Effect of an argon–nitrogen carrier gas mixture on the sensitivity of a gas chromatographic ionisation detector

The Pye Argon Gas–Liquid Chromatograph is easily modified for work on a preparative scale. The main problem was how to control the highly sensitive detector; an overloaded detector will give a full scale deflection together with a series of false peaks where there should be only one peak ("peak doubling"). We needed to adapt the detector to give nearly full scale deflections on the recorder for fractions ranging from micrograms to 1 g.

By using a carrier gas mixture of argon and nitrogen we can vary the sensitivity of an argon ionisation detector continuously between the limits obtained with pure argon and pure nitrogen. The detector will give full scale recorder readings without overloading or "peak doubling" for sample fractions varying in size from micrograms to over 1 g. Any user of a Pye Argon Chromatograph should be able to convert the instrument for this type of versatile preparative scale working.

Methods of increasing detector sensitivity range

We wished to avoid the complication of using a by-pass system, and we considered the following three methods for increasing the sensitivity range of the detector.

(1) Decreasing the detector voltage below 750 V. Lowering the detector voltage to about 250 V and 50 V lowers the amplitude of the peaks, but it does not stop "peak doubling".

(2) Using nitrogen as the carrier gas and altering the recorder range from 0–10 mV to 0–1 mV. Pure nitrogen reduces the sensitivity of the detector, but then sample fractions of hundreds of milligrams are needed to get a reasonable response on the recorder. This would only satisfy our requirements for the largest fractions, and we would be near the limit for overloading the column. The apparent sensitivity can be increased by altering the range of the recorder from 0–10 mV to 0–1 mV, but this increase is not sufficient and it is spoiled by a high noise level.

(3) Using a carrier gas mixture of argon and nitrogen. This method gives the detector the sensitivity range that we require. By altering the percentage of nitrogen in the mixture, the detector can be made to work at any sensitivity between those obtained with pure argon and pure nitrogen. This was selected as the only suitable method.

Modification and operation of the Pye Argon Chromatograph

Three stainless steel columns (4 ft. × 2 cm diam.) joined by steel capillary U-tubes are housed in a pipe (2½ in. diam.) which fits within the usual heater jacket. This pipe is packed with aluminium powder which forms the heat conductor. A Variac transformer controls the heat input to the column, vapouriser and outlet tube, which are not controlled by thermostats.

The two carrier gases are controlled by separate needle valves and rotameters before being mixed at a glass Y-junction and passed through a final rotameter. Both

gases are kept at the same pressure at the cylinder heads. As we use the rotameters under different conditions from those for which they were calibrated, all our nitrogen percentage values are nominal.

The column was packed with 20 % M. S 710 silicone oil on Embacel (60/100 mesh). The total flow rate was nominally 800 ml/min, the inlet pressure was 25 lb./sq. in., the temperature was 90° and the detector voltage was 2000 V.

Results

The same experimental conditions apply to the results shown in Figs. 1 and 2.

Fig. 1 shows the effect of varying the nominal nitrogen percentage from 1 % to 100 % on a chromatogram of 50 mg of impure *n*-pentanol. The impurities help to

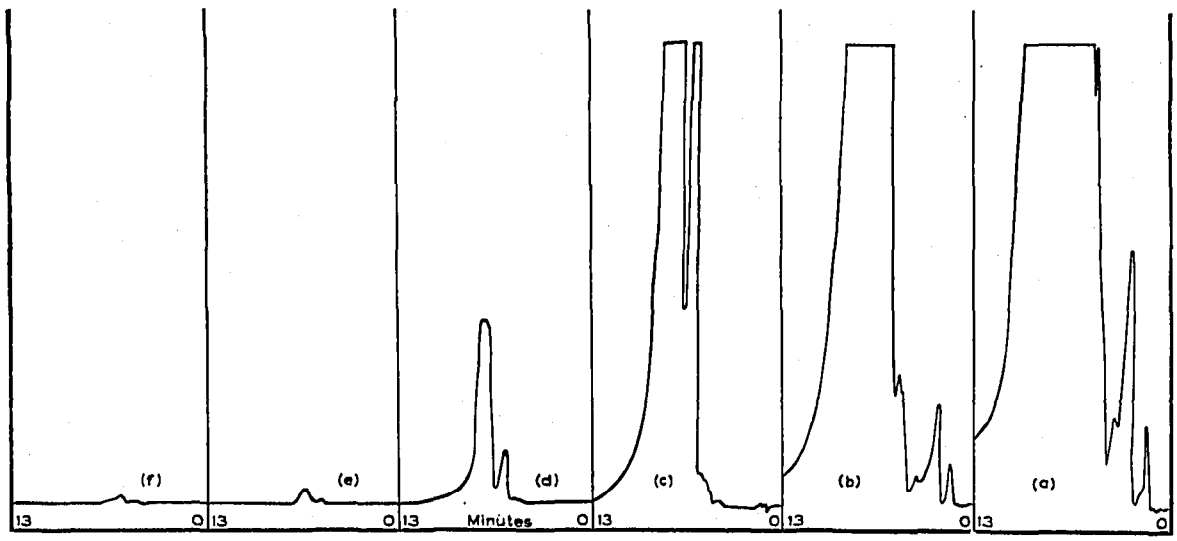

Fig. 1. Chromatogram of impure *n*-pentanol with various mixtures of nitrogen–argon carrier gas. (a) 1 % nitrogen, 99 % argon; (b) 2 % nitrogen, 98 % argon; (c) 5 % nitrogen, 95 % argon; (d) 10 % nitrogen, 90 % argon; (e) 50 % nitrogen, 50 % argon; (f) 100 % nitrogen.

show up the differences more clearly. Pure argon gives a straight line along the top of the chart and this is not shown on Fig. 1.

The largest decrease in the sensitivity of the detector takes place as the nominal nitrogen percentage increases from 0 to 10 %. This low percentage level of nitrogen means that the flow-rate settings are critical for good reproducibility. It is therefore better to use the highest possible nitrogen percentage. This is done by adjusting the two main variables that effect the sample vapour concentration in the detector, *i.e.* flow rate and temperature. The flow rate must be as high and the temperature as low as possible.

Although the detector voltage has no control over peak doubling, it does affect the amplitude of both single and double peaks. Provided that doubling has been avoided, the detector voltage can be used in conjunction with the nitrogen percentage, flow rate and temperature to give the optimum control over the detector sensitivity.

The maximum and minimum sample sizes are detected when the carrier gas is either pure nitrogen or pure argon. Using nitrogen and overloading the column, we

can deal with more than 1 g of a single substance. Using a nominal 5 % nitrogen in argon as an example of a mixture, our limits of detection of a single substance are about 0.5 mg to 100 mg under the experimental conditions given for Figs. 1 and 2. The exact amount increases with the retention time.

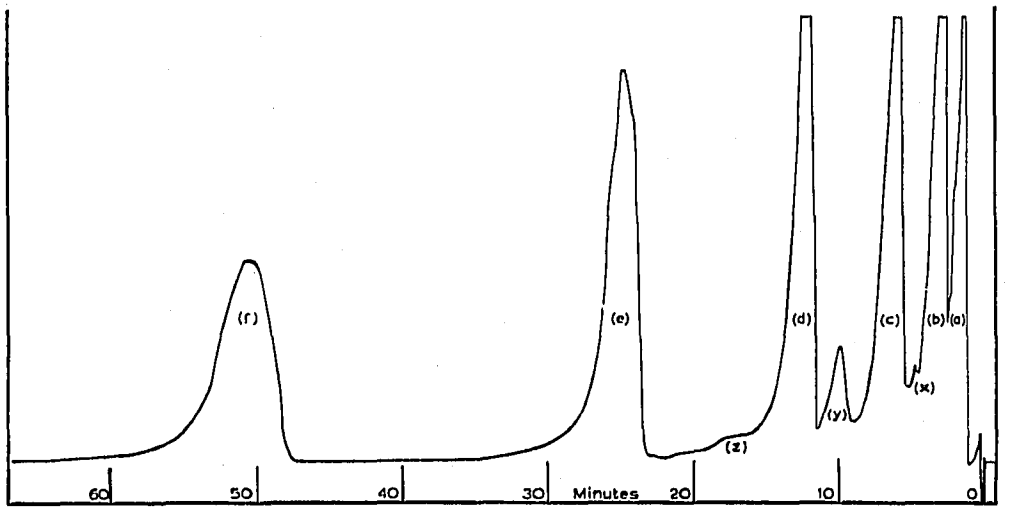

Fig. 2. Chromatogram of a 110 mg mixture of normal alcohols. (a) *n*-propanol; (b) *n*-butanol; (c) *n*-pentanol; (d) *n*-hexanol; (e) *n*-heptanol; (f) *n*-octanol; (x), (y) and (z) impurities.

Fig. 2 shows a separation of a 110 mg mixture of equal quantities of *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol. The carrier gas contained a nominal 5 % of nitrogen in argon.

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Unilever Ltd., Food Research Department, Colworth House, Sharnbrook, Bedford (Great Britain)

D. WELTI
T. WILKINS

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Paper chromatography of *Withania somnifera* alkaloids

Although *Withania somnifera* have been previously studied[1–3] no simple method has been reported in the literature for the detection and separation of its alkaloidal components.

In a previous paper we already showed the possibility of this separation, by employing a circular chromatographic technique, with which at least five of the alkaloidal components could be detected[4].

On the basis of these results and by employing paper disks with suitable diameter, we succeeded in separating and observing all eight components at the same time.