CHROM. 6069

THE GAS–LIQUID PARTITION DETECTOR

A NEW PRINCIPLE FOR INDIRECT NON-DESTRUCTIVE DETECTION OF NON-VOLATILE SOLUTES*

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SUMMARY

A moving carrier detector is described. The principle of operation of this detector can be summarized as follows: A moving chain or other carrier is wetted with a chromatographic effluent, consisting of volatile solvent and a (relatively) non-volatile solute. Next the carrier passes a solvent elimination zone, as in conventional wire detectors. Hereafter the carrier enters a zone, where a suitable (*e.g.* for electron capture detection) gaseous substance or mixture is partitioned into the residual at appropriate conditions. An indirect solute signal is obtained in the next zone, where this gaseous substance is eluted from the original solute in a stream of carrier gas and through an appropriate specific (*e.g.* electron capture) or general (flame ionization) gas detector.

The application of the above principle is being illustrated using a circulating chain detector system. The apparent observations of performance have been tentatively studied.

It seems, that the direct application of the principle to chromatogram monitoring is unpracticable due to the number of variables involved. The main emphasis then lies in the "new" way of employing gas–liquid partition.

INTRODUCTION

In gas–liquid chromatography, the partition between different solutes and a uniform phase forms the basis for the separation of the solutes. Solutes are usually characterized by their retention or partition parameters in such a chromatographic system. However, the reverse process can also be carried out: if an unknown substance is used as the stationary phase, then under given conditions the behaviour of known solutes in a gas–liquid partition system characterizes to some degree at least the quality and quantity of the stationary phase. As the partition equilibrium is

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a relative concentration-constant system, this means that the amount of a stationary phase can be measured if, under given conditions, the partition coefficient and the concentration of the solute are known.

With the moving carrier detectors for liquid chromatography[1–3], the detection of non-volatile solutes in a (relatively) volatile solvent is carried out by eliminating the solvent by evaporation, followed by final gas-phase detection of the non-volatile residue either directly on the carrier[2,3] or after pyrolysis of the residue[1].

The general principle of these detectors is illustrated in Fig. 1. In spite of some structural differences, the moving carrier detectors basically operate on a destructive gas-phase detection principle.

However, the residual solute zones on a moving carrier can also be considered to form a stationary phase, which can be characterized by its uptake of a gaseous solute through gas–liquid partition under appropriate conditions. This gaseous solute can then be eluted and detected in a stream of carrier gas at a higher temperature. The principle is illustrated in Fig. 2.

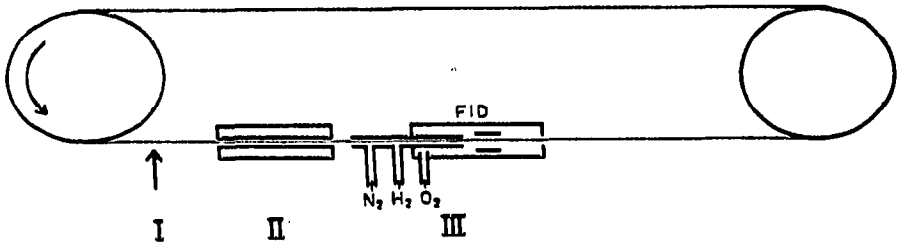

Fig. 1. Schematic illustration of conventional circulating chain detector. I, Wetting of chain with sample or effluent; II, elimination of solvents by evaporation; III, detection of non-volatile residue by FID.

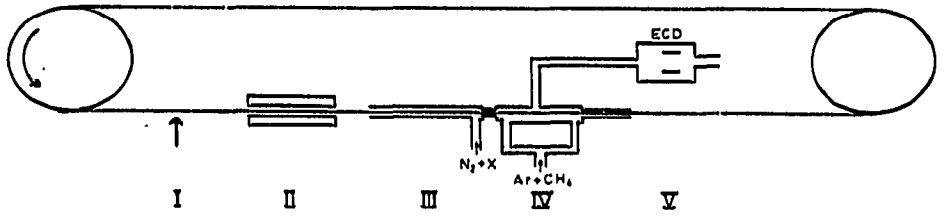

Fig. 2. Schematic illustration of the new gas partition detector. I and II as in Fig. 1.; III, partition chamber, to permit volatile solute X to dissolve in non-volatile residues on moving carrier; IV, stream-splitter compartment, where solute X is eluted from the non-volatile "stationary phase"; V, gas-phase detector (ECD) monitoring the eluted solute X in a carrier gas stream.

As sensitive specific detection methods such as that involving the use of the electron capture detector (ECD) are available, it is an advantage to select the partitioning solute so that a high specific sensitivity is achieved.

This detection principle seemed to us to be attractive and of particular interest because of the following *a priori* features:

(1) The method is non-destructive in relation to the solute.

(2) The gas–liquid partitions at stages III and IV (Fig. 2) allow fast operation, as only the equivalent of one theoretical plate is needed.

(3) The principle can be extended to a "physical multiplication" (*cf.* chemical multiplication[4]), by including several partitioning solutes and/or several partitioning stages in series.

EXPERIMENTAL

Apparatus

A circulating-chain apparatus was constructed according to the schematic diagram shown in Fig. 2. Linear chain speeds of 1–10 cm/min were attained with a step-motor, and gas flows were controlled with standard equipment. The partitioning chamber (III) is supplied with a stream of nitrogen, previously saturated with the partitioning solutes in a gas washing tube. The temperature of the partitioning chamber is regulated by a water jacket. The elution stage (IV) consists of a stream-splitting system through which an argon–methane mixture is led to the chambers. From the mid-point of this chamber an exit line leads to the ECD (Fig. 3). The temperature (here always higher than that at stage III, in order to achieve elution of the partitioned solute) is regulated by direct electrical heating.

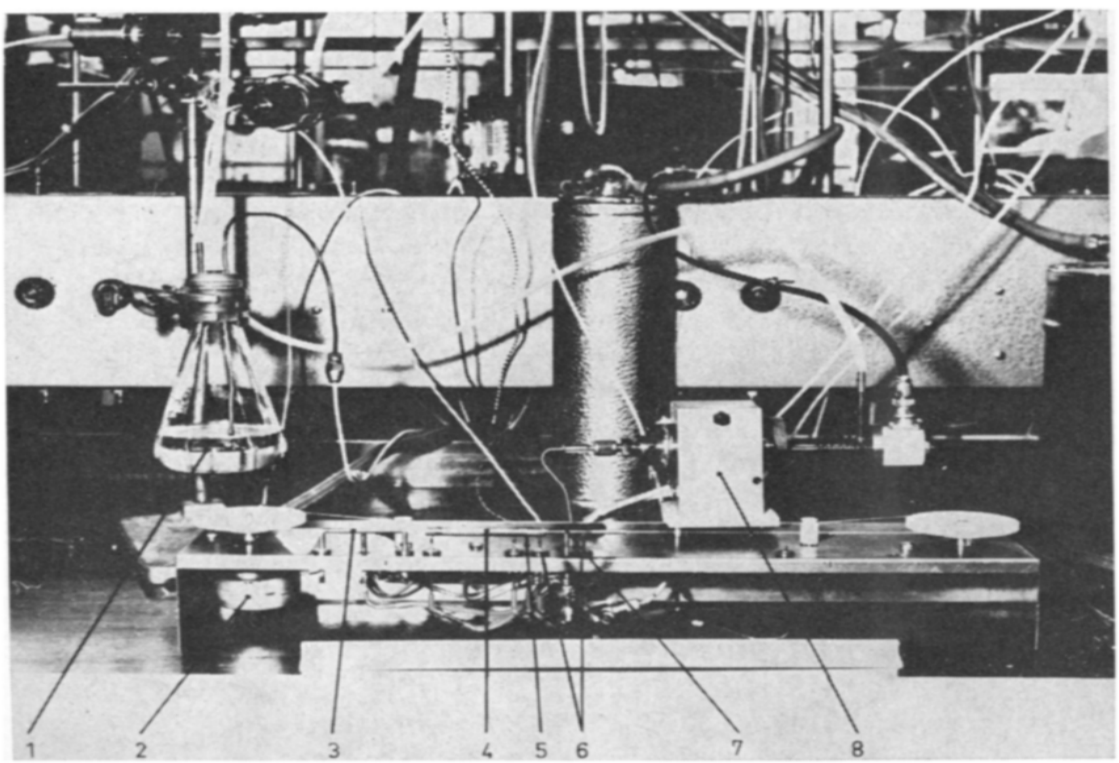

Fig. 3. Photograph of the new partition detector. 1, Saturation bottle for partitioning agent (CCl_4); 2, driving motor for moving (circulating) carrier (chain); 3, evaporation zone to eliminate original solvent of sample or effluent; 4, thermostated gas-partition chamber with 5, inlet for carrier gas saturated with partitioning solute; 6, inlets for elution gas ($Ar–CH_4$); 7, heated elution chamber with central exit leading to 8, ECD detector.

The initial balancing of the system is carried out as follows. The argon–methane stream to stage IV is set to a pressure such that the flow through the ECD is 50–60 cc/min. After reaching maximum steady background on the ECD, the nitrogen,

saturated with partitioning solute (carbon tetrachloride, Freons), is turned on; the flow is then adjusted to a level just below that which produces a signal on the ECD. The presence of a signal would indicate that a higher pressure exists in the left-hand arm of the stream-splitter (see Figs. 2 and 3), resulting in a "leak" of nitrogen and partitioning solute gas into the elution chamber IV.

The chain (a clean blank) is then set to an advance of approximately 5 cm/min. If the ECD signal changes (decreases), the nitrogen flow should be decreased to re-establish the stream-splitter balance as above. In the prototype used for this work (Fig. 3), the following ranges of conditions were used:

Chain speed	1–7 cm/min
Nitrogen + partitioning solute	10–50 cc/min
Argon-methane input	80–120 cc/min
Argon-methane through ECD	40–60 cc/min
ECD (Becker Model 714), ^{63}Ni, temperature	300–350°
Partitioning chamber temperature	Ambient to 90°
Elution chamber temperature	50–150°
Partitioning solutes	carbon tetrachloride, acetone, chloroform, Freons (technical) and mixtures of these substances

Performance of the system

The performance was tested by spotting known amounts of standard glycerides, sterols and hydrocarbons on the chain. It was immediately observed that, in spite of mechanical contact at the drive wheels, the signals recorded by passage of the spots through the elution chamber repeated for each full turn of the chain, even when the apparatus was operated overnight. Within the adjustable ranges of variables, the following preliminary observations can be made.

(1) The partitioning chamber temperature should be above the melting point of the spots. Below the melting point, the signal decreases sharply to a level of only 1–5%. This is due to the fact that, instead of gas–liquid partition in chamber III, gas–solid partition occurs.

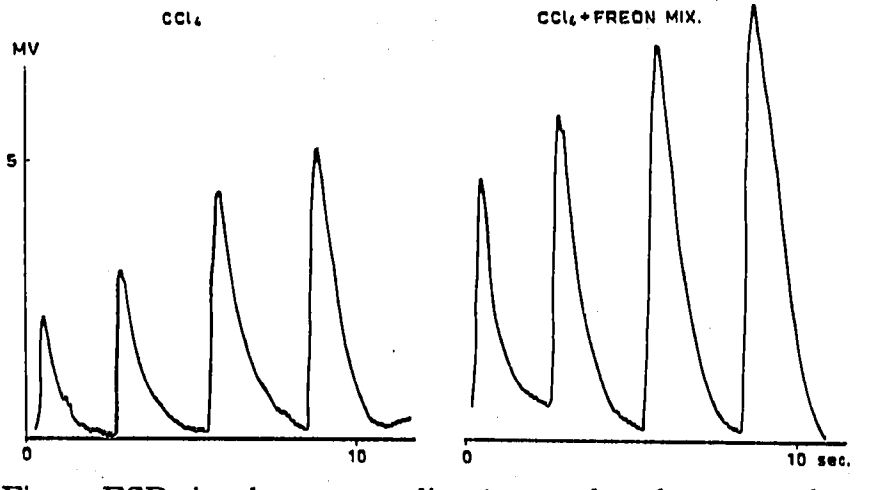

Fig. 4. ECD signals corresponding to samples of 5–20 μg of a standard glyceride mixture on the chain. Partitioning solutes: left, carbon tetrachloride; right, same, plus a Freon mixture with a boiling range of 30–60°.

(2) At slow chain speeds (1–2 cm/min), a decrease in signal could be observed for a series of spots. This was interpreted as partial elution of the solute in the stream-splitting region, where the direction of flow of the argon–methane mixture is towards chamber III. This effect has an understandable relationship to the temperatures of chambers III and IV.

(3) If a multicomponent partitioning gas was used, an increase in signal (compared with that obtained with single component solutes) could be observed (Fig. 4). Theoretically, each of the dissolved solutes has its own characteristic partitioning coefficient that is basically independent of the others. The total solute eluted at stage IV and producing the signal is thus the sum of the amounts of each partitioned solute component, *i.e.*, a "physical multiplication" effect is achieved. However, as partitioned solutes can serve as stationary phases for each other, the over-all situation in chamber III becomes complicated.

(4) As the gas–liquid partition in stages III and IV, *i.e.*, the "play-out", proceeds rapidly, whereas the "play-in" (the chromatogram) may take a long time, these stages can be separated so that a slow carrier speed is used in the "play-in" stage and a fast speed in the "play-out".

(5) The non-destructive method of detection permits a fast repetitive monitoring, thus rendering possible the elimination of random noise by an averaging process.

(6) Experiments were carried out in which the ECD was replaced by a flame ionization detector (FID) and benzene, light petroleum, etc., were used as the partitioning solutes (Fig. 5). The FID signals obtained for known spots on the chain indicated that the recovery of the amount of benzene was of the order 1:1000 of the amount of the sample spot.

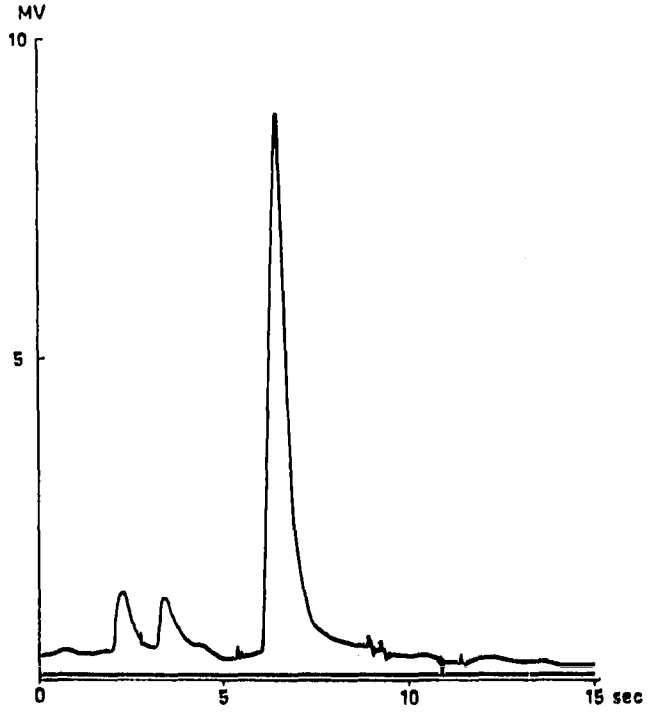

Fig. 5. FID signal of two 5-μg and one 50-μg sample of a standard glyceride mixture with benzene as partitioning solute.

Owing to the number of variables involved in the method, it seems, however, that the direct applicability of the principles for chromatogram monitoring is limited. However, the use of gas–liquid partition in a "perverse" way (by conventional standards) may prove useful for a variety of other applications.

ACKNOWLEDGEMENTS

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