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NOVEL TRANSPORT DETECTOR FOR LIQUID CHROMATOGRAPHY

I. PRELIMINARY EXPERIMENTS

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SUMMARY

A transport detector mechanism is being developed for the removal of volatile solvents from a chromatographic eluent and the detection of residues using a flame ionization detector. The mechanism employs a number of novel features, which allow close control over solvent removal and permit the detector to be used for relatively volatile sample materials. A number of results obtained using normal phase chromatography are presented, and the characteristics of the experimental system are discussed.

INTRODUCTION

High-performance liquid chromatography (HPLC) has become one of the most widely used techniques for routine analyses¹, and this is due in part to the quality and relatively low cost of many of the commercial chromatographic systems available. Over the past decade the reliability of pumping systems, the efficiency of columns and the sensitivity of detectors have improved considerably, and the wide range of detection systems now available is capable of dealing with the majority of application requirements. However, it is still the case that there is no universal, high sensitivity detector available to compare with the flame ionization detector of gas chromatography (GC). The most popular HPLC detector remains the UV absorption detector¹, with other detectors, such as fluorescence and electrochemical, being used where the sensitivity of absorbance detectors is inadequate. However, for many compounds none of these detectors is suitable, and the only commonly encountered alternative is the refractive index monitor, which tends to operate with rather poor sensitivity.

Many attempts have been made over the past 20 years to utilize the sensitivity of flame ionization detection (FID) in liquid chromatography. The approach has generally involved the deposition of the chromatographic eluent onto a moving chain²⁻⁹, belt¹⁰⁻¹⁸, wire¹⁹⁻³⁰ or disc³¹⁻³⁸ (the transport mechanism), which may then be heated to evaporate the volatile components of the eluent, leaving any less volatile residue on the support. The problem was then reduced to that of transferring the residue to the detector.

Hahti and Nikarri² used a 1-mm diameter gold chain driven by a synchronous motor at a velocity of 1 mm s^{-1} as the transport mechanism. Solvent was removed by air heated to 120°C and the chain passed directly into an FID flame, *ca.* 2 mm above the jet, with the chain biased to *ca.* 10 V above the jet potential. The system was used for classical chromatography, although quantitative measurements were not successful owing to the loss of components from the chain and the electrical noise generated by the chain mesh. Some of these problems were tackled by Stouffer *et al.*³, who used a platinum chain that passed vertically through the FID flame, so that the collector electrode was concentric with the chain. Karmen^{4,7} used a continuous metal chain from which the eluent was evaporated, followed by strong heating in a nitrogen-filled tube. Volatile vapours and pyrolysis products were swept into a flame ionization detector. This system had difficulties with non-volatile material melting and spreading over the chain, and with crystalline material spattering before pyrolysis. It was really limited to moderately volatile compounds that could be pyrolysed below 250°C .

A major improvement was made by Scott and co-workers^{20,24} who employed a nickel wire that passed through the eluent and through a two-stage glass tube, through which argon was passed. The first stage was heated to evaporate the solvent, with the vapour being swept away by the argon. The second stage was heated much more strongly to pyrolyse the eluent residue. The argon pressure forced the pyrolysis products into a flame ionization detector. A subsequent enhancement²⁵ passed the wire directly into the flame. The device was developed into a commercial product, which became known as the moving wire detector. There were several difficulties with this approach: the relatively small amount of the eluent collected by the wire; the dimensional changes in the wire as it was heated; contamination of one part of the wire by contact with structural components; and the general lack of reliability of the mechanism.

In the more successful disc detectors eluent is deposited on a rotating disc. Owens *et al.*³⁵ used a rotating perforated metal disc (a 2.5-in. diameter platinum screen) to carry eluent from a gel permeation column into the flame (the disc was insulated at its hub). This system relied on relatively small gel permeation columns (0.01–0.125 in. I.D.) and low flow-rates, and was successfully applied to the detection of polystyrenes separated in THF. Dubsy^{36,37} used an 8-in. diameter ceramic disc, heated by an infrared lamp to evaporate solvent prior to passage through a two-part detector (the flame below the disc and the electrodes above), which could also be used as a thermoionization detector by continuously applying an alkaline metal salt to the disc. Szakasits³⁸ and Szakasits and Robinson³⁹ used a vertical spinning porous alumina disc, which passed through an oven to evaporate the solvent before the disc itself met a dual-nozzle flame. After passing through the flame, the edge of the disc was cooled by air drawn over the disc by a fan. Fischer and Kohl⁴⁰ employed a transport mechanism consisting of a rigid ring coated with a porous ceramic material to transfer eluent from a column to a pyrolysis oven fed by hydrogen (or helium) and nitrogen. The pyrolysis products were swept into a flame ionization detector or mass spectrometer. Dixon and Hall¹⁷ used a quartz-fibre belt mounted at the periphery of a rotating disc, with volatile solvent being allowed to evaporate within the heated housing, leaving any residue on the belt. The belt rotated into flame ionization detector and then into a hydrogen–oxygen “clean-up” flame, before cooling to receive further eluent. The principal difficulty with most of these approaches is that precise control of

evaporation is difficult. The disc needs to be cool to receive eluent and yet pass through the flame to combust the residue. The thermal mass of the disc makes it difficult to accommodate these conflicting requirements.

Transport mechanisms based on metal belts have also been used. Yang *et al.*¹⁸ described a device using a stainless-steel belt that is loaded using thermospray vaporization followed by subsequent pyrolysis (typically at 420°C) in the presence of a carrier gas, such as helium, which sweeps the pyrolysis products into a GC detector (in this case most of the work was carried out using a photoionization detector, although an electron-capture detector was also used). Hoskin¹⁹ has also described a two-part nickel belt onto which discrete droplets of eluent may be loaded, followed by evaporation and pyrolysis. This system forms the basis of a transport detector manufactured by Analink Ltd. With these systems the principal difficulty is the requirement of a limited temperature pyrolysis stage to avoid damage to the belt, coupled with the high thermal conductivity of the belt material.

We have designed a transport mechanism that attempts to overcome the limitations imposed by the continuous "analogue" mechanisms used in the past. By treating the eluent flow as a series of discrete packets of liquid it becomes possible to use a low conductivity support material and yet keep the thermal mass small enough to allow evaporation of the solvent and cooling of the support material to be carried out by controlled-temperature air-flows. In this paper the basic structure of the transport mechanism is described, and the parameters that effect the separation of solvent from sample component are discussed. A number of preliminary results are presented to demonstrate the practical operation of the detector.

DETECTOR

The detector consists of five components: the transport mechanism, the evaporation and cooling air-flow systems, the flame ionization detector, the controlling and data logging microcomputer, and the interface between the computer and the other components. During the design and construction of the detector there was a fairly clear distinction between each of these components, but a description of the system produces an unavoidable overlap between them. A major feature of the design is that the entire operation of the system is under the control of software in the microcomputer—there are no manual controls of any kind on the detector. Thus the transport mechanism is a specific item of hardware but its operation is governed by the computer system, which defines transport parameters to the interface electronics. In describing the system we will discuss each component in turn, even though this must result in aspects of the operation being described before the controlling mechanism has been detailed.

The transport mechanism consists of a two-part disc mounted on the shaft of a stepper motor fixed to the main chassis of the instrument. From the disc protrude a number of 1-mm diameter drawn quartz rods (40 on the experimental system), as shown in Fig. 1. Each rod is 12 cm long, protruding 10 cm from the disc, is located in a groove machined into the lower part of the disc and is held in place by an O-ring located in the upper part. The rods are not treated before use, apart from several passages through the FID flame, and the surface of the rods can be described as smooth but not polished. The stepper motor is operated so that the disc steps around

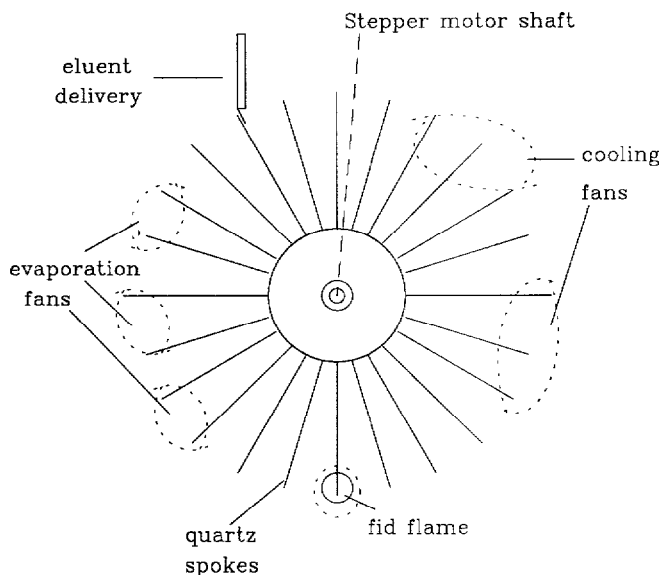


Fig. 1. Quartz rod assembly of the transport mechanism shown in relation to the other major components, the eluent delivery tube, evaporators and coolers.

maintaining one rod under the eluent delivery point, several rods over the evaporation points, one rod in the flame, and several rods over the cooling air-flows. Eluent is deposited on the rod at the delivery point, where the liquid is applied *ca.* 2 mm from the end of the rod. The disc mechanism is positioned at a slight angle from the horizontal (*ca.* 2°), so that the liquid tends to flow towards the end of the rod. While the actual amount of liquid deposited on any rod may be up to *ca.* 20 μl , in normal operation we deposit *ca.* 10 μl per rod. The rate at which the disc steps around may be varied up to about six steps per second, although again in normal operation the rate is likely to be about one step per second.

Once liquid is deposited on a rod, the rod moves over the evaporating air-flow, whose flow-rate and temperature are carefully controlled. In the experimental system three stages of evaporation are used, and different combinations of flow-rates and temperature may be used to evaporate different multicomponent eluents. The rods step from one evaporation stage to the next, remaining in a given stage for three steps. By the end of the third stage, the volatile eluent should have been evaporated. The rod is then stepped into the centre of the flame, where any carbon-containing residue is combusted and current is produced. The rods then step over two stages of cooling air-flow to ensure that they are cool enough to receive another drop of eluent by the time they reach the eluent delivery point again.

The air-flow systems are all based on variable speed fans, with the speed set by the computer. The air-flow system is outlined in side view in Fig. 2. The cooling fans are fixed under the main chassis of the system and blow their air through holes in the chassis. The evaporation fans are mounted at the ends of tubes that contain the mains-powered heating elements, and the heated air is also blown through holes in the chassis. Temperature sensors located in the evaporation air-flows ensure that the

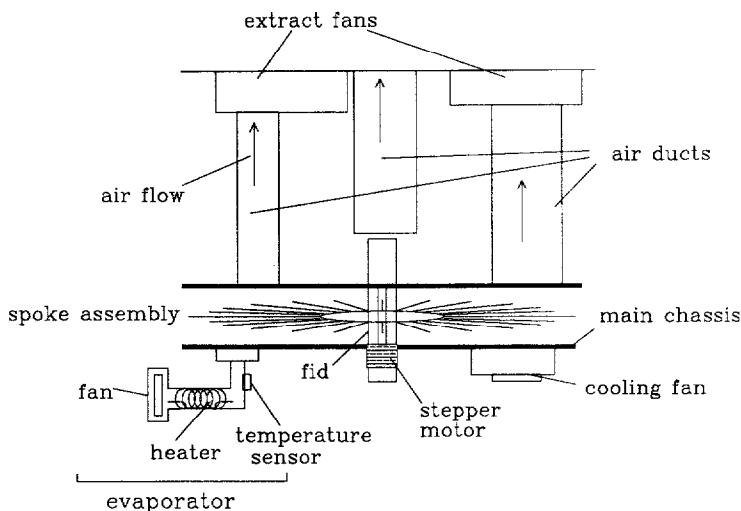


Fig. 2. Side view showing position of evaporator and cooler fans on the mounting plate.

forced-air temperature is maintained as required. Air-flows from the evaporation and cooling stages are kept separated from one another and from the ambient air in the instrument's housing; this prevents solvent-laden air from being drawn into the detector. The separation is maintained by allowing blown air to pass through holes in a baffle plate and then into tubes, which are maintained at a slight negative pressure by a pair of pressure balance exhaust fans mounted in the cabinet roof. The experimental system uses three evaporators, two coolers and two pressure balance fans, so that seven fan speeds and three evaporator temperatures must be specified by the computer during operation.

The FID system is shown in Fig. 3. Essentially the detector is a conventional one, *ca.* 70 × 15 mm I.D., with a slot cut in the outer wall to allow the rods to pass into the flame *ca.* 8 mm above the base of the flame. In the experimental system the collector consists of a 6-mm diameter platinum mesh held *ca.* 10 mm above the FID jet by a length of stainless-steel tubing. The hydrogen is brought into the detector through similar tubing, insulated from the support brackets and operated at a potential of *ca.* 300 V. The outer wall of the detector is mounted on a small plate, which slides under the rod path through a cut-out in the chassis using a drawer arrangement. The outer wall is grounded electrically. The collector current is passed to a transresistance amplifier, which generates a voltage signal that is digitized using a dynamic analog input interface to the computer.

The computer system controls all aspects of the detector's operation and the flow-rate of the chromatographic eluent (this avoids the risk of flammable eluents being accidentally pumped into a box containing mains-powered heaters!). The software is required to adjust the stepper motor's stepping rate to suit the user-specified eluent flow-rate, to adjust the evaporation temperatures and air flow-rates to suit the eluent composition and its flow-rate, and to adjust the pressure balance fans to ensure that the evaporation and cooling areas of the detector are operating under a negative pressure. The software also collects the detector signal data.

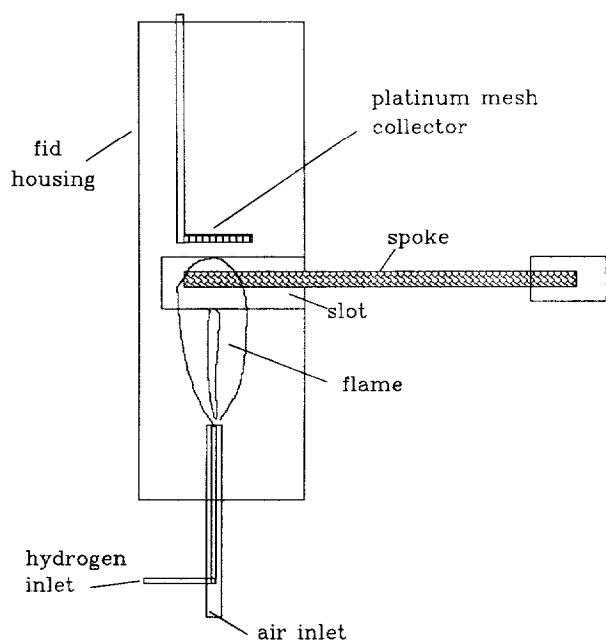


Fig. 3. Detector assembly, showing a spoke in position at the tip of the flame.

Because the detector operates in a sequential mode (*i.e.* one rod at a time is passed into the flame) the signal (at least when a component is eluting) actually consists of a series of rapidly changing peaks, each caused by a single spoke entering the flame, its residue starting to combust, and then combustion reaching completion. While the many ways of handling such data can become complex, they all require that the computer samples the signal at specified times after the rod enters the flame. Thus the computer must synchronize the signal readings with the stepping of the stepper motor. The computer must also display the chromatogram, and it is desirable to have this carried out in real time. Our software also provides facilities for plotting the chromatograms on a graphics plotter, although this is usually carried out after the chromatogram has been collected; the chromatograms reported below were produced in this way by plotting onto a laser printer. Finally, as the detector consists of a large box containing mains-powered heaters and a flame, and into which is passing flammable eluent and hydrogen gas, the computer system must monitor various safety aspects of the system and be able to take appropriate action in the event of a problem. In the experimental system the computer monitors the hydrogen flame (using a temperature sensor mounted in the detector chimney) and can shut off the hydrogen supply if the flame goes out. It also monitors the movement of the rods and can turn off the HPLC pump if the rods cease to move. Several other eventualities are catered for, and in response to most of these the heaters are all turned off while the fans speeds are all set to maximum and appropriate warning bleeps are delivered.

Although the detector's working is simple in principle, it will be clear that there are a number of parameters that are specified, monitored or controlled by the computer during operation. In designing the computer-detector interface it became

clear that either the computer could do everything (send the pulses to the stepper motor, monitor the evaporator temperatures and adjust the heater power several times a second, read the signal, etc.) or that some of these activities must be handled by purpose-designed electronics. We chose the latter approach, and an outline diagram of the control system is shown in Fig. 4.

An initial study has been undertaken to obtain an indication of the range of hydrocarbons to which the experimental version of the detector responds. It is difficult to present preliminary results without the reader arriving at incorrect conclusions, but it must be emphasized that the result reported below were obtained by selecting operating conditions that seemed reasonable. No attempt has been made to optimize the operating conditions (*i.e.* temperatures and air flow-rates), and the range of application would be reasonably expected to be increased by such optimization.

EXPERIMENTAL

A diagram showing the major components of the experimental detector is shown in Fig. 5. The chromatographic system consisted of a Knauer pump, a Rheodyne Model 7125 injection valve fitted with a 20- μ l loop, and a 150 \times 4.6 mm I.D. column packed with Partisil 5 μ m. The sample materials consisted of pyrene (SLR, Aldrich) and in some cases hydrocarbon standards provided by BP Sunbury Research Centre. All were used without further purification. Apart from pyrene, samples are identified by carbon number, *e.g.* C12 is dodecane.

Samples of 20 μ l of test compounds diluted in hexane were loaded onto the column and eluted with hexane-dichloromethane (3:1, v/v) at a flow-rate of 0.6 ml

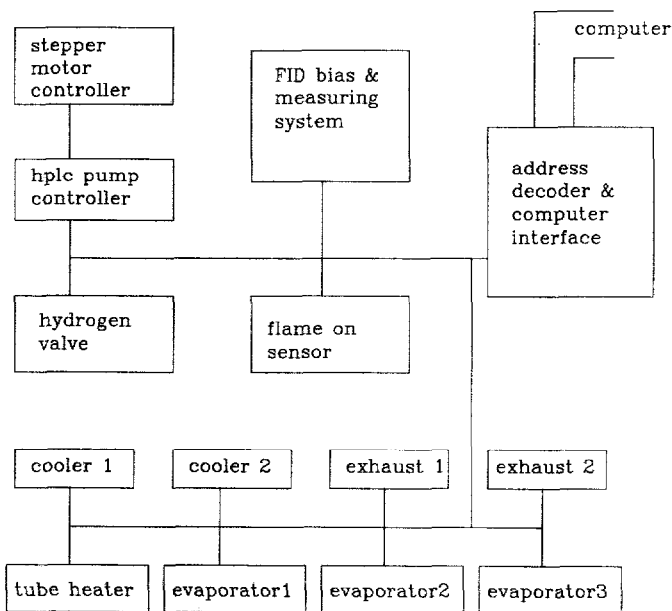


Fig. 4. Block diagram of major elements of the control system used to operate the transport detector under computer control.

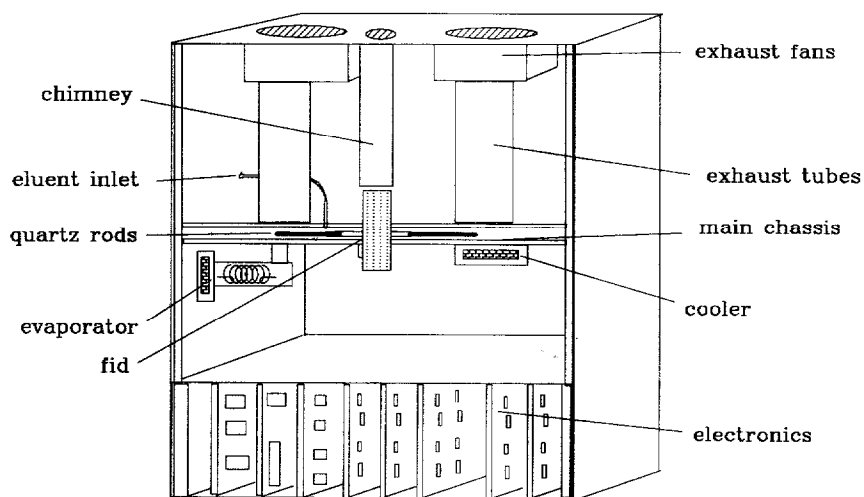


Fig. 5. Outline of the prototype detector showing the major components of the detector system.

min^{-1} . The detector was operated with the following parameters: eluent temperature, 55°C ; evaporator 1: speed, 98%; temperature, 120°C ; evaporator 2: speed, 68%; temperature, 130°C ; evaporator 3: speed, 56%; temperature, 130°C ; detector jacket temperature, 110°C ; step speed, *ca.* 1 s/spoke; detector amplifier gain, 33.

RESULTS AND DISCUSSION

The results presented represent initial studies of certain areas of interest associated with a transport detector system. The first question asked of any detector concerns its reproducibility, and results typical of many we have obtained are illustrated in Fig. 6. In this case the peaks arise from four samples each of $10\ \mu\text{g}$ of

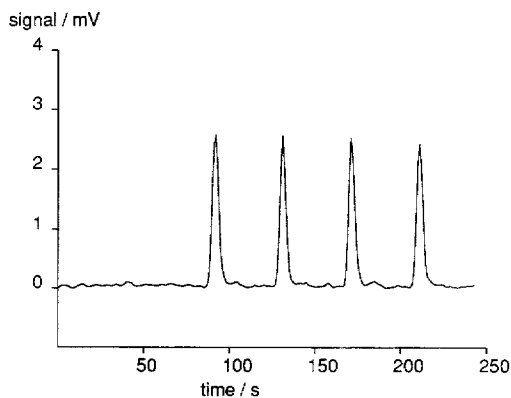


Fig. 6. Chromatographic signals recorded from four successive samples, each containing $10\ \mu\text{g}$ of pyrene in hexane, eluted with hexane-dichloromethane (3:1, v/v).

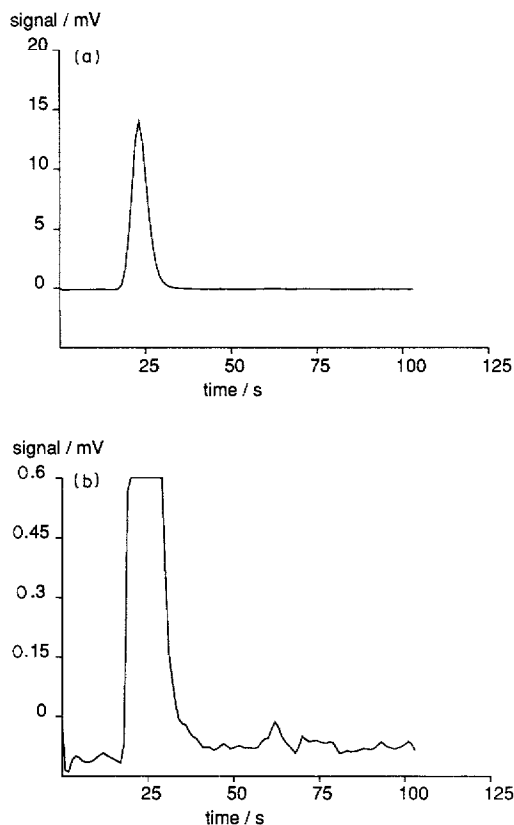


Fig. 7. Demonstration of the minimal carry-over exhibited by the detector. (a) The response from a large sample of Arab heavy oil tar injected directly into the detector (no column). (b) The same record expanded 33-fold: the small carry-over peak is seen at 65 s.

pyrene, and the variance of the peaks shown is better than 2% (and better than 1% for the first three peaks).

Carry-over (*i.e.* material from one component appearing a second time when the spoke re-enters the flame) is another important characteristic of a transport mechanism. Fig. 7 shows the results of injecting a relatively concentrated solution of Arab heavy oil tar (actual concentration unknown, but estimated to result in an injected mass of *ca.* 100 μg). In this case no column was used! Fig. 7a shows the "chromatogram" recorded, and Fig. 7b shows the same data scaled up by a factor of 33. The very small degree of carry-over is shown by the peak at *ca.* 65 s, representing a carry-over of less than 0.5%.

Linearity of response was examined by injecting samples containing 20.8, 10.4, 5.0, 2.6, and 1.04 μg of pyrene. The chromatographic responses are shown in Fig. 8a, and a plot of peak height *vs.* sample mass is shown in Fig. 8b. We believe that 20 μg is sufficient to overload the detector, so the 20- μg point has been ignored in drawing the solid line in Fig. 8b. The correlation coefficient for the solid line drawn was 0.998.

Carbon number response is of particular interest for a detection system based on

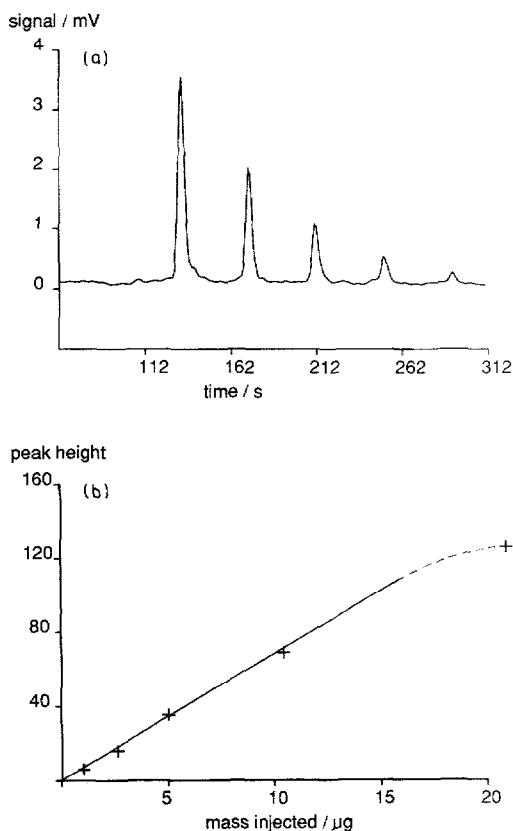


Fig. 8. Linearity of response illustrated by responses from samples containing 20.8, 10.4, 5.0, 2.6, and 1.04 μg of pyrene (eluted as described for Fig. 6): (a) the chromatographic responses; (b) a plot of the peak heights as a function of sample mass.

FID, and this aspect of the performance was examined by injecting 10- μg samples of C12, C14, C16, C20, C24, C28, C32, C36 and C40. The results in Fig. 9 indicate that, under the conditions chosen for this preliminary study, the response is essentially flat down to *ca.* C22, and then falls steadily down to C12. It must be noted that changing the evaporation conditions (fan speeds and temperatures) significantly modifies this response curve, and the one presented does not represent an optimum response curve. Thus we have routinely used the detector for detecting C10 using a hexane eluent under the following detector conditions: eluent temperature, 55°C; evaporator 1: speed, 98%; temperature, 80°C; evaporator 2: speed, 68%; temperature, 90°C; evaporator 3: speed, 56%; temperature, 95°C; detector jacket temperature, 110°C; step speed, *ca.* 1 s/spoke; detector amplifier gain, 33.

As the results of Fig. 7 indicated, we also expect the detector to function with hydrocarbons of substantial molecular weight.

Fig. 10 illustrates a typical chromatogram recorded with the detector. In this case the sample consists of 10 μg each of C36 and pyrene. Analysis of this and similar

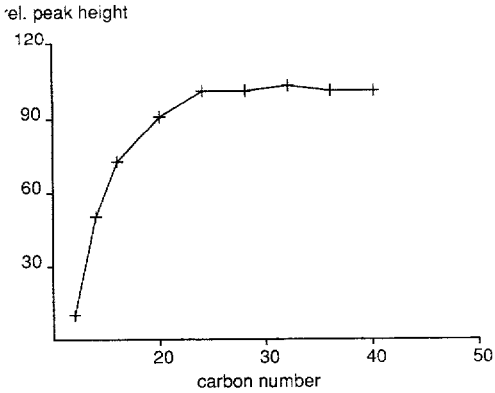


Fig. 9. Response as a function of sample carbon content: the variation of peak height as a function of sample carbon number for 10- μ g samples of C12, C14, C16, C20, C24, C28, C32, C36 and C40, all eluted as described for Fig. 6.

chromatograms leads to a preliminary estimate of the limit of detection of the order of 100 ng for either component.

The detector has been in operation for several months and we are confident that the major aspects of the design are sound. We have demonstrated that the detector functions reliably, results in acceptable sensitivity and linearity of response with sample size, exhibits minimal carry-over, and can deal with a useful range of carbon-number samples. There remains a considerable amount of work to be carried out to optimize the detector's performance in relation to the air flow-rates and temperature. However, with the precise control of these parameters available through the use of direct computer control, we hope to demonstrate that the design offers significant advantages over earlier designs of transport detector.

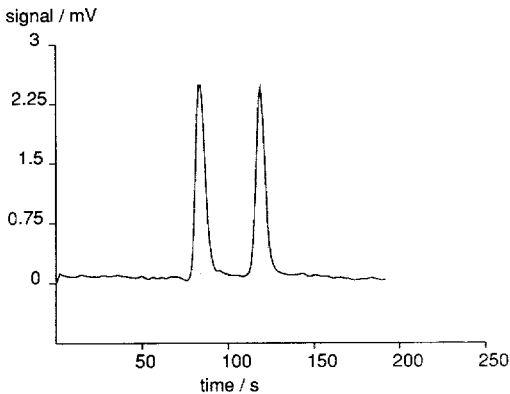


Fig. 10. Typical chromatogram record with the transport detector. Sample of 10 μ g each of C36 and pyrene, eluted as described for Fig. 6.

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