DETECTOR FOR LIQUID–SOLID CHROMATOGRAPHY

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INTRODUCTION

The need for a means of indicating or recording changes in the composition of liquids flowing from liquid–solid chromatographic columns is long-standing. Methods that have been used include the continuous measurement of refractive index[1], conductivity[2,3], dielectric constant[4], pH[5] or absorption of light of suitable wavelength[6]. These methods often involve costly and complicated equipment and are highly sensitive only when liquids having very different physical properties are involved.

The detector described in this report depends upon the differences in the heat of adsorption of liquids on suitable adsorbents. The liquid leaving the chromatographic column is passed through a tube containing the adsorbent in which a thermocouple is embedded. As the composition of the liquid passing through the detector changes, the temperature of the adsorbent and the thermocouple changes. These temperature changes are a function of the heats of adsorption and desorption of the components of the liquid passing through the detector.

After passing through the detector the liquid may be collected in fractions for further examination and signals from the thermocouple may be used to operate a fraction collector.

The detector is simple and easily constructed in the laboratory and has a fairly high sensitivity. It is suitable for the detection of the different classes of hydrocarbons that occur in benzole, petroleum and similar complex mixtures and can also be used for the detection of metals in eluates obtained from chromatography on ion-exchange resins.

THEORETICAL CONSIDERATIONS

The adsoprtion of gases and liquids on surfaces of solids is accompanied by the evolution of heat due to a decrease in free energy of the system. This heat is called the heat of adsorption. The evolution of heat that occurs in the detector described in this report is due to the replacement of one substance adsorbed on the solid by another. The replacement may be of air by a liquid, of one liquid by another, or of a liquid by a solute dissolved in the same liquid.

The most important factors influencing the amount of heat evolved in the detector are:

1. The nature of the material being displaced from the adsorbent.
2. The nature of the displacer.

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3. The quantity of solid adsorbent in the detector.
4. The adsorbent capacity and nature of the adsorbent.
5. The quantity of material replacing that originally on the adsorbent.

If the quantity of adsorbent in the detector is small compared with the quantity of any one component in the liquid leaving the column, the heat evolved when a new component reaches the detector will be a characteristic of the compound concerned but will be independent of the quantity of the compound present. Fig. 1 shows this

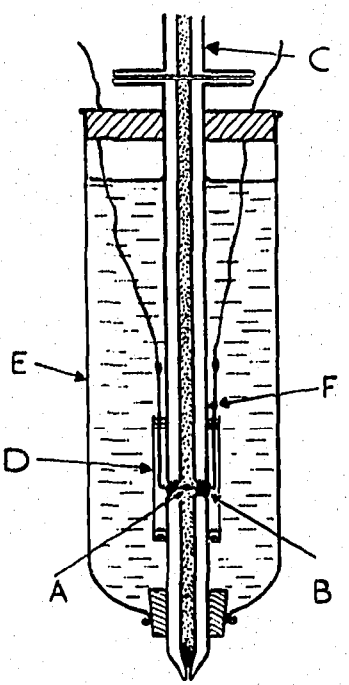

Fig. 1. The detector.

type of detector. It is the temperature change and not the heat evolved that is measured in the detector, and the following will affect the temperature change:

a. Thermal capacity of the body of the detector and the thermocouple.
b. Specific heat of the liquid in the detector.
c. Quantity of liquid in the detector.
d. Heat losses from the detector by conduction away from the detector and normal heat losses to the surroundings.
e. Rate of flow of the liquid through the column.

For a detector intended only to indicate changes in the composition of the liquid leaving the column, these factors are of little importance.

DESIGN AND OPERATION OF APPARATUS

The detector, shown in Fig. 1, indicates changes in the composition of the liquid that passes into it. It is attached to the bottom of the chromatographic column C by a flat-flange or taper joint, which is suitably lubricated and clamped to be leak-proof.

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The detector consists of a length of capillary tubing, 1.6 mm I.D., carrying a thermojunction A so placed that the junction is in the centre of the bore of the capillary. The thermocouple wires pass through the holes B and are sealed in place with litharge–glycerin cement. The tube D is fitted on to the capillary tube with rubber bungs so that the part of the capillary near the thermojunction is enclosed in an air jacket. The wires pass through the upper rubber bung and the cold junction F is made just above this bung. The detector is surrounded by a tube E containing water. This water jacket keeps the walls of the detector at a constant temperature, thus ensuring a uniform rate of heat loss. It also keeps the cold junction F at a constant temperature. The lower end of the capillary tube is drawn out to a fine jet and a few coarse granules of silica gel are placed in the jet to retain the adsorbent. Suitable thermocouples may be made from wires, 0.004 in. in diameter, of 40% palladium in gold and 10% iridium in platinum. The thermojunctions are best made by carbon-arc welding.

This detector may be used to indicate any changes in composition of liquids supplied to it. Its use in conjunction with displacement development is one of its more obvious applications. The dimensions of the detector described are such that it can be attached to the column used for the analysis of hydrocarbon types by the Fluorescent Indicator Adsorption (FIA) Method (I.P. 156/58T)[7].

The detector is fitted by means of flat flanges or taper joints to the lower end of the analyser section of the FIA column, the detector and the column being filled with

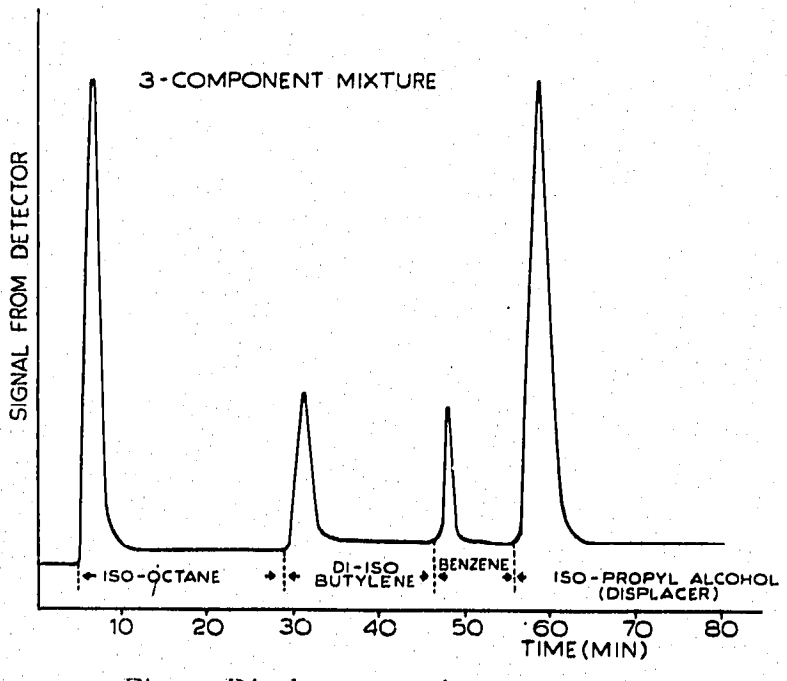

Fig. 2. Displacement chromatography.

silica gel in the normal way. The sample is introduced on to the silica gel, followed by the displacer, isopropyl alcohol. The bands corresponding to saturated, unsaturated and aromatic hydrocarbons develop and as each boundary reaches the detector the heat generated raises the temperature of the thermocouple. The thermocouple cools

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again after the boundary has passed it. The output from the thermocouple is supplied to a suitable galvanometer or recorder. On larger columns the output may be used to operate a fraction changer, thus enabling the various types of hydrocarbons to be collected separately. Fig. 2 shows the results obtained on a mixture of iso-octane, di-isobutylene and benzene. The boundaries are quite sharp. The time axis does not provide an indication of the quantities of the hydrocarbon types present, due to variations in flow rate, which was not accurately controlled.

DISCUSSION AND CONCLUSIONS

The qualitative detector is a simple device that will give a signal when a boundary reaches it during a chromatographic separation. As it is merely a thermocouple inserted in the column, it can obviously be used in any system in which temperature changes occur at the boundary between components. In addition to liquid–solid adsorption chromatography, it has been found to be applicable to separations carried out on ion-exchange resins, the detector being filled with the resin.

ACKNOWLEDGEMENTS

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SUMMARY

A detector is described that is suitable for indicating changes in the composition of liquids flowing from chromatographic columns.

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