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A DISC DETECTOR FOR LIQUID CHROMATOGRAPHY

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SUMMARY

This detector for liquid chromatography is reliable and cheap. Its main component is a rotating circular net. Column effluent is continuously deposited on the net, which enters a flame ionization detector after the evaporation of the liquid phase.

The detector can be used with advantage as a so-called thermionic detector (AFID). It can be connected to the amplifier of any gas chromatograph with flame ionization detection or to any other electronic amplifier.

INTRODUCTION

While gas chromatography (GC) is used in the analysis of volatile substances, liquid chromatography is used primarily in the analysis of compounds that cannot be vaporized. Both of these methods necessitate the use of a device that detects a compound to be analyzed after the separation of individual fractions. The flame ionization detector, used in GC, is one of the most versatile and sensitive detectors, and efforts have been made to extend its use to liquid chromatography.

The use of the flame ionization detector in liquid chromatography requires a device to transfer the sample from the column to the detector. JAMES *et al.*[1,2] and SCOTT[3,4] used a wire that passes from one coil to another through the point at which the sample is deposited on it, through the chamber in which the solvent is removed and then into the pyrolysis chamber in which fractions are converted into volatile portions that are swept into the ionization detector. HAAHTI *et al.*[5] used, in place of the wire, a closed loop formed by a gold chain.

The disadvantage of these "wire detectors" is the problem of depositing the sample from a chromatographic column on to the wire. The carrier wire must have a relatively small cross-section in order to be easily re-wound, which is a disadvantage owing to the small carrier surface. Only a small portion of the solution from the column is transferred on to the wire, while an unused portion is retained in a waste reservoir. The fractions are deposited less quantitatively as the extent to which the mobile phase coats the wire decreases. Hence, if the mobile phase is pure water, the fraction is deposited on the wire in such a small amount that it cannot be detected. The system in which the wire or the chain is passed directly through the flame of the detector cannot be used, in spite of its simplicity, owing to the large amount of noise.

The disc detector described in this paper is a flame ionization detector with a disc transfer of fractions, which permits the relatively simple transfer of the liquid from the column into the combustion space of the detector. The disc is most frequently a net, the surface of which can be enlarged either chemically, electrolytically or mechanically. The net also permits impregnation materials to be deposited (even continuously), and such material can serve either as a combustion catalyst or as an ionization medium for a thermionic detector.

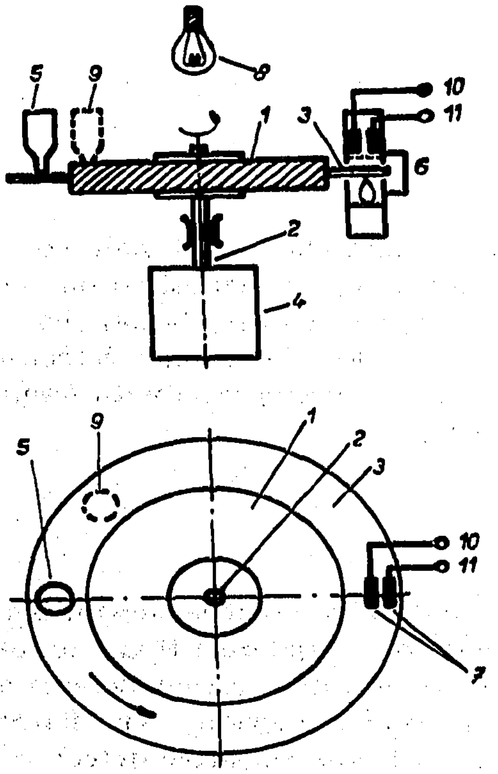

Fig. 1. Diagram of transfer device. 1 = Rotating body; 2 = shaft; 3 = net; 4 = motor; 5 = column; 6 = flame ionization detector; 7 = electrodes; 8 = infrared lamp; 9 = solution for impregnation of the net; 10, 11 = connectors to the amplifier.

The disc detector is shown in Fig. 1, and consists of a rotating body (1) on a shaft (2), which is connected to a driving motor (4). The circumference of the rotating body is formed by a collecting plate (net) (3), which can be heated with an infrared lamp (8) during the operation. Over the collecting plate (3) is situated a chromatographic column (5) and the ionization detector itself (6), part of which is formed by the electrodes (7), the connectors of which (10, 11) are connected to a detector amplifier.

The device operates as follows. The shaft (2) of the motor (4) revolves the rotating body (1) in the direction of the arrow-head. The effluent drips from the chromatographic column (5) on to the collecting plate (3). If necessary, an impregnation substance can be deposited on the collecting plate (3) from a container (9). As the collecting plate is heated with the infrared lamp (or with the heat from the detector), the mobile phase evaporates before the fraction reaches the detector itself. Here the fraction is combusted and the products, produced by passing through the electrodes, cause a change in ionization. After being amplified, these changes are registered on a recorder.

The detector can also be adjusted in such a way that the fraction is only pyrolyzed on the collecting plate and combusted in the burner above the plate, and the change in ionization is then measured.

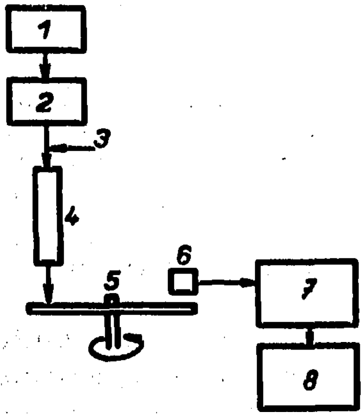

Fig. 2. Diagram of the chromatograph. 1 = Container for mobile phase; 2 = damper of pressure impacts; 3 = sampler; 4 = column; 5 = rotating net; 6 = detector; 7 = amplifier; 8 = recorder.

EXPERIMENTAL AND RESULTS

A liquid chromatograph, the design of which is shown in Fig. 2, was used for the study of the disc detector. The mobile phase (light petroleum + 20% of benzene or 1% of isopropyl alcohol) is pumped from a reservoir (1) with a pump (Mikrotechna, Prague) through a damper of pressure impacts[6] (2) and a sampling device[7] (3) into a column (4).

A stainless-steel column, 100 cm long with I.D. 2 mm, was packed with silica gel of 50–71 μm mesh (Lachema, Brno) that had been activated for 5 h at 180°. The weight of packing was 2.16 g. The solvent flows out from the column on to the rotating net (5). The mobile phase is removed from the sample during the rotation of the net and the pure sample is carried into the detection unit (6). The signal is amplidfied by a Vibron Electrometer 33 B-2 amplifier (7) set at an input resistance of $10^8\,\Omega$, with a range of scale of 1000 mV. Any other suitable equipment, *e.g.*, for the amplification of the signal of the flame ionization detector used in GC, can be used in place of the amplifier mentioned here. After being amplified, the signal is registered on an EZ 3 compensation recorder (Laboratory Equipment, Prague) with the range set to 5 mV.

The transfer device used in this work was the rotating net. Because of the lack of suitable material, a circular iron net, usually used for Pyrex glass vessels, was used. The net used influences the design of the device and the selection of the operating conditions for the detector (platinum net, which could be used for only a short time,

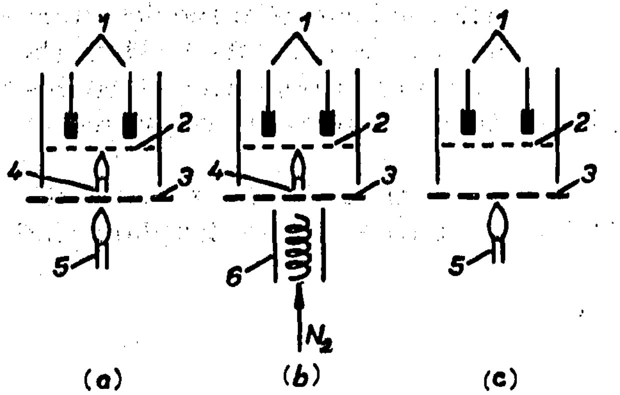

Fig. 3. Diagram of the flame ionization detector setting. (a) Double-flame detector; (b) single-flame detector with an electric pyrolysis furnace; (c) single-flame detector. 1 = Electrodes; 2 = screen; 3 = rotating net; 4 = upper burner; 5 = lower burner; 6 = electric pyrolysis furnace through which nitrogen passes.

was especially useful as it gave good wettability and excellent heating of the net in the detector space).

All three detection systems shown in Fig. 3 were tested for detection. Only simple experimental models were used in each experiment, for which the operating conditions used were far from optimum. The use of the flame for the heating of the rotating net (Figs. 3a and c) is successful if a mixture of air and hydrogen is used. With these two systems, the combustion products are transferred by the draught of hot combustion products upwards between the two electrodes.

The arrangement according to Fig. 3c in a prototype model gives a large amount of noise. The ionization efficiencies obtained for the systems shown in Figs. 3a and c are comparable with the results obtained for the system in Fig. 3b, which was the preferred system.

The use of an electric furnace is advantageous, especially for easy manipulation. In this arrangement, nitrogen passes through the furnace and transfers vapours or pyrolysis products from the net into the combustion space of the detector. With the use of hydrogen, not only is the sensitivity of detection increased but also the amount of noise is decreased.

Reproducibility of analyses and ionization efficiency of the detection

The sample was injected with a Chrominject syringe with a PTFE piston at an inlet pressure of the mobile phase of 5 atm, with good results. A 10-μl volume of 10% squalane diluted with the mobile phase was sampled. The length of the stroke of the piston was 15 mm for a 10-μl volume and the estimated error of sampling was $\pm$ 0.2 μl.

The average area under the curve was 153 $\pm$ 5 mm^2 for 10 μl of squalane and for ten measurements. The total error of the determination (including sampling) was 4%.

The ionization efficiency was calculated and for the present prototype equipment it is 3.4×10^{-2} C/g-atom of carbon, or $3.5 \cdot 10^{-5}$ %. The results are therefore ten times better than those obtained with the liquid chromatograph with a wire fraction carrier (the comparison holds for both systems without the use of hydrogenation).

Response linearity

The dependence of the response on the sample size was investigated over the range 0.1–2 μl of squalane. Larger samples could not be taken as it was impossible to decrease the sensitivity of the recorder in the described arrangement. The value of the response is dependent on the temperature of the hot nitrogen that heats the net, on the profile of hot air flow lines, on the secondary thermal radiation of the furnace and, to a great extent, on the leakage of the ionization current, which affects the detection sensitivity by one order of magnitude (with a prototype of the original device).

The results are reproducible with any furnace arrangement but the dependence of the response on the sample size need not always be linear. In general, it was found that the higher the temperature of the nitrogen, the higher was the detector response. If the furnace is insufficiently large, pre-evaporation of the sample takes place. Then the graph of the dependence of the response on the sample size does not pass through the origin of the ordinates but intersects the axis on which the sample size is plotted.

The dependence of the response on the sample size is shown in Fig. 4 for the furnace which was formed by a 150 W body from a brazing solder into which was inserted a metal jet with a V-shaped opening. In the experiments performed, the net was cooled in order that sample evaporation might be achieved on the unwanted spots. The values for samples of 1 and 10% squalane solutions diluted with the mobile

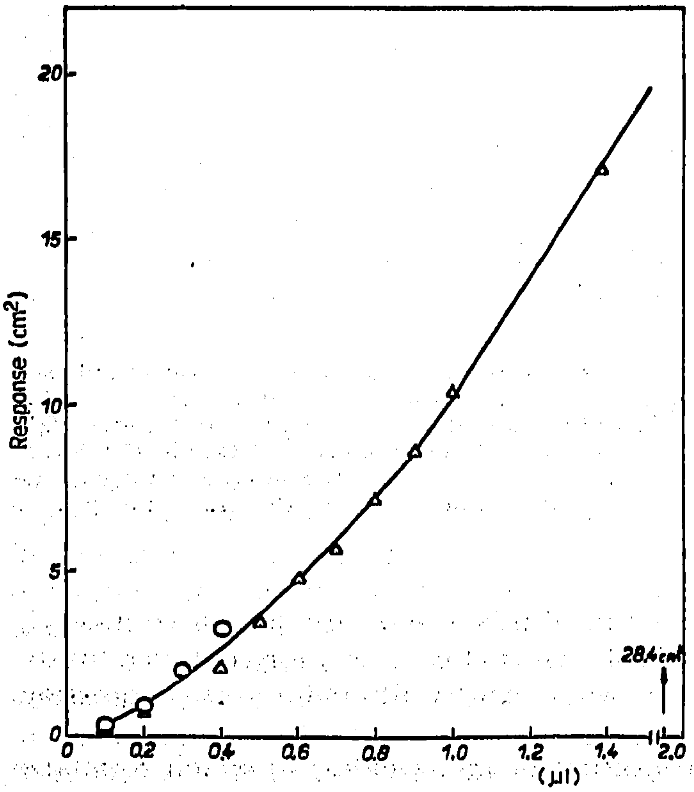

Fig. 4. Dependence of the response on the sample size. Column: length 1 m, I.D. 2 mm; packing, 2.16 g of silica gel L 50/71 (Lachema, Brno). Mobile phase: light petroleum + 20% of benzene. Sample: squalane diluted with mobile phase; △ = 1% and ○ = 10% solution.

phase are given in Fig. 4. The dependence found was not linear, as the detector prototype used did not meet all the design requirements. The response is in no instance dependent on the flow-rate of the mobile phase.

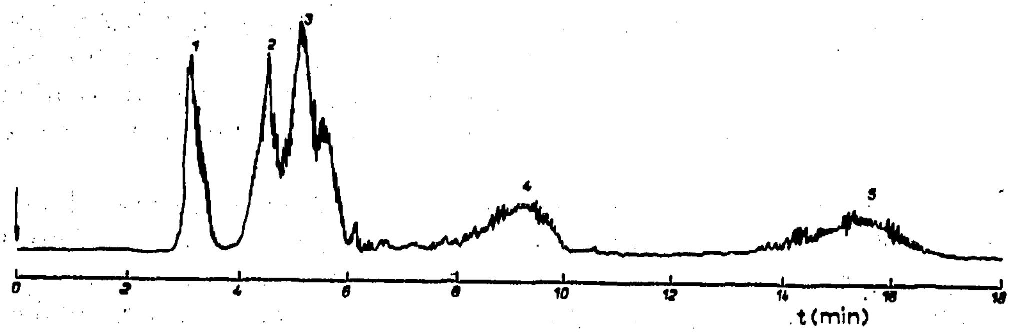

Fig. 5. Analysis of squalane with a mixture of phthalic acid esters. Column: length 1 m, I.D. 2 mm; packing, 2.16 g of Silica Gel L 50/71 (Lachema, Brno). Mobile phase: light petroleum + 1% of isopropyl alcohol. Sample: 5 μl of a mixture containing squalane (1) and technical esters of phthalic acid: dioctyl (2), dibutyl (3), diethyl (4) and dimethyl phthalate (5) in the ratio 1:1:2:5:10. No RC filter[8] was used for noise suppression.

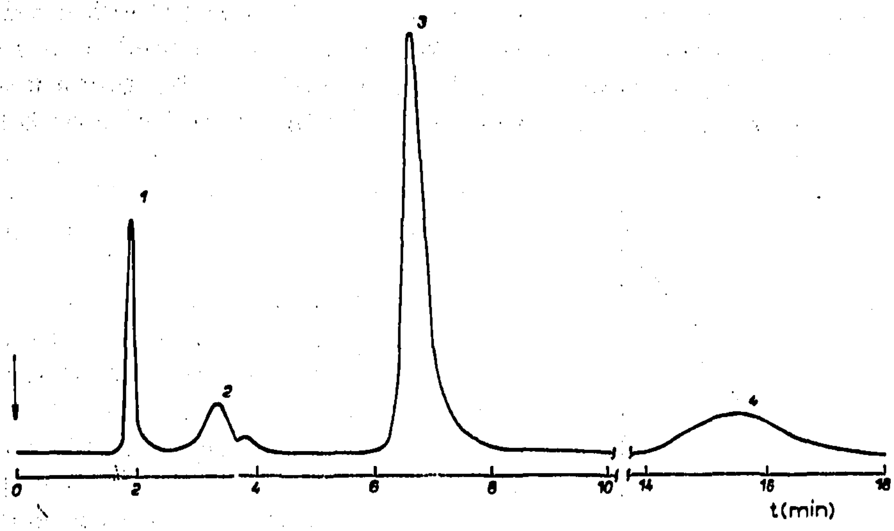

Fig. 6. Analysis of squalane with a mixture of insecticides. Column: as in Fig. 4. Mobile phase: light petroleum + 20% of benzene. Sample: squalane (1) and saturated solutions of lidykol (2) containing mainly DDT, lindane (3) containing mainly hexachlorocyclohexane, and endrin (4). The saturated solutions were filtered before use so that the sediment containing talc might be removed. An RC filter[8] was used for noise suppression. A 20-μl volume of the injected sample contained squalane with the saturated extract of lidykol, lindane and endrin in the ratio 1:40:30:30.

Examples of analyses

An example of the separation of an artificial mixture of squalane with dioctyl, dibutyl, diethyl and dimethyl phthalates is shown in Fig. 5. A more detailed study of the admixtures was not carried out in this work. An RC filter[8] for noise depression was not used in this work.

An example of the separation of a mixture of insecticides, to which squalane was added, is shown in Fig. 6. The figure shows the chromatogram obtained with the use of filters. If a suitable filter is selected, the curve is not much distorted and the area under the curve is not affected[8]. The flame ionization detector with a tip saturated with sodium sulphate (*i.e.*, in the arrangement identical with that with an alkali flame ionization detector) was used for the analysis of insecticides (Fig. 6). The sensitivity of the detection increases substantially for compounds that contain chlorine or phosphorus. For example, in the pesticide sample of lidykol used, so little DDT was contained that proof of its presence (fraction 2) was possible only after the use of sodium sulphate on the tip in the vicinity of the electrodes.

DISCUSSION

The flame ionization detector that is used in liquid chromatography has, in direct use[4], a higher level of noise than that which is common in GC. This is the reason why an indirect method of detection[9] is used.

The increase in noise can be explained by changes in the capacity between the electrodes and also by changes in the temperature of the electrode space. Both of these changes are caused by the movement of the transporter, whether it is a wire or a disc formed by a net.

No change in capacity should appear with an ideally flat, rotating disc. In practice, however, two variable distances of the net from the electrodes must always be considered. The metal net as a whole is always uneven and the grid consists of wires that are connected to one another in two mutually perpendicular directions, and therefore the shape of the net mesh with regard to the electrodes varies with time. The smaller is the collecting electrode, the more will this inequality apply. On the contrary of course, if the collecting electrode is as large as the net, in the boundary case, this effect cannot apply to a substantial extent, provided that the temperature is the same everywhere. In the place where it is heated, the net will affect the electrodes more strongly. Therefore, it is not suitable for the electrodes to be placed directly over the flame that is used to heat the net.

Changes in temperature occur if the flame of the lower burner is very narrow in comparison with the net mesh. Then, there are occasions when the flame heats the wire filaments and other occasions when the flame passes through the mesh of the net. If the net sinks in the direction of the flame it is heated, and if it rises then it becomes cooler.

The flame of the burner under the net is adjusted in such a way that a greater surface area of the net is heated. The position of the jet of an air–hydrogen burner, its distance from the rotating net and the ratio of the air to hydrogen are decisive for the optimum use of the detector in the systems shown in Figs. 3a and c. The lower burner can, however, be replaced with an electrical furnace through which flows nitrogen (Fig. 3b), hydrogen or a hydrogen–nitrogen mixture. The temperature of the hot nitrogen can easily be adjusted and the amount of the gases flowing through the furnace can be well defined.

The new disc transporter is formed by the circular net or by a plate with a suitable porosity. The disc is compressed between two smaller stabilizing flat discs, and if it is formed by the net then it must be relatively thick and the mesh must be fine. The margin of the disc only is used for the transfer of sample. It is advantageous if the circumference of the disc moves between ball bearings.

A platinum net would be an ideal disc, especially if it is coated with platinum black, as it is easily wettable and has a catalytic effect during the combustion. The net can be very thin and the sample can be well combusted on it. The disadvantage of platinum is its high price and its considerable softness. A stainless-steel net is acceptable for its availability and mechanical properties, but unfortunately its wettability is poor. The required characteristics can be obtained by chemical treatment, electrolytic coating, impregnation with appropriate salts or merely by sand or metal blasting. A fine annealing will also improve the coatability.

If the net is impregnated with salts that have catalytic activity, the character of the decomposition process that is expected in the space where the sample is removed from the rotating net must be considered. In hydrogenation or pyrolysis (see the diagram of the detector in Fig. 3b), it would be suitable if the net were made of nickel or coated with a hydrogenation catalyst. In oxidation (see the diagram of the detector in Fig. 3c), the impregnation of the net with cobalt oxides is advantageous. As the sample on the net is transferred in a negligible absolute amount, conditions for perfect decomposition of the sample are obtained.

The speed of the movement of the transporter is very important. The speed at which the sample on the wire is introduced into the detector was studied with a so-called "wire" detector[10,11]. The sensitivity was found to increase with increasing wire speed. However, with some compounds, the sensitivity decreased at a very high speed. The wire speed recommended for most compounds is 6 cm/sec with the wire detector studied. YOUNG[10] mentions also that compounds that have boiling-points below 200° evaporate before they reach the required space.

The dependence of the sensitivity of the detection on the transporter speed can, however, be explained by a simple experiment. A sample, *e.g.*, of an oil, is deposited on a thin wire. If the wire is inserted into the flame, the sample has a tendency to move in the direction opposite to the flame and to evaporate at the same time. If the movement in the direction of the flame is more rapid than the movement of the sample in the opposite direction, the sample is carried into the flame and, provided that the flame temperature is sufficient for heating the wire to the appropriate temperature, the sample is combusted. If the temperature is not high enough or the movement of the wire too rapid, the sample passes through the flame without being combusted.

The use of the circular net in place of the wire enables the quality of the introduction of the sample into the detector to be changed substantially. The surface area of the net itself is much larger than the surface of one filament of the wire that is used with a "wire" detector, where the wire must have a very small diameter so that it can be wound on the coil. In addition, the meshes among the wires, or the places where the wires of the wire net come into contact, influence setting of the sample on the net very favourably. An active or mechanically enlarged net surface aids in the pyrolysis of the sample. Surface treatment, however, cannot easily be achieved with a carrier medium for which the proper body varies with time, or twists, as does the so-called "chain" detector[5] with which complete combustion or pyrolysis of the sample does not occur.

A better "settlement" of the sample on the net prevents the sample from travelling into a colder position. The sample is better able to enter the pyrolysis space of the detector as it is well spread out and combusted. The net can also be immediately cooled before the entrance. Rapid pyrolysis can be achieved with a small but very hot air–hydrogen flame. This flame is hot enough to pyrolyse quantitatively even a sample adsorbed in a thin layer of silica gel on a rotating mica plate. A high pyrolysis temperature can also be obtained by using a small porcelain jet that is wound with a platinum wire. If the jet tip is metallic, the effects of radiated heat and of hot nitrogen apply simultaneously.

The detection of the sample on the net can be carried out with the aid of the three detector systems shown in Fig. 3. It is common to all three systems that a thin net-screen is placed between the electrodes of the flame ionization detector and the rotating disc. This screen functions as a Faraday cage and as a stabilizer of the flow of gases and vapours.

The sample is combusted on the net and the ionization is measured between the electrodes with a single burner system. But in the case of a double burner system, the flame of lower burner is much smaller and the noise level is thus decreased. The sample is partially combusted, partially pyrolyzed or also hydrogenized. The flame of the upper burner is very small and is situated above the screen, and is used to increase the conductivity between the ionization and collecting electrodes and to combust entirely organic compounds.

The advantage of a small upper flame is retained with the single burner system with an electric furnace. According to the type of gases that are carried to the vicinity of the net, the sample is pyrolyzed or hydrogenized. The electrical connections and design requirements differ for the individual systems.

CONCLUSIONS

A new system for the transfer of fractions from a chromatographic column into the flame ionization detector is described. The results obtained are very favourable. A great success is the fact that the detector is not dependent on the intensity and changes in the flow-rate of the mobile phase through the column, which is unavoidable for any gradient or programmed elution in liquid chromatography.

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