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Note

Simultaneous detection of halogenated and other compounds by electron-capture and flame-ionization detectors combined in series

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To monitor the effluent from a gas chromatograph a number of detectors based on different principles are available. The flame-ionization detector (FID) is probably the most common and versatile detector, while electron-capture detection (ECD) remains the method of choice for halogenated and other electron-absorbing compounds when high sensitivity is required. The FID is not a selective detector but records any compound containing carbon. The extent of ionization reflects the number of carbon atoms in the molecule. The ECD favours detection of compounds containing halogens, and its sensitivity depends on the number of halogen atoms in the molecule and their location. Thus a combination of flame ionization and electron capture may result in information superior to that obtained by a single detector. Furthermore, combining ECD with alkali-FID gives the pesticide residue analyst the advantage of detecting, in the same sample, both organochlorine and organophosphorus compounds.

Much work has been devoted to combining two or more detectors to give complementary information from a single sample injection[1]. Most of the techniques presented have accomplished this by splitting the sample before a parallel detection system. As a result the sensitivity of the system is decreased, since only part of the injected sample is fed to each detector. Furthermore, it may be difficult to quantify the detected compounds since the splitting ratio, usually estimated by measurement of the carrier gas stream, may be affected by the size of the molecules eluted from the column.

The aim of this study was to combine the ECD and the FID in series to obtain a dual detection system capable of simultaneous detection of environmental pollutants of different character, *e.g.*, organochlorine residues and oil and lipid constituents in samples from aquatic environments. In order that the limit of detection should not be adversely affected when using capillary columns, a split-less system without a scavenging gas was required.

MATERIAL AND METHODS

A modified all-glass ECD[2] was connected to the FID of a Varian 2700 gas chromatograph (Fig. 1). Since electron capture is a non-destructive process, the effluent from the column passes undisturbed through the ECD. The effluent is then

directed to the jet-tip of the FID by means of a glass capillary tube. The voltage applied to the ECD was 92 V (d.c.), and the volume of the detector cell was 0.35 cm^3. Despite the increase of the dead volume of the system caused by the ECD, no effects on the operation of the FID were noted.

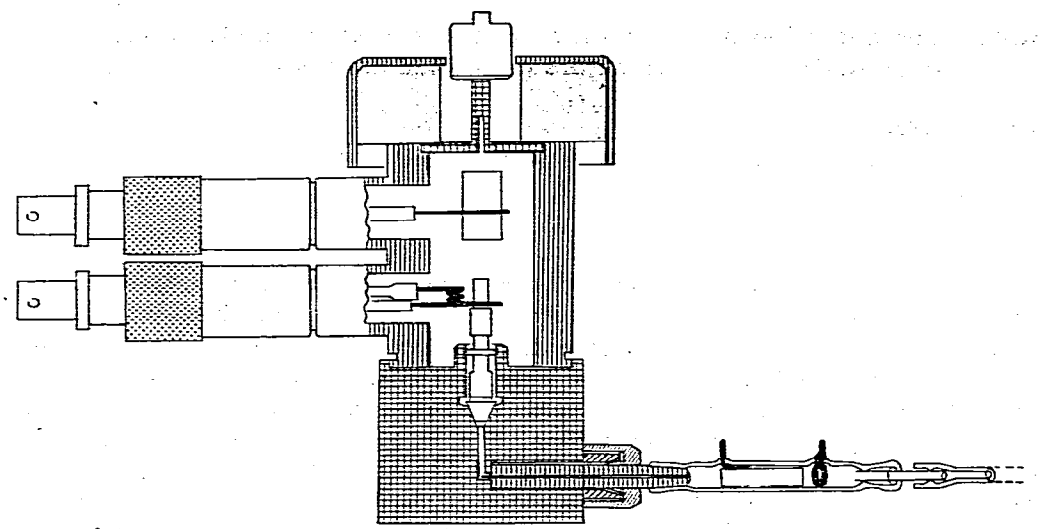


Fig. 1. Serial ECD–FID dual detection system.

The detector system was connected to the column by means of a PTFE tube[2]. Glass columns (190 cm × 1.5 mm I.D.) were used, and the stationary liquid phases (SF-96–QF-1, 3:1) were supported on Gas-Chrom G HP AW DMCS (100–120 mesh). The support was prepared in a fluidized bed. The capillary column (30 m × 0.4 mm I.D.) was coated with OV-101 by a dynamic procedure[3].

Unless the temperature of the column oven was programmed, the temperatures of the injector, column and detector were 225, 185 and 220°, respectively. With packed columns the flow-rate of the carrier gas (nitrogen) was adjusted to *ca.* 20 ml/min. With capillary columns a minimum flow-rate of 1.9 ml/min was required to operate the ECD. The flows of hydrogen and air to the FID were *ca.* 25 and 250 ml/min, respectively.

To prepare the detection system for open-tube capillary columns, a low-volume detector was developed. The ECD is sensitive to solute concentration, and the use of a scavenging gas dilutes the sample and lowers the sensitivity. By modification of the arrangement of the tritium foil in the detector cell (Fig. 2), a cell volume of 0.15 ml

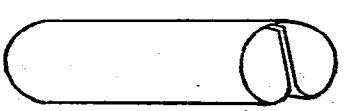


Fig. 2. Modified arrangement of the tritium foil in the ECD cell.

was obtained. The detector was operated with comparable sensitivity to that of a conventional cell at a carrier gas flow-rate of 1.9 ml/min.

RESULTS AND DISCUSSION

Organochlorine pesticides and methyl esters of fatty acids were simultaneously detected (Fig. 3). The ECD was apparently not affected by the fatty acids, and the FID showed no response for the organochlorine compounds at the concentrations used. No interferences or abnormal behaviours were observed in the detection system when the two classes of compounds were injected separately (Fig. 4). Obviously, the responses of the detectors are equal to those obtained when the detectors are operated singly.

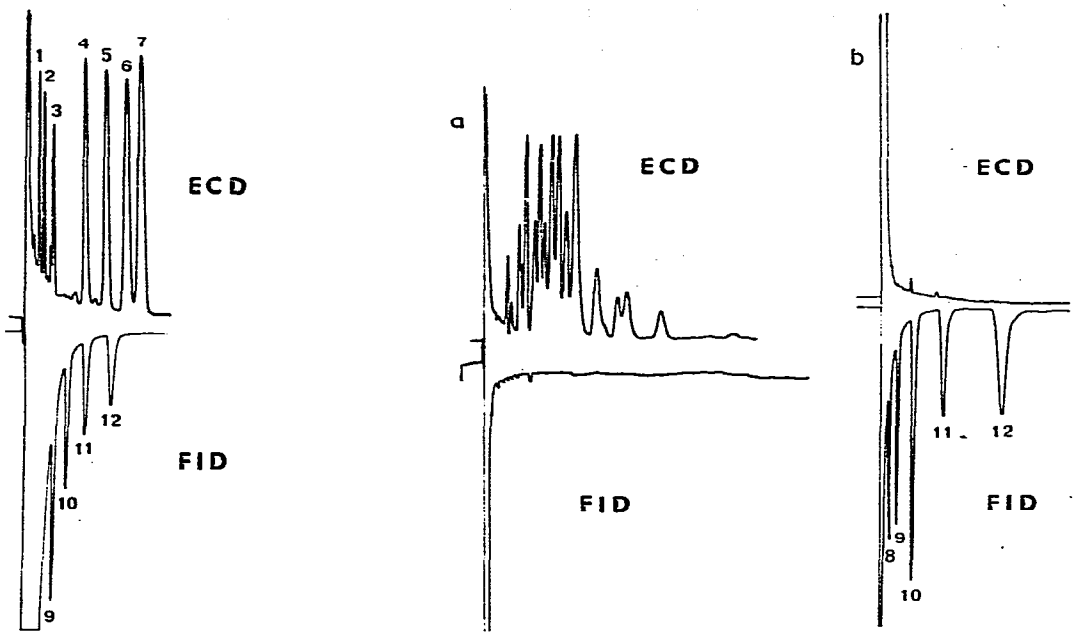


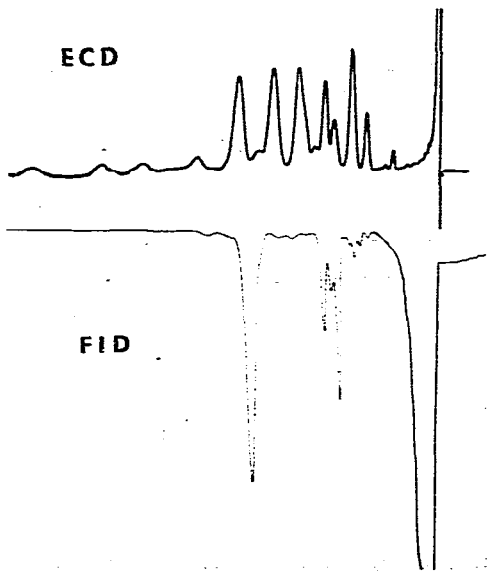
Fig. 3. Simultaneous response of ECD–FID to a mixture of organochlorine pesticides and methyl esters of fatty acids. Peaks: 1 = lindan; 2 = BHC; 3 = aldrin; 4 = *p,p'*-DDE; 5 = dieldrin; 6 = *p,p'*-DDD; 7 = *p,p'*-DDT; 8 = lauric acid; 9 = myristic acid; 10 = palmitic acid; 11 = stearic acid; 12 = oleic acid.

Fig. 4. Response of ECD–FID to a mixture of PCBs (Clophen A 50: (a)) and to a mixture of methyl esters of fatty acids (b). For peaks, see Fig. 3.

The detection system has been used to study the degradation and fate of persistent pollutants in aquatic model ecosystems. Usually these pollutants are closely associated with lipids. Therefore, it is an advantage to be able to study the occurrence and amount of both lipids and, for example, organochlorine residues. A cell extract from a continuous flow culture of the green alga *Chlorella pyrenoidosa* to which polychlorinated biphenyls (PCBs) had been added was hydrolyzed by treat-

ment with a solution of acetyl chloride in methanol and then presented to the detection system (Fig. 5). The PCBs added to the culture were efficiently taken up by the algal cells; the lipids detected in the extract were palmitic acid and stearic acid.

Lipids and substances of lipophilic character tend to accumulate in aquatic environments at the interface between water and air. To assess the ability of the ECD–FID system to simutaneously detect mineral oil and PCBs, a mixture of these substances was injected into the water of an aquarium below the surface. The surface film thus created was sampled[4], extracted and an aliquot of the extract injected into the gas chromatograph equipped with a capillary column and a low-volume ECD and an FID (Fig. 6). The mineral oil was eluted before the main PCB components appeared. Due to the high sensitivity of the ECD to changes in temperature, programming the column resulted in severe baseline drift at the beginning of the run. However, neither class of components affected the detection of the other. Thus both the mineral oil and halogenated compounds can be conveniently analyzed and quantified simultaneously after a single injection.



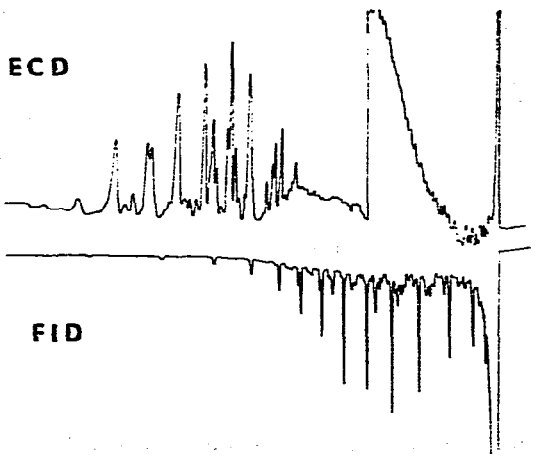


Fig. 5. Fatty acids and PCBs in cells of the green alga *Chlorella pyrenoidosa*. For peaks, see Fig. 3.

Fig. 6. Simultaneous detection of PCBs and mineral oil in a surface film. Glass capillary column (30 m); stationary phase, OV-101. Column temperature programmed from 80° to 180° at 4°/min.

The widespread occurrence and transport of pesticides and other pollutants in the air are well documented. An airborne fallout sample from the southern part of Sweden[5] reveals that in addition to organochlorine residues (mostly PCBs) a number of non-halogenated unidentified substances are present (Fig. 7).

When the distance between the electrodes of the ECD was decreased, the detector also responded to other, non-halogenated compounds. A mixture of methyl esters of fatty acids resulted in reversed peaks in the EC mode (Fig. 8). One peak

(lauric acid) not separated from the solvent peak by the FID was readily detected by the ECD. In this case, the detector responds as an electron cross-section detector in addition to its function by electron absorption and may as such aid in recognizing unknown peaks.

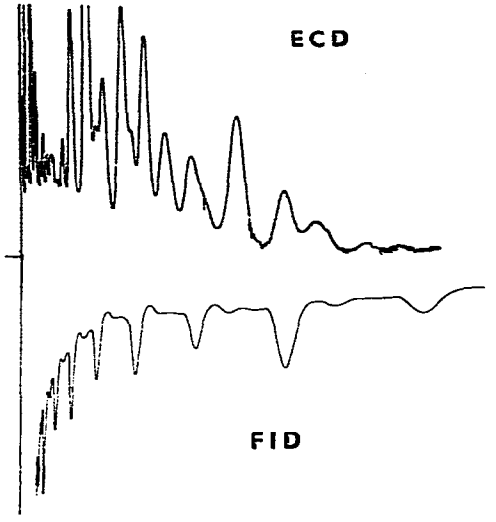


Fig. 7. Response of ECD–FID to a sample of airborne fallout from south Sweden.

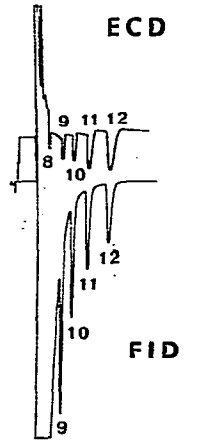


Fig. 8. Simultaneous response of ECD–FID to methyl esters of fatty acids, after decreasing the distance between the electrodes of the modified ECD cell. For peaks see Fig. 3.

CONCLUSIONS

The combination of ECD and FID in series offers the advantage of simultaneously detecting compounds with different properties in the same sample. The system is simple in construction and maintenance and requires no major modification of the gas chromatograph. Since no splitting is used, the accuracy of the quantitative determination of compounds eluted from the column is comparable to that of a single system. Capillary columns and low-volume ECDs which require no scavenging gas increase the separation efficiency of the system without a loss in sensitivity. By a careful choice of operational parameters to optimize the performance of the detectors, samples of different origin are conveniently handled, resulting in additional information to that normally obtained by a single injection into a gas chromatograph.

ACKNOWLEDGEMENTS

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