable power supply than was given by the step-down transformer. Replacing the latter by a heavy duty 6 volt accumulator proved satisfactory, except that the high current consumption resulted in a gradual drift of the recorder baseline as the accumulator was discharged. The latter was therefore replaced by a comparatively inexpensive transistorised Zener-diode stabilised d.c. power supply, specially designed for the purpose.

In this more sensitive circuit the signal from the cathode was led through a 1-megohm input resistor in an Electronic Industries Ltd. model A33B current- and resistance-measuring bridge, backed off similarly to the one described above, and then passed into an E.I.L. Vibron model 33B vibrating-reed electrometer, before being fed via appropriate series - parallel matching resistors to the 1-mV recorder.

Under the same operating conditions as described above, the limit of detection for aldrin with this circuitry was about 0·1 nanograms at the 100-mV attenuation setting. Again, good linearity of response with increase in pesticide load was observed up to recorder full-scale deflection at the 1000-mV (maximum) attenuation setting, which for aldrin occurred with 30 nanograms.

A similar evaluation of the ceramic-protected Ozotron Type J halogen-sensitive element was also undertaken. The performance characteristics observed were similar in some respects to those outlined above.

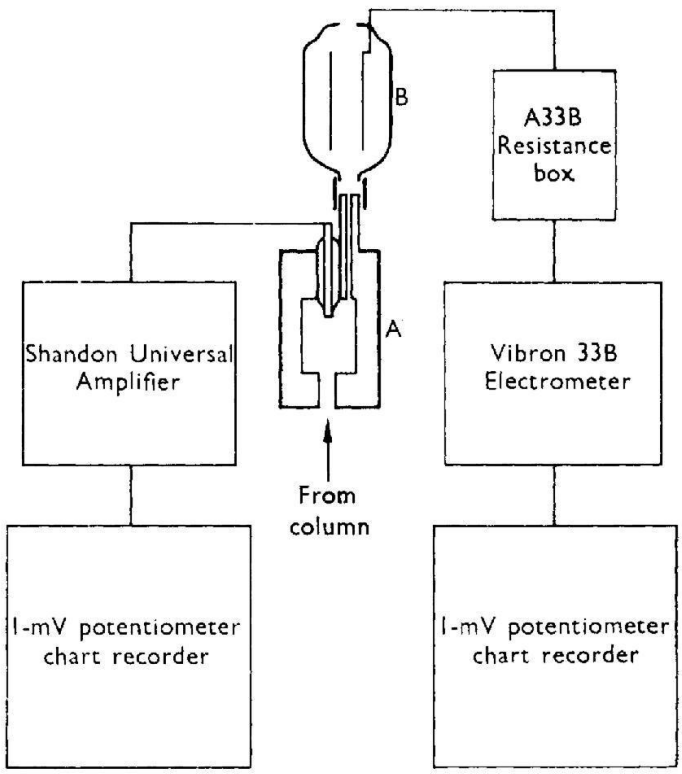
In this work it was found essential to ensure that all signal-carrying leads were fully screened by using co-axial cable, and that electrical connections, particularly the leads to the heater elements, were soundly made, *e.g.*, brazed or silver-soldered.

The two least satisfactory features of the Type H and J detectors when used in the manner described, were their general electrical instability and the need for conditioning them appreciably before high sensitivity could be achieved. The tendency towards electrical instability was considered to be caused partly by some lack of rigidity in the location of the concentric platinum electrodes (in the Type H) and partly by shorting of the electrodes, perhaps by carbonaceous deposits resulting from pyrolysis of the samples. Such deposits could easily be removed by cleaning the electrodes in acetone; this was facilitated for Type J by the ease with which the cell could be taken apart.

The conditioning of the cells and their maintenance in a state of high sensitivity was the biggest problem encountered, and has not yet been completely solved. A variety of conditioning processes were tried with five such cells, including pre-treatment with air, nitrogen or massive loads of chlorinated material, and washing the anode and gentle abrasive cleaning of the cathode in acetone. Of these, pretreatment with air shows promise of being the most effective. The results quoted above were obtained on the most sensitive of the detectors examined and this one (a Type H) was used to produce the halogen-detector chromatograms reproduced in this paper.

EVALUATION OF HALOGEN-SENSITIVE AND ELECTRON-CAPTURE IONISATION DETECTORS IN COMPLEMENTARY OPERATION—

An Ozotron Type H halogen-sensitive element was connected by means of a short brass capillary tube and silicone rubber sleeve on to the outlet port of an electron-capture ionisation detector. This, in turn, was connected to a 4 feet × 0·125-inch bore copper column that was packed with 2·5 per cent. w/w of silicone oil *plus* 0·25 per cent. w/w Epikote 1001, supported on 100- to 120-mesh plain Celite. The column was operated at a temperature of 163° C, and a nitrogen flow-rate of 100 ml per minute was maintained. For the Ozotron, the more



A = Electron-capture detector **B** = Halogen-sensitive detector

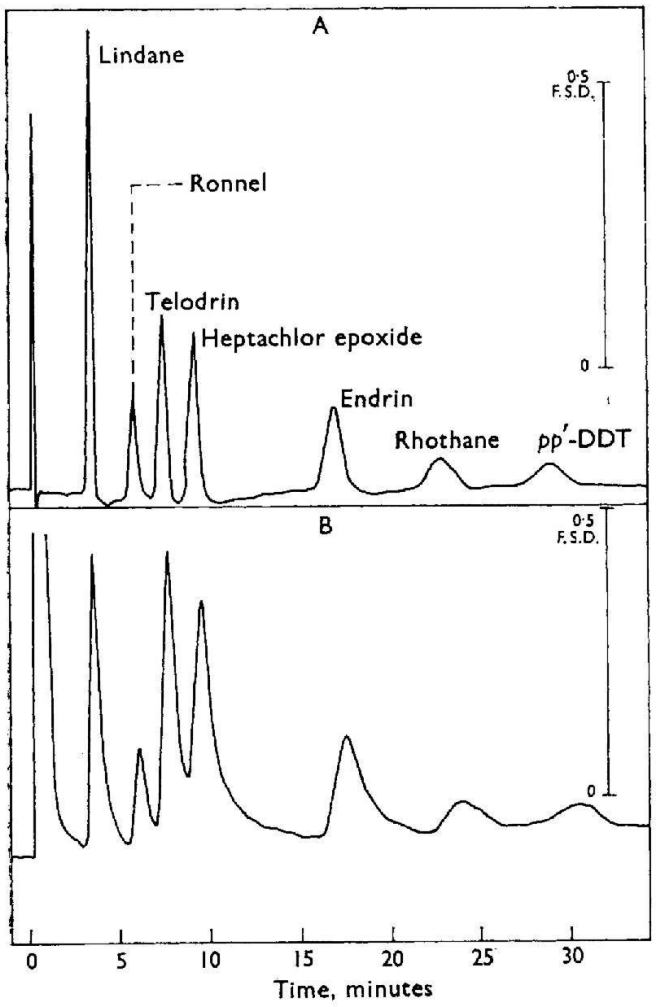
Fig. 3. Simultaneous complementary detection system

sensitive circuit was used, and the signals from both detectors after attenuation or amplification as appropriate were fed, as shown in Fig. 3, into separate 1-mV recorders running at the same chart speed. By this arrangement simultaneous chromatograms from these two different detection systems could be produced for solutions containing nanogram amounts of the chlorinated pesticides.

An example of this is illustrated in Fig. 4, in which the simultaneous halogen-sensitive and electron-capture chromatograms were produced on the injection of 2·3 μl of a petroleum spirit solution, containing 2·3 nanograms each of lindane, ronnel, Telodrin, heptachlor epoxide, endrin, Rhothane and *pp'*-DDT. It will be noted that the relative response of the two detectors is different, particularly for lindane, Telodrin and endrin.

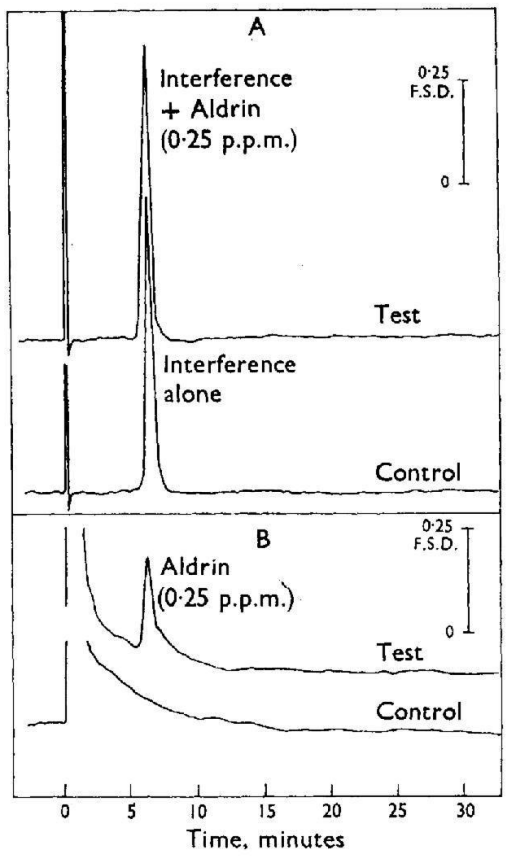
This difference in relative response can be more marked when sensitivity to chlorinated and non-chlorinated material is considered. In the top half of Fig. 5, the electron-capture chromatogram of "control" wheat before and after the addition of 0·25 p.p.m. of aldrin can be seen. As has been previously pointed out,[1] this control sample, typical of the grain crops, exhibits massive electron-capture interference from a naturally occurring co-extractive, whose retention time is the same as that of aldrin. In the simultaneous halogen-sensitive chromatograms, no such interference is evident. The complementary use of the two detectors could therefore be of much value in increasing the certainty of identification of any pesticide indicated as present in the sample.

The value of the difference in relative response of the two detectors to individual pesticides is shown in Fig. 6, in which, under standard operating conditions, reproducible relative responses (as measured by peak area ratios) provide good confirmatory evidence for the



A: Electron-capture detector
B: Halogen-sensitive detector

Fig. 4. Simultaneous complementary gas chromatograms of seven chlorinated pesticides: 2·3 nanograms of each pesticide.



A: Electron-capture detector
B: Halogen-sensitive detector

Fig. 5. Simultaneous complementary gas chromatograms of control and aldrin-treated wheat: injection, 5 μl ≡ 6 mg of crop.

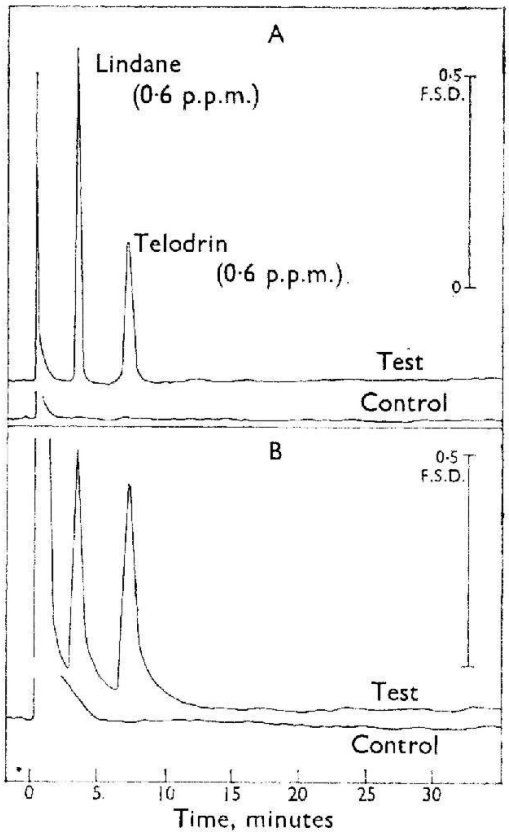
identification of the pesticides lindane and Telodrin, added to spring cabbage to the extent of 0·6 p.p.m.

In the last-mentioned chromatogram, the area of the halogen-sensitive detector peak for Telodrin (chlorine content, 68·8 per cent.) is greater than that for lindane (chlorine content, 73·1 per cent.), indicating that, for this detector, the response obtained is not simply a function of the chlorine content of the molecule.

Another example of simultaneous complementary halogen-sensitive - electron-capture gas - liquid chromatography is illustrated in Fig. 7, which shows the dual chromatograms produced by the addition of 1 p.p.m. of either dieldrin or *pp'*-DDE to "control" lamb. The retention times of these two pesticides on a single silicone - Epikote column are nearly coincident, with the consequent possibility of confusion between them. With the complementary detector system, however, the calculated peak area ratios, 1·3 and 1·1 for dieldrin and *pp'*-DDE respectively, could provide sufficient evidence to permit reasonable distinction between the two pesticides.

Discussion and conclusions

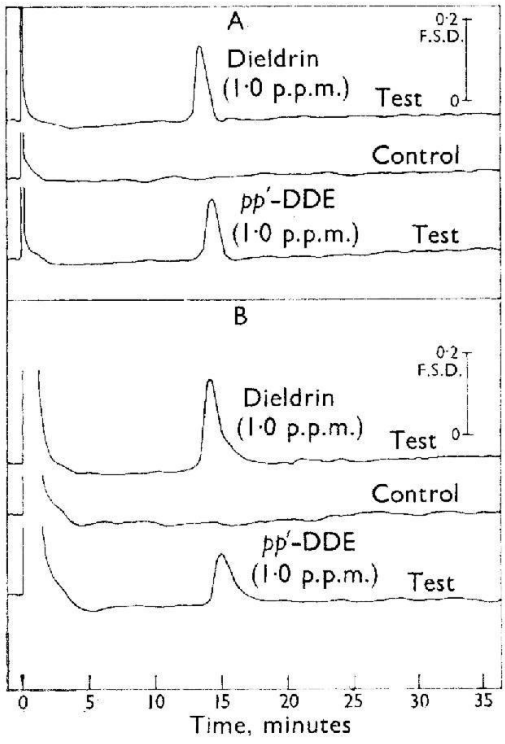
One of the chief merits of the halogen-sensitive detectors described lies in their exceptional selectivity towards the halogenated pesticides compared with natural materials co-extracted from crops, soils or tissues. There is evidence that this selectivity is significantly superior to that shown by the electron-capture ionisation type of detector. This is particularly marked in the example shown in Fig. 5. Certainly, in the screening of a wide range of crops with the halogen-sensitive detector, no sample containing non-pesticidal material gave a response greater than that for electron-capture ionisation detection, and there were indications that in general the superiority in selectivity was about tenfold.



A: Electron-capture detector (EC)

B: Halogen-sensitive detector (HS)

Fig. 6. Simultaneous complementary gas chromatograms of control and lindane - Telodrin treated spring cabbage: injection, 5 μl = 6 mg of crop. Relative peak areas, HS/EC: lindane 1·1; Telodrin 2·5



A: Electron-capture detector (EC)

B: Halogen-sensitive detector (HS).

Fig. 7. Simultaneous complementary gas chromatograms of control lamb and lamb containing dieldrin or *pp'* - DDE: injection, 5 μl = 2·5 mg of tissue. Relative peak areas, HS/EC: dieldrin 1·3; *pp'*-DDE 1·1

Another feature in favour of the halogen-sensitive element is that there is linearity of response with increase in load up to at least 100 nanograms. This could be of advantage in quantitative work, by reducing the need for repeated dilution and injection in the analysis of extracts of unknown pesticide concentration.

The cost of these detectors (£15 to £18) is not high, and in tests where the highest sensitivity (0·1 nanogram) is not required, simple and inexpensive circuitry that does not involve the use of either an electrometer or amplifier is adequate. This arrangement could be of immediate value in analyses in the near-residue range, *e.g.*, for chlorinated pesticides in field-strength dusts, fertilisers, wool, wood, plastics and hardboard, and after a tenfold concentration of the sample extract (by partition or evaporation, or both), could be applied to the low residue range. Indeed, it is probable that this concentration step can be eliminated simply by using a larger input resistor, and feeding the signal directly into a high-impedance 1-mV recorder.

The main disadvantages of these halogen-sensitive detectors, as has been already indicated, lie in their indifferent electrical stability under the conditions used, and the difficulty of conditioning the cells rapidly and maintaining them at high sensitivity. It must be remembered, however, that the detectors have been used in a manner quite unlike the one for which they were designed. It is possible, therefore, that design and development work on halogen-sensitive elements for use in gas - liquid chromatographic residue analysis could overcome both of these problems and, moreover, effect sufficient increase in sensitivity to make them of even greater value than the electron-capture type.

Most of the work reported here was performed with the Ozotron Type H detector, but the Type J shows considerable promise. The unglazed ceramic sheath of the latter, however, may not be as impervious as the glass of the former. Against this, the Type J is easier to clean and, perhaps, to condition since it can be taken apart. Further, it possesses a higher thermal capacity, which makes it somewhat less sensitive to slight fluctuations in the power supply to the heater filament.

In conclusion, it is considered that the halogen-sensitive detector when used in combination with the electron-capture ionisation detector in the manner described, provides a technique with a potential value at least comparable with that of the multi-column "spectro-chromatogram" (described in Part I of this paper), for improving the certainty of identifying chlorinated pesticides in analysis of residues. Apart from its complementary operation with the electron-capture ionisation type, it has great potential value as an alternative detector in gas - liquid chromatographic analysis of chlorinated pesticides, both on the residue and near-residue scales.

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References

1. Goodwin, E. S., Goulden, R., and Reynolds, J. G., *Analyst*, 1961, **86**, 697.
2. Watts, J. O., and Klein, A. K., *J. Assoc. Off. Agr. Chem.*, 1962, **45**, 102.
3. Taylor, A., *Analyst*, 1962, **87**, 824.
4. "Aerograph Research Notes," Wilkens Instrument and Research Inc., Walnut Creek, California, Summer Issue, 1962.
5. Lovelock, J. E., *Anal. Chem.*, 1963, **35**, 474.
6. Goulden, R., Goodwin, E. S., and Davies, L., *Analyst*, 1963, **88**, 941.
7. Cremer, E., Kraus, Th., and Bechtold, E., *Chem.-Ing.-Tech.*, 1961, **33**, 632.
8. "Leak Detector Type HA," *Instruction book* (*reference* 4092–61. *Ed. A.*), Associated Electrical Industries Ltd., Electronic Apparatus Division, Leicester.

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