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CHROMSYMP. 130

GAS CHROMATOGRAPHY JUDGED BY OPTIC FIBRE TECHNIQUES

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SUMMARY

A technique is described for measuring the plug length of volatile fluorescent compounds at the beginning and at the end of a gas chromatographic process. In this way the contribution of injection and separation to the registered end signal can be quantified.

INTRODUCTION

The end signal of a gas chromatographic (GC) process reflects three main events: injection, separation and detection. To establish the influence of each separate event on the end signal, one must observe and quantify the GC process as it goes through these stages. Observation of a GC process by using highly fluorescent compounds has been described earlier[1,2]. In this paper, a technique for the quantitative measurement of injection and separation is presented.

EXPERIMENTAL

Instrumentation

A heat-resistant box with two windows was constructed on top of a Packard-Becker 420 oven[2]. Outside this box, in front of one of the windows, a UV source (Osram HBO, 200 W) with three filters (infrared filter, UG1 filter and BG38 filter) was placed, limiting the excitation light to a wavelength band of 360 ± 50 nm (Fig. 1).

The column had a modified shape, and both ends were mounted in a device equipped with two slits, each of 1 × 12 mm, which made it possible to observe the passing fluorescent plugs through the slits at the column inlet and outlet (Fig. 2).

Behind each slit, a quartz rod (diameter 4 mm, length 12.5 cm) to which an optic

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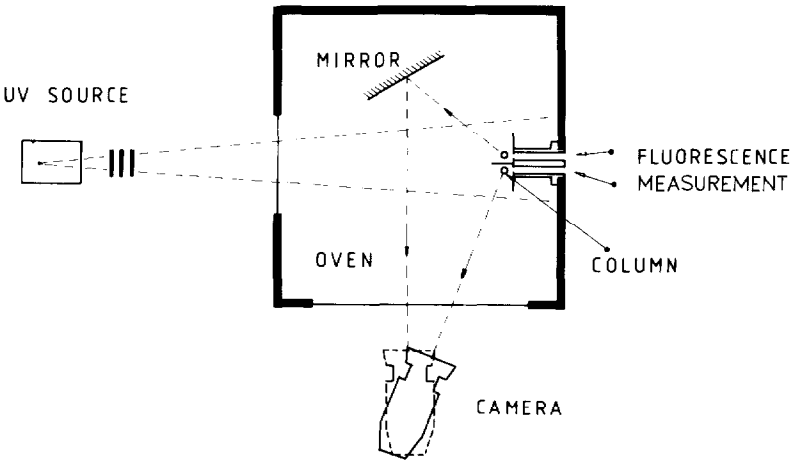

Fig. 1. Schematic view of apparatus from above. The heat-resistant box (in bold lines) is mounted on top of the oven, between the oven and a vertically movable oven cover.

fibre was connected, could be pushed into the device. This rod carried the light emitted by the fluorescent plug out of the oven (Fig. 3).

The light was transmitted by the optic glass fibre to a photomultiplier (EMI 6094 with S_{11} cathode) and subsequently registered by a recorder (Fig. 4).

In addition to the described set-up; the fluorescent plugs at the beginning and at the end of the column were registered by a video camera (Fig. 1).

As the device in which the column was mounted had a metal light separator in the middle section to prevent light scatter from one column end to the other, only a mirror could show the plug in the column outlet to the camera.

More detailed information about the instrumental set-up can be found elsewhere[3].

Gas chromatographic conditions

A wall-coated open-tubular (WCOT) column of Duran 50 glass (11.6 m × 0.45 mm I.D.) was leached, persilylated and statically coated with OV-101[4].

The carrier gas (nitrogen) flow-rate was 5 ml/min., the oven temperature was 205°C and the injection and detection temperatures were 220°C. For injection an all-glass falling needle system was used. Flame-ionization detection (FID) was employed.

Fluorescent compounds and the measurement of plug length

Two vividly fluorescent and volatile compounds, pyrromethene BF_2 pigments, were used[1,2,5], one of which is shown in Fig. 5.

On injection, the plug length was measured at the column inlet slit. After the plug had passed, the quartz rod was plugged into the other hole, in front of the outlet slit. In this way only one measuring system (photomultiplier) was used. Plug lengths observed through the slits were registered in seconds and measured at half peak height using the equation peak area / (peak height × 0.939). The duration of the signal depends on: (a) the intrinsic length of the passing fluorescent plug and (b) the speed with

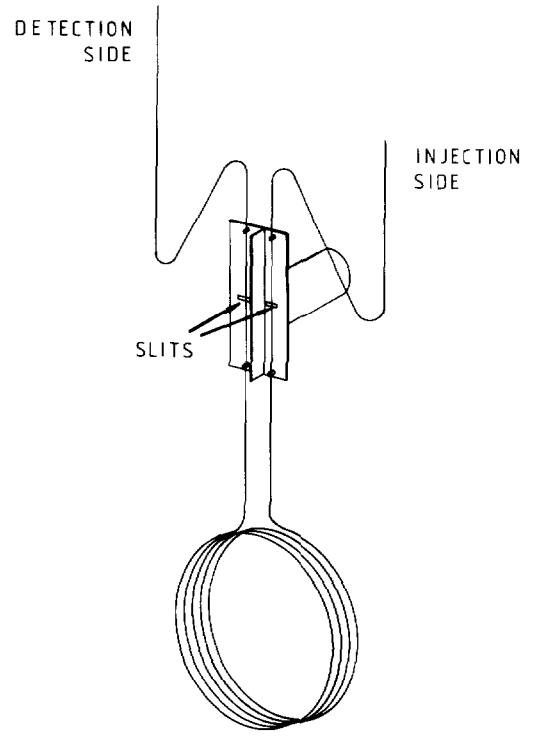

Fig. 2. Column used in the device. The shape of the column has been changed, because the measuring spots must be near to each other, being illuminated by the same UV bundle.

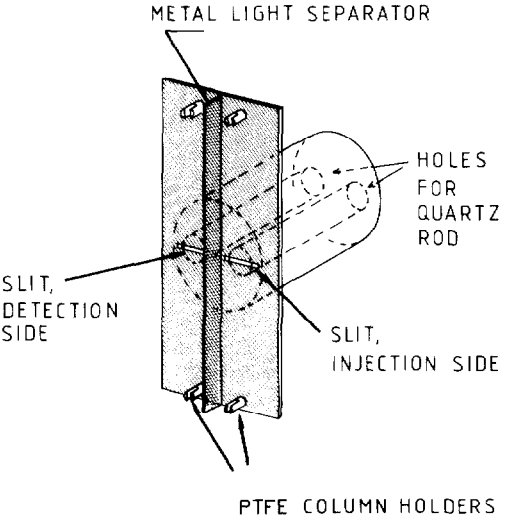

Fig. 3. Device in which the column and quartz rod with optic fibre are mounted.

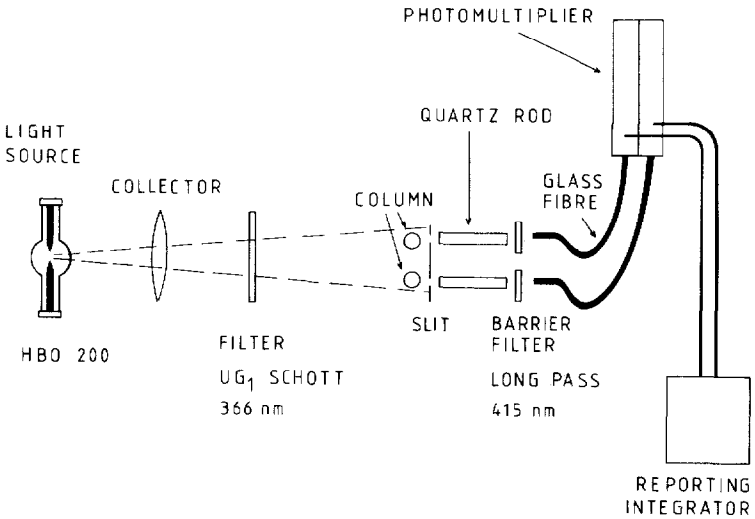

Fig. 4. Schematic view of the experimental set-up designed to measure fluorescent plug length at the column inlet and outlet.

which the plug is moving. The latter, especially, depends on the thickness of the liquid phase at the point of measurement. A destroyed liquid phase, for instance, will result in a very fast moving plug[2].

As the column parts are not uniform, the measured plug lengths must be matched for plug speed. The speed was estimated as follows: at the injection side, by measuring the time between injection and appearance of plug at injection slit; at the detection side, by measuring the time between peak maximum in slit and peak maximum of subsequent FID signal.

RESULTS

The details of the instrumental set-up and the registration of the fluorescent plugs by the camera on video tape are not given here; for information, contact the authors.

Peaks from which plug lengths at the column inlet and outlet are derived are given in Fig. 6, which contains an example of the signals registered through the slits of the device. There are two tracks in Fig. 6: one derived from the photomultiplier, yielding the signals of the fluorescence as seen through the slits, and one obtained from the FID instrument. At the beginning of the experiments it was ascertained that there

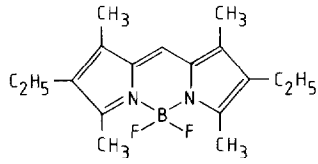

Fig. 5. Pyrromethene BF_2 pigment: 2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3*a*,4*a*-diaza-S-indocene.

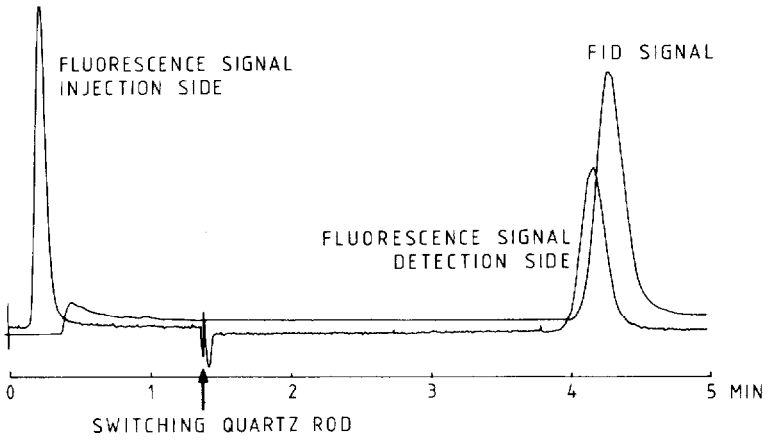

Fig. 6. Recorder signals after injection of 25 ng of the compound depicted in Fig. 5. FID signal: attentuation ×128 (1 mm absolute peak height = $1.25 \cdot 10^{-14}$ A). Recorder speed: 5 cm/min.

was no systematic difference in measurement between the two measurement points at the column inlet and outlet[3].

Table I gives the plug length in seconds after several injections of the same amount of compound as depicted in Fig. 5, observed just after injection at the column inlet and after passing through the column, as registered at the outlet. From the table it appears that the falling-needle system produced broad peaks on the column inlet, while the transport of the compound through the column caused additional substantial peak broadening.

TABLE I

MEASUREMENTS WITH COMPOUND DEPICTED IN FIG. 5

Injection of 25 ng.

Injection temperature (°C)	*Injection No.*	*Peak width at half-height (sec)*			*Correction for speed difference*	*Peak width at injector slit, matched for speed (sec)*	*Difference between fluorescent peaks (detector slit minus matched injector slit)*	
		Injector slit	*Detector slit*	*FID signal*			*sec*	*%*
220	1	6.0	12.9	12.8	5.0/3.8=1.32	7.9	5.0	62
	2	5.4	11.9	12.6	5.8/5.4=1.07	5.8	6.1	107
	3	6.5	12.6		6.2/5.0=1.24	8.1	4.5	56
	4	6.0	12.7	13.8	7.9/5.8=1.36	8.2	4.5	55
	5	6.7	13.2	12.6	6.7/5.8=1.16	7.7	5.5	71
	6	6.2	13.7	14.4	6.7/4.2=1.60	9.9	3.8	38
	7	6.1	13.4	14.0	6.3/5.4=1.17	7.2	6.2	87
	Mean							68
	S.D.							23
250	8	4.8	8.2		3.8/2.5=1.52	7.3	0.9	12
	9	4.7	8.0		4.2/2.9=1.45	6.8	1.2	18

DISCUSSION

The technique used shows that by simple means it is possible to distinguish between the two major factors that contribute to peak broadening in a GC experiment: injection factors and column factors. By using this technique, it should be possible to optimize injection techniques and column manufacture more readily. In the set-up described, the plug speed at the moment it passes the slits is only roughly estimated. Therefore, the measurements in Table I, corrected for plug speed, will yield results that give only a rough indication of what happens in the system. This aspect of the method will be improved, making the results more reliable.

It should be stressed that only highly fluorescent compounds can be used, such as pyrromethene pigments. For initial experiments, some of these pigments can be obtained from the authors.

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