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COMPACT DUAL-CHANNEL FLAME IONIZATION-CUM-THERMIONIC DETECTOR FOR HIGH-SPECIFICITY CHROMATOGRAPHIC ANALYSIS

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SUMMARY

A compact dual-channel flame ionization-cum-thermionic detector was constructed by duplicating the burner of a conventional flame ionization detector.

Any commercial apparatus can be modified in this way, the result being an increase in the selectivity and the efficiency of the chromatograph. The new detector has been found to be particularly useful in the qualitative and quantitative chromatographic analysis of organic phosphorus, halogen, and nitrogen compounds.

Normally interfering organic compounds not containing these hetero-atoms can be automatically suppressed, or identified by comparing the two responses given by the detector units.

INTRODUCTION

The simultaneous use of more than one selective detector is on the increase, partly because laboratories and manufacturers have solved the problem of instrumentation, so that the resulting multidetectors are relatively easy to operate.

Multidetectors have been found useful for the detection of traces of insecticides in food, because a single operation provides all the required information about the phosphorus, halogen, and carbamate content of the sample. Most insecticides are chlorinated derivatives, phosphates, or carbamates, and are readily analysed gas chromatographically with the aid of a detector system composed of an electron capture detector (ECD) and an alkali-metal thermionic detector¹ (TD). The latter has been improved, and new models using potassium chloride and cesium bromide have recently been developed^{2, 3}.

In the analysis of insecticides in food, the extracts prepared from the samples contain entrained organic compounds other than insecticides. Normally these have to be removed in a pre-purification step (clean-up). However, this may involve serious losses of the insecticide components. High-specificity detectors can come to our aid by ignoring the entrained substances. As a result, time is saved by omitting or simplifying the pre-purification.

However, the entrained substances may be present in such large amounts that

they impair the selectivity of the detectors and thus give rise to spurious peaks. To avoid this, one must couple the detector with a conventional hydrogen flame ionization detector (FID), this latter detector monitors the entrained organic compounds. This is useful even when the extract has been purified, for it gives a check on the results. It should be noted that, when a thermionic detector is used, the signal given by a few micrograms of an interfering hydrocarbon is comparable to that given by 0.1 ng of the insecticide Parathion; furthermore, it is also known that when different types of thermionic detectors are used¹⁻⁴ organic carbon can always give rise to positive or negative interfering peaks.

To eliminate such interference, two-stage detectors have been developed. In these systems, the sample is first burned in a normal flame-ionization detector, and then the combustion products are analysed by a selective thermionic detector for halogens, phosphorus, and nitrogen compounds. Organic compounds do not interfere, because they have all been burned to CO₂, which remains undetected. These systems include KARMEN's detector^{5,6}, with two hydrogen flames in series, and the detector of ABEL *et al.*⁷ which differs from the former in the position of the salt reservoir and in it being heated by an electrical current rather than by the hydrogen flame. The selectivity with which these detectors pick out phosphorus derivatives from other organic compounds is about a hundred times as good as with conventional thermionic detectors. On the other hand, the two-stage detectors are less sensitive. This is probably due to the fact that not all the gas can be made to react in the active volume of the second flame.

EXPERIMENTAL

Our task was to find a rapid method for detecting nano and sub-nanogram amounts of phosphate and carbamate insecticides in non-purified extracts from fruit, vegetables and related food products. Our choice fell on gas chromatography with a hydrogen flame ionization detector and a potassium chloride thermionic detector⁸ connected in parallel. This thermionic detector can detect sub-nanogram amounts of phosphorus compounds and some of the carbamates of interest here, but is insensitive to chlorinated substances, and gives a positive response to organic carbon. This response is similar to, but smaller (by a factor of about 2) than, that of conventional flame ionization detectors; for the correct comparison of the responses the amplifier of the flame ionization detector must be adjusted to obtain the same sensitivity toward organic carbon as that of the other detector. The aim of using the FID was to reveal any possible co-extracted natural products capable of upsetting the detection of insecticides by the thermionic detector. When the FID gave no peaks, the peak of the KCl-TD could be attributed to phosphorus compounds or carbamates. FID peaks indicated the presence of entrained substances in the extracts, and comparison between the peak areas obtained from the FID and the TD led to the correct qualitative and quantitative evaluation of the chromatograms.

The two detectors were combined in a single unit, the quartz burner (0.5 mm I.D.) and the collecting electrodes of one being duplicated. The new device may be called parallel-flame thermionic detector (PFTD), whose arrangement is shown in Fig. 1. The advantages offered by this compact dual-channel detector are discussed below.

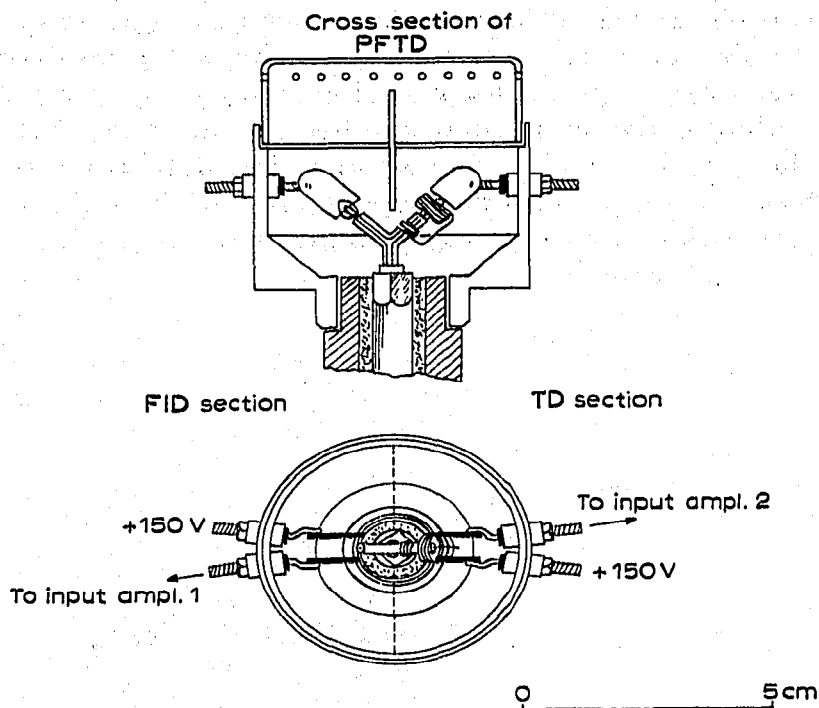


Fig. 1. Diagram of parallel-flame thermionic detector.

1. Two detector channels, FID and TD or (in the doubly thermionized case) TD' and TD'' with different salts, can be used in the same analysis without having to employ stream splitters in the oven. The air, the hydrogen, and the nitrogen circuits need not be modified or integrated—all this results in a greater versatility of the apparatus.

2. The sample components reach the active volume of the two flames at the same time, and there are minimal interchannel delays. (In the conventional dispositions using splitters such delays can arise from asymmetric adsorption phenomena in the outlet tubes and from the presence of dissimilar dead volumes in the column-detector connections.) Strictly simultaneous detection is important in order to be able to compare the retention times and to carry out the electrical differentiation of the signals. This is done by combining the information from the two detectors into one signal, in which the parasite signals, being in-phase, are suppressed. The resulting signal is then relayed to *e.g.*, a single-track recorder (a chromatogram obtained by electrical differentiation will be shown later).

3. The method of selective detection with FID + TD systems (or TD' + TD'' systems with different salts) can be applied in conjunction with capillary columns without any loss in the resolving power due to the use of capillary stream splitters or other devices complicating the connection between the column and the detectors.

The new detector was attached to a Fractovap D/AI chromatograph (Carlo Erba Ltd., Milan) fitted with a glass column (length 2 m, I.D., 4 mm) having a built-in vaporizer. The stationary phase was 1% SE-30 on a 100-120 mesh silanized Gas Chrom P support. The flow rate of the nitrogen carrier gas was 42 ml/min (at 202°), that of the air being 428 ml/min. The current of the KCl-thermionic detector was $3 \cdot 10^{-9}$ A (about full scale recorder deflection with attenuation $\times 100$ input, $\times 8$

output). This was obtained at total hydrogen flow rates varying between 45 and 60 ml/min according to the degree of depletion of the salt reservoir. The latter needed replenishment when the hydrogen flow rate required for reaching a detector current of $3 \cdot 10^{-9}$ A exceeded the indicated limits. Under normal conditions, one can work for months without any servicing. The current in the flame ionization detector was $2 \cdot 10^{-10}$ A. The signals of the two detectors were amplified separately with the aid of two electrometers connected to two recording channels or to a single channel recorder, according to versions A or B, respectively in Fig. 2.

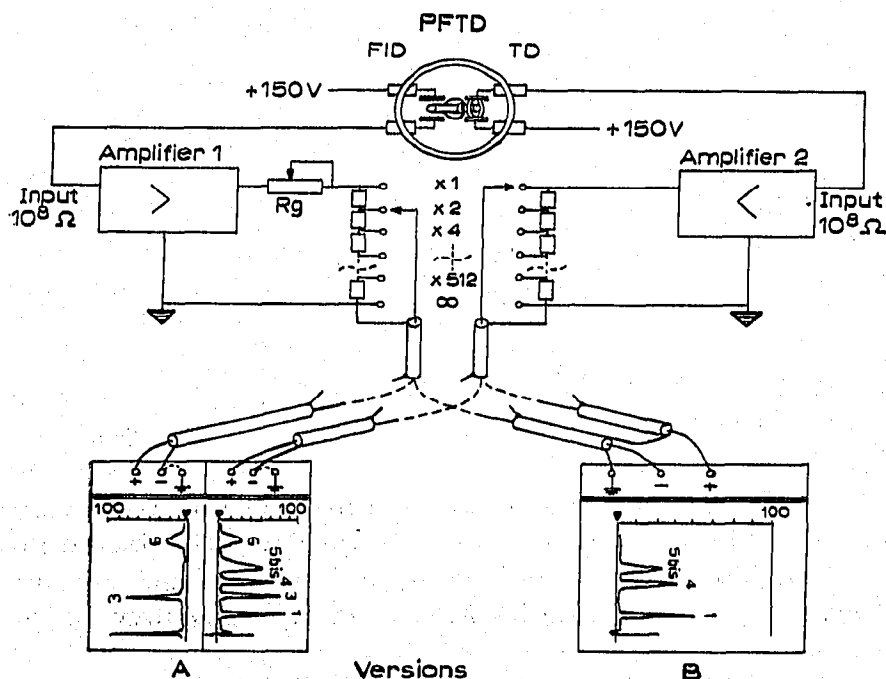


Fig. 2. Diagram showing two different methods of connecting the electrometers and recorders.

The output of one of these amplifiers could be continuously varied through a variable resistor R_g inserted in the output circuit as shown in Fig. 2. Working with version A, a $10\text{-}\mu\text{g}$ sample of an organic compound (*e.g.* methyl pentadecanoate) containing no phosphorus, halogen, and nitrogen was then injected, and the output attenuators were adjusted together with R_g until peaks of the same height were obtained in the two detector channels, this—as mentioned before—being essential for the correct comparison and interpretation of the chromatograms.

DISCUSSION

Fig. 3 shows the results obtained in the chromatographic analysis of a reference mixture and two non-purified fruit extracts (extracting solvent: 50:50 hexane-benzene). Curve "e" resulting from the direct analysis of a non-purified peach extract shows that the parallel-flame thermionic detector has a high sensitivity.

The Parathion peak was given by 0.04 ng (0.04 p.p.m.) of the substance; $2 \mu\text{l}$ of the extract were injected, and only $1 \mu\text{l}$ reached the KCl-thermionic detector. The reference mixture had the composition shown in Table I, the peaks being listed in

the order in which the substances left the column under the conditions specified above.

This analysis, carried out in the presence of chlorinated compounds and a large excess of methyl esters, confirmed the high selectivity of the PFTD detector. Chromatogram "a", obtained with the aid of an electron capture detector (gain $\times 100 \times 16$), shows that this device responds to both chlorine and phosphorus derivatives with different sensitivities. The distorted peaks originating from the two methyl esters (peaks 3 and 6) indicate that the amount of these was so high as to override even such a selective detector as the ECD.

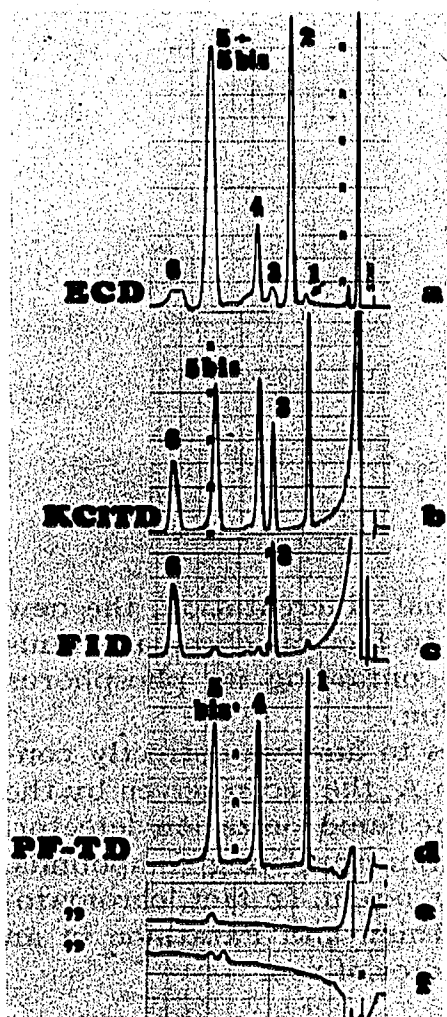


Fig. 3. Chromatograms of the standard mixture of insecticides (see Table I) using: (a) electron capture detector (tritium source); (b) KCl-thermionic detector; (c) hydrogen flame ionization detector; (d) parallel-flame thermionic detector; (e) and (f): analysis of fruit juices with the PFTD.

Chromatogram "b", obtained with a KCl-thermionic detector (gain $\times 100 \times 8$), indicates only phosphorus derivatives (peaks 1, 4 and 5 bis), together with excess methyl esters (peaks 3 and 6). The last two substances masquerade as phosphorus derivatives, and incorrect interpretation is only avoided by noting that in chromatogram "c" the flame ionization detector also gave these two peaks, with the same size

and in the same position, which proves that they must correspond to organic compounds containing no phosphorus or nitrogen.

Finally, the signals from the two detector channels were differentiated and passed into a single recorder. The resulting chromatogram "d" shows that the interfering compounds No. 3 and 6 containing no phosphorus have been automatically suppressed. The arrangement shown in Fig. 2 as version B simplifies the presentation of the analytical data and exhibits an increased detector specificity. Fine adjustment of one of the two detector signals ensures the best automatic suppression of carbon

TABLE I
COMPOSITION OF REFERENCE MIXTURE

Peak No.	Compound	Concentration, p.p.m.
1	Thimet	0.5
2	Lindane	0.5
3	Methyl pentadecanoate	10,000
4	Methyl Parathion	1
5	Aldrin	1
5 bis	Parathion	1
6	Methyl heptadecanoate	10,000
-	Solvent 50:50 hexane-benzene	
	Retention time of Aldrin = 5 min	

compounds. The results show that, in the system of signal differentiation, the new multidetector has a selectivity of $3 \cdot 10^5$ for phosphorus. In fact, as chromatograms "b" and "d" show, 10,000 ng of organic compounds containing no phosphorus simulate the presence of not more than 0.03 ng of Parathion.

The detector system proposed here thus enables us to analyse correctly concentrated extracts without first purifying them. In version A, the record given by the KCl-thermionic detector is compared with that given by the flame ionization detector. In version B, the chromatogram is automatically freed from interfering compounds. The sensitivity of the detector system is better than 0.001 p.p.m. In fact, chromatogram "f" shows the detection of 0.0002 p.p.m. of Malathion and Parathion in an apple, the extract of which had been concentrated by a factor of 100.

CONCLUSION

Thermionic detectors are sufficiently sensitive to detect traces of phosphate and carbamate insecticides in food. However, the results in some cases are unambiguous only when they are compared with corresponding chromatograms obtained with the aid of a conventional flame ionization detector. This fact calls for the combination of the two detectors, which has now been done in a simple and efficient way, the two parts forming a single compact unit. The resulting device may be called a parallel-flame thermionic detector (PFTD). This device has been tested in the analysis of fruit extracts for the presence of insecticide residues.

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