THE APPLICATION OF A LONG-PATH INFRA-RED CELL IN GAS CHROMATOGRAPHY

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INTRODUCTION

Several recent papers[1-4] have described the use of gas–liquid chromatography to separate the components of mixtures containing unknowns, followed by infra-red spectroscopy for their identification. Other papers have described the combination of gas–liquid chromatography with other spectroscopic techniques[5-7]. Two approaches may be distinguished. The fractions after leaving the column and detector may be condensed out and subsequently transferred to a suitable gas or liquid infra-red cell. This procedure has obvious advantages with relatively involatile samples, provided the quantities are large enough to be manipulated.

Alternatively the gas stream may be led directly from the detector into an infra-red gas cell. This approach avoids the loss of time, and possible loss of sample involved in condensing it before examination. It has, however, the disadvantage that under normal gas–liquid chromatographic conditions, the concentrations, at least of minor components, are too small for sufficiently intense spectra to be obtained in a normal infra-red gas cell of about 10 cm path. One means of overcoming this difficulty is the use of mechanical or electrical scale expansion on the infra-red spectrometer. The degree of expansion is, however, limited to about five-fold, if a wide wavelength range is to be scanned, by imperfections of the background trace obtained with a double-beam spectrometer. Scale expansion also leads to loss of sensitivity, which must be compensated for by increasing the amplifier gain or slit-widths.

A long-path cell therefore offers a better method of obtaining the necessary band strength. The present paper describes the construction of such a cell, and illustrates its use in obtaining the infra-red spectra of chromatographically separated components.

EXPERIMENTAL

(a) *Long-path cell*

Since long-path cells of small volume are not normally available for commercial spectrometers, a simple cell has been constructed to fit the double-beam unit of the Grubb-Parsons G.S. 2A spectrometer. The design uses the conventional 3-mirror arrangement. Fig. 1 shows how the cell is arranged with respect to the spectrometer optics. The path of the central ray through the cell is indicated for sixteen passes. In order to retain a sharp image on the entrance slit, the horizontal axis of the long-path cell is inclined at approximately 20° to the normal beam direction, so that the

final image falls at the correct distance from the slit. The two mirrors M_1 and M_2 (2.2 cm square) and the larger mirror M_3 (3.0 by 1.7 cm) were all cut from a single concave mirror of 7½ cm focal length, and subsequently surface aluminised. These mirrors and the plane mirrors M_4 and M_5 were mounted on a ¼ in. brass plate, which in turn was fixed at the correct height by a support screwed on to the double beam unit. The cell could thus be removed and replaced as required without loss of alignment.

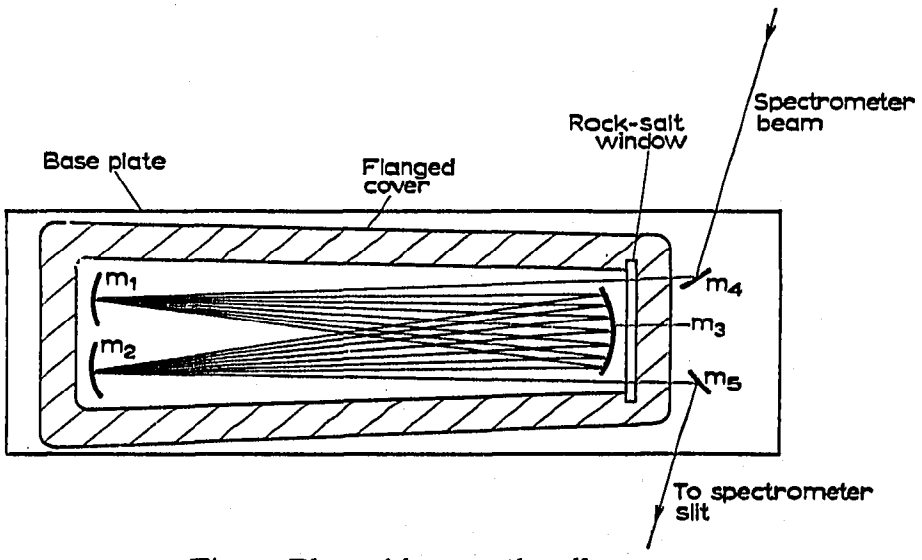

Fig. 1. Plan of long-path cell.

Up to 7 images could be obtained on M_3, corresponding to 16 passes, giving a path-length of 240 cm. After the optical adjustments were made, the cell was completed by covering the mirrors with a flanged brass cover of minimum volume (about 130 c.c.), one end of which was fitted with a rock-salt window. The flange rested on a rubber ring which fitted into a groove in the base-plate. Sufficient pressure could be obtained on the flange by means of clips to provide a gas tight seal. With this arrangement about 40 % transmission was obtained through the cell. An attenuator was placed in the blank beam so that full scale deflections could be obtained.

(*b*) *Gas chromatography*

A 4 ft. by 4 mm column packed with 20 % dinonyl phthalate on 60–30 mesh "Celite", was used, and could if necessary be heated by means of an electrically heated jacket. A flame ionisation detector was used, in which about 5 % of the carrier gas stream (nitrogen) was diverted to the flame. This flame was maintained by independent supplies of air and 50/50 hydrogen/nitrogen. Satisfactory signal-to-noise characteristics were obtained when this detector was connected to an amplifier of Type 1E/114 (Gas Chromatography Ltd.) and a Type DSP (2) Sunvic Recorder. Minimum lengths of polythene tubing were used to connect the detector to the column and long-path cell, so as to avoid remixing of fractions. The column was operated with its outlet at atmospheric pressure.

(*c*) *Mode of operation*

Because of the relatively large volume of the cell, it was not feasible to flow the

effluent gas continuously through it, since remixing of the separated components would occur. The following procedure, however, proved satisfactory, using two three-way taps connected as shown in Fig. 2.

Gas flow through the system was started, tap T_1 being turned to waste by-passing the long-path cell, until the emergence of a fraction from the column was indicated by the detector. The gas flow was then diverted to the cell and the infra-red spectrum

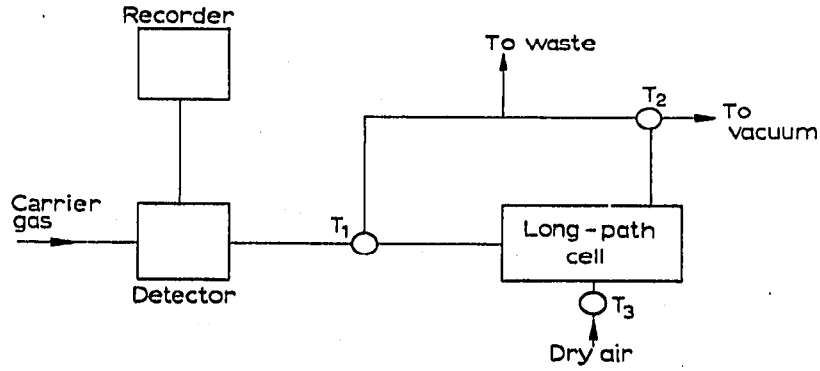

Fig. 2. Arrangement of chromatograph and long-path cell.

scanned rapidly by hand until a band was found. The spectrometer was held at this wavelength until maximum absorption was obtained. About 30 sec normally elapsed between attainment of maximum concentration in the detector and in the gas cell. Taps T_1 and T_2 were then closed, the gas flow stopped and the spectrum of the fraction measured, usually from 5–15 μ. This takes about 4 min. Except with very close sample peaks, diffusion on the column during this period was insignificant. The long-path cell was then evacuated via T_2, and refilled with dried air through T_3, after which gas flow was restarted, by-passing the cell until the next fraction was detected. The procedure was then repeated.

RESULTS

The apparatus was tested by separating several synthetic mixtures, and obtaining the infra-red spectra of the components. Three examples are illustrated below.

(*a*) *Separation of ketones*

One drop (about 3.5 μl) of a mixture of equal amounts of acetone, methyl ethyl ketone, methyl isopropyl ketone and diethyl ketone was placed on the column with a hypodermic syringe, and eluted at room temperature by nitrogen at 20 ml/min. Fig. 3 (a) shows the resulting spectra. They are sufficiently strong for the components to be readily identified by comparison with the spectra of the corresponding liquids given in the Sadtler collection.

(*b*) *Separation of esters*

Fig. 3(b) illustrates an identical experiment involving ethyl formate, ethyl acetate, isopropyl acetate and ethyl propionate. Again a spectrum of good quality was obtained from each component.

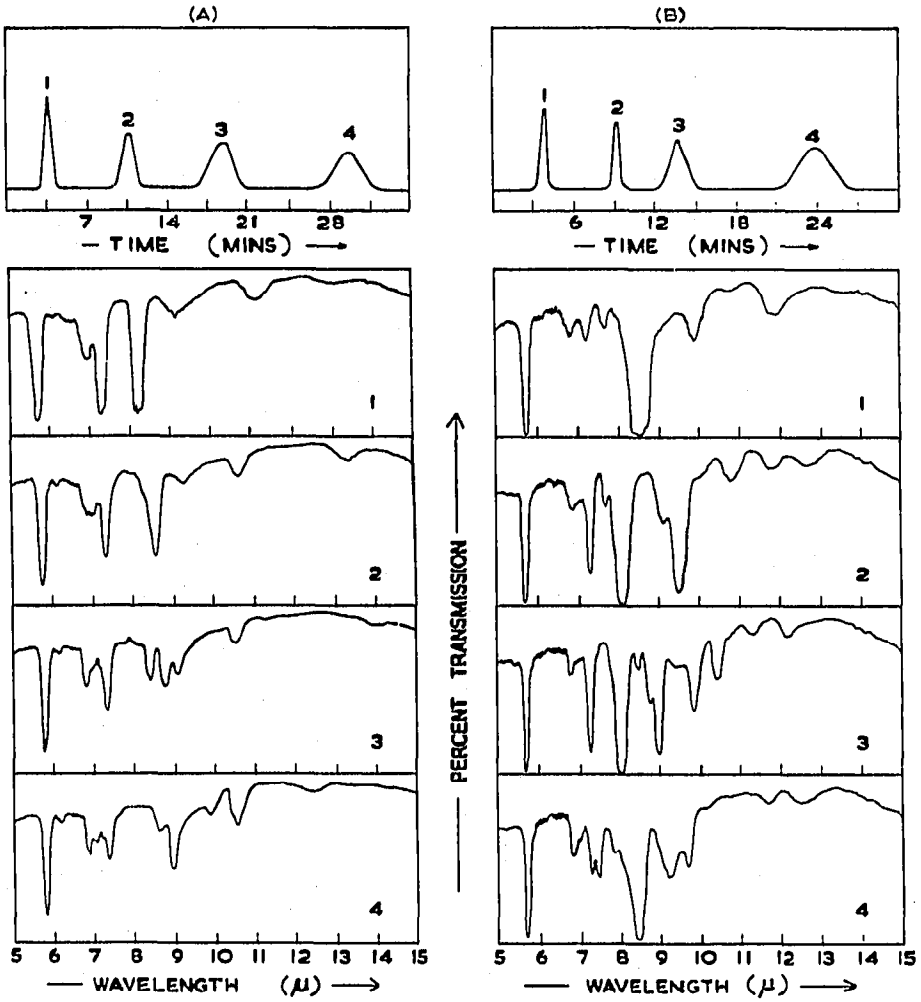

Fig. 3. Gas chromatograms and infra-red spectra. (a) Separation of ketones. (1) acetone; (2) methyl ethyl ketone; (3) methyl isopropyl ketone and (4) diethyl ketone. (b) Separation of esters. (1) ethyl formate; (2) ethyl acetate; (3) isopropyl acetate and (4) ethyl propionate.

(c) *Separation of a ten-component mixture*

A rather more rigorous test was made on a mixture of equal parts of diethyl ether, diisobutyl ether, acetone, methyl isopropyl ketone, isopropyl acetate, ethyl propionate, cyclohexane, toluene, 1-pentanol and cyclohexanol. Two drops (7 μl) of sample were used, and because of the wide variation in the volatility of the components, the column temperature was increased from 37° to 90° during the experiment. Once again, as shown in Fig. 4, an adequate spectrum of each component was obtained. Similar separations involving mixtures of ethers, hydrocarbons and alcohols were also carried out. It must be stressed that in separations of this kind, the limiting factor in the quality of the infra-red spectra is the degree of separation of the components on the column. Satisfactory spectra can be expected only if resolved peaks are obtained in the chromatogram.

In order to assess the value of the method in the identification of small amounts of impurity, one drop of a solution of 1 % of acetone in ethyl acetate was added to the column, and the spectrum of the acetone determined. The three strongest peaks in its

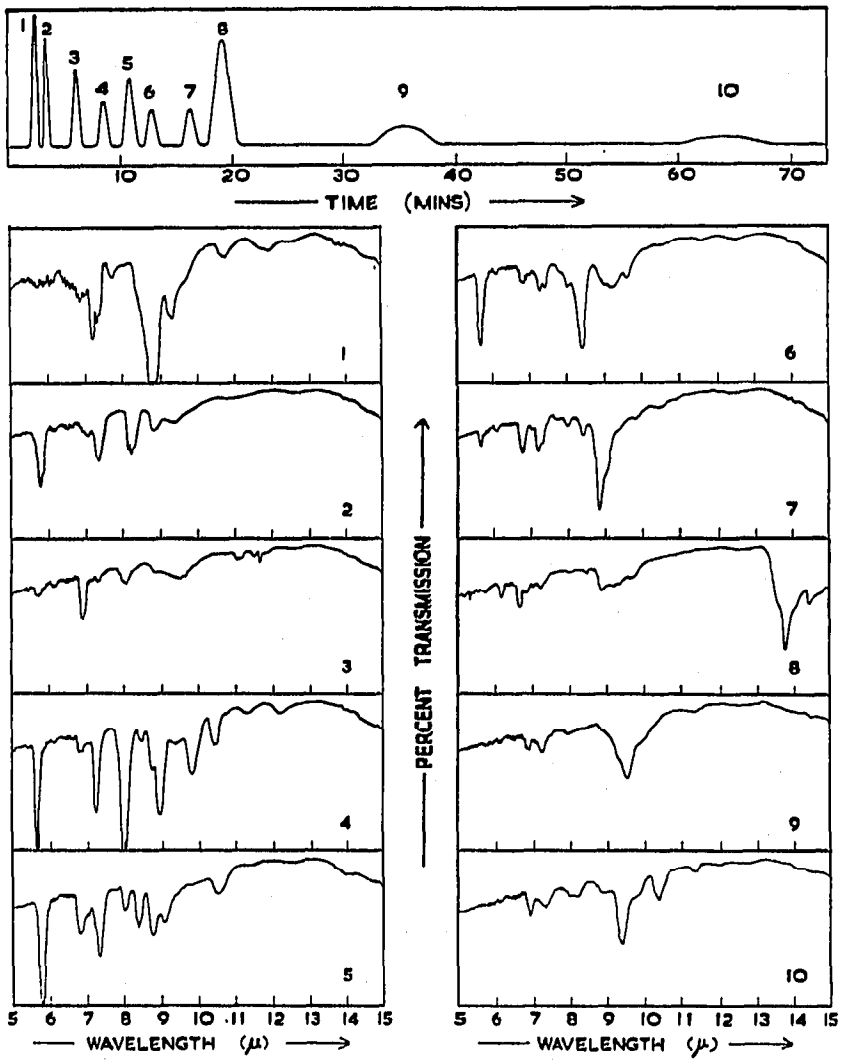

Fig. 4. Gas chromatogram and infra-red spectra of components of a ten-component mixture. (1) diethyl ether; (2) acetone; (3) cyclohexane; (4) isopropyl acetate; (5) methyl isopropyl ketone; (6) ethyl propionate; (7) di-isobutyl ether; (8) toluene; (9) 1-pentanol; (10) cyclohexanol.

spectrum, at 5.75, 7.3 and 8.2 μ showed optical densities of about 0.1. This indicates that in favourable cases as little as 0.00003 g of an impurity could be identified.

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SUMMARY

A long-path infra-red cell has been used to obtain the spectra of the separated components of mixtures, as they emerge from a gas chromatograph. The advantages and limitations of this method of identifying these components are considered.

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