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Short Communication

Study of large sample volume injection in a capillary gas chromatographic–Fourier transform infrared system using a retention gap column

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ABSTRACT

In the work reported here, the technique of large sample volume injection based on the retention gap method proposed by Grob (*J. Chromatogr.*, 237 (1982) 15) has been applied successfully to increase the relative sensitivity of a gas chromatography–Fourier transform infrared (GC–FTIR) system. By regulating the make-up gas in the lightpipe (the interface which connects the GC system with the FTIR system) and the flow-rate of the carrier gas, the interference from the large volume of solvent is resolved and the sensitivity of the system is retained. Using this method, a sample as large as 100 μl can be injected with excellent results. By using this method the relative sensitivity was increased by 100 times and therefore the detection range of the GC–FTIR system is expanded.

INTRODUCTION

As a result of the limited sensitivity of infrared detection, it is often difficult to determine trace amounts of analytes by gas chromatographic–Fourier transform infrared (GC–FTIR) techniques. To solve this problem, the technique of capillary column chromatography with large sample volume injection has recently been developed. Fehl and Marcott [1] used an injection trapping technique to inject a 100-μl volume [1]; Chow *et al.* [2], with the aid of an injection–Cu^{2+} pre-column technique, have expanded the injection range. It is therefore possible to obtain satisfactory detection results for trace amounts of some analytes.

In this study, the more simple retention gap technique [3] was used to inject a large sample volume in capillary GC–FTIR. The results showed that the method allowed the efficient removal of solvent vapours, such that the large sample volumes had no negative effect on the GC–FTIR resolution and sensitivity. When the injection begins, the lightpipe make-up gas is added; when the solvent peak has decreased sufficiently, the make-up gas is no longer required.

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EXPERIMENTAL

A Model 9A gas chromatograph (Shimadzu) was used, coupled with a Model 5SXC Fourier transform infrared spectrometer (Nicolet). Fig. 1 shows a schematic diagram of GC–FTIR system. The gold-coated lightpipe was 15 cm × 1 cm I.D. The separation column was a cross-linked quartz capillary column (9 m × 0.32 mm I.D.) coated with a 0.5-μm OV-1 film. The retention gap column was a soft glass capillary column (37 m × 0.32 mm I.D.) deactivated by silylanization with hexamethyldisilazane. The separation column and the retention gap column were connected by a stainless-steel butt connector. The separation column outlet stretched into the lightpipe inlet.

The following conditions of analysis were used: carrier gas, nitrogen; flame ionization detector temperature, 200°C; lightpipe and transfer line temperature, 190°C; on-column injection.

A test mixture of decane, octanol, 2,6-dimethylphenol, 2,6-xylidine, 2,4,6-trimethylphenol, dodecane, decanol, diphenyl, 2,6-dimethylnaphthalene, dicyclohexylamine, acenaphthene, methyl dodecanoate, hexadecane and fluorenone was used. The solvent was *n*-pentane.

RESULTS AND DISCUSSION

When a large sample volume is injected, a long section of the capillary column is flooded by the solvent; the length of the flooded zone is proportional to the volume of injection (about 15–30 cm/μl [4]). The resultant broadening of the initial solute bands causes a loss of resolution from the separation column. Fig. 2 shows the gas chromatogram obtained by the on-column injection of a 100-μl volume of *n*-pentane solution

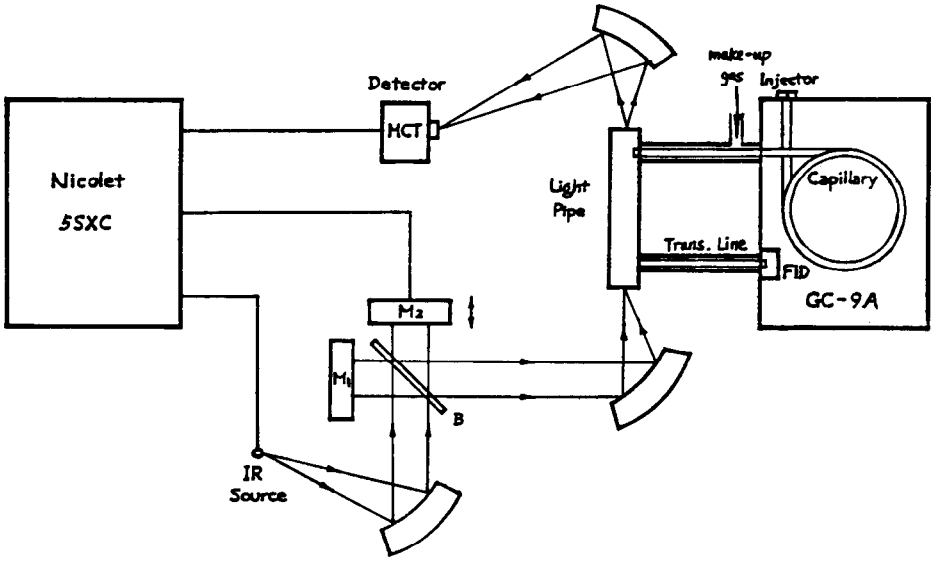

Fig. 1. Schematic diagram of the GC–FTIR system.

Fig. 2. On-column injection of a 100-μl volume without using a retention gap column. *n*-Pentane solution, 38°C for 17 min, then 6°C/min up to 170°C.

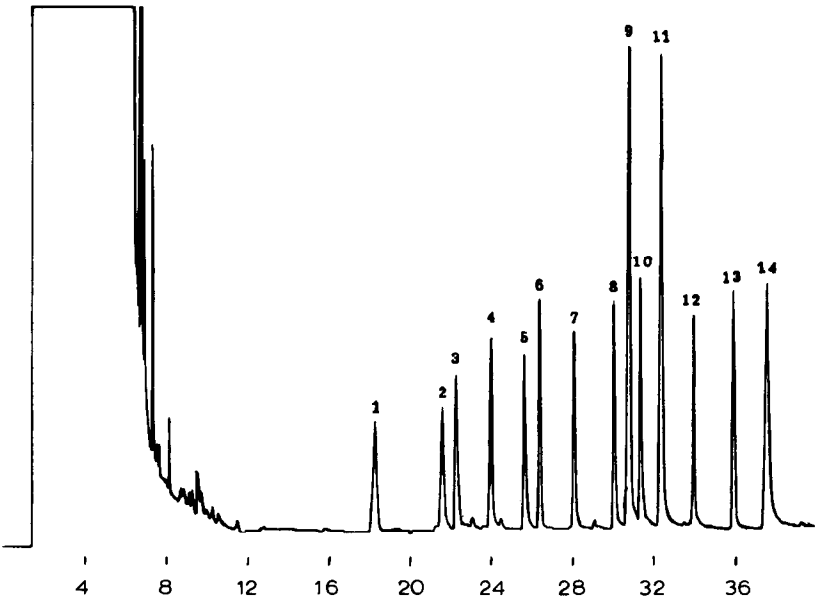

Fig. 3. Injection as in Fig. 2, but using a retention gap column. A 37-m retention gap column was connected to a 9-m separation column at 38°C for 17 min, then 6°C/min up to 170°C. On-column injection, injection volume, 100 μl; carrier gas flow-rate, 2.4 ml/min. Peaks: 1 = decane; 2 = octanol; 3 = 2,6-dimethylphenol; 4 = 2,6-xylidine; 5 = 2,4,6-trimethylphenol; 6 = dodecane; 7 = decanol; 8 = diphenyl; 9 = 2,6-dimethylnaphthalene; 10 = dicyclohexylamine; 11 = acenaphthene; 12 = methyl dodecanoate; 13 = hexadecane; 14 = fluorenone.

without the use of an uncoated pre-column. The peaks cannot be clearly seen. However, when a retention gap column without any separation ability is fitted to the head of the separation column satisfactory results were obtained with the same injection volume and separation column (Fig. 3).

Effect of carrier gas flow-rate on solute peak separation

In GC–FTIR, the carrier gas flow-rate affects the resolution and sensitivity of the system. Fig. 4 shows the Gram–Schmidt reconstruction chromatograms for a 1-μl sample at various carrier gas flow-rates. When the carrier gas flow-rate is less than or equal to 2.4 ml/min, the system maintains the higher sensitivity. However, when the rate is increased, the signal-to-noise ratio decreases. Therefore a lower carrier gas

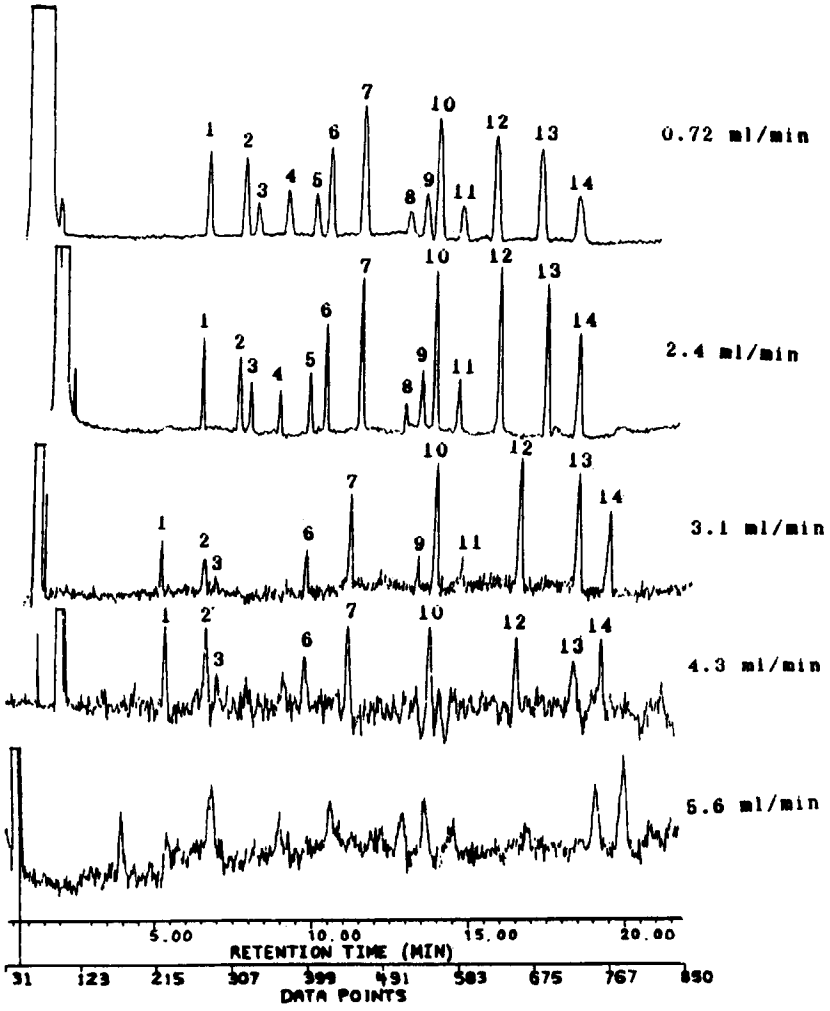

Fig. 4. Gram–Schmidt reconstruction chromatograms with different carrier gas flow-rates. *n*-Pentane solution, 27°C for 1 min then 6°C/min up to 180°C; injection volume, 1 μl. Peak identification as in Fig. 3.

flow-rate increases the sensitivity of the system. In addition, the evaporation rate of the solvent in the column inlet is proportional to the carrier gas flow-rate [5]. As a higher solvent evaporation rate will decrease the analysis time, a carrier gas volume flow-rate of 2.4 ml/min was used in this experiment.

Effect of the make-up gas of the lightpipe on a large volume of solvent

Fig. 5 shows that the injection of large volumes may cause distorted solvent peaks when using FTIR as a detection method. The internal diameter of the capillary column of the GC–FTIR system was 0.32 mm, but that of the lightpipe was 1 mm. When the carrier gas passes from the capillary column into the FTIR lightpipe, the average linear velocity decreases ten times as a result of the change in pipe diameter. At these low gas velocities, longitudinal diffusion, *i.e.* broadening of the solvent band, becomes important. To improve the shape of the solvent peak, it is necessary to add a make-up carrier gas at the connection between the chromatography column and the lightpipe. Fig. 5c shows the gas chromatogram of a 100-μl injection after adding a 40 ml/min make-up gas to the lightpipe. The shape of the solvent peak is substantially improved.

Effect of the make-up gas of the lightpipe on the solute peak

Griffiths [6] studied the problem of matching the chromatography fraction half-peak width volume ($V_{1/2}$) to the volume of the lightpipe (V_L). He concluded that only when the average value of the carrier sample half-width volume is greater than or

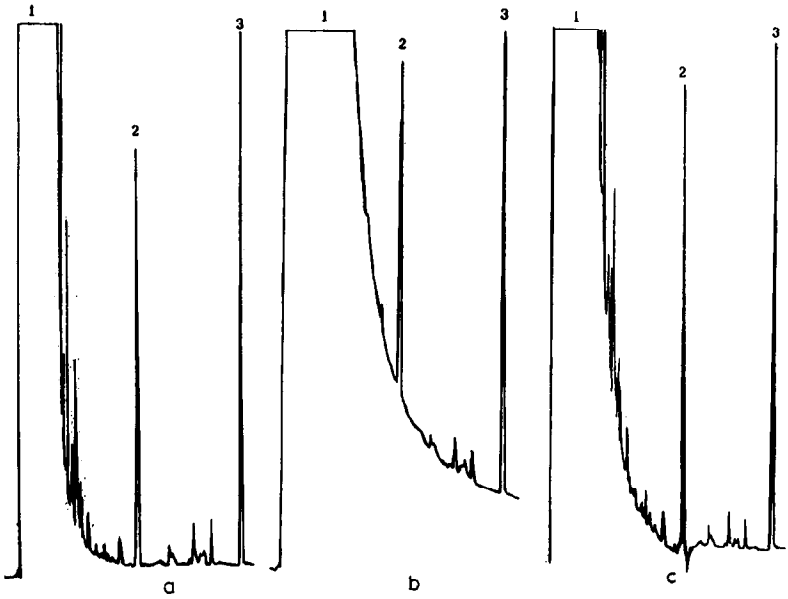

Fig. 5. Chromatograms for 100-μl on-column injection. (a) Capillary column outlet connected to flame ionization detector; (b) capillary column outlet connected to lightpipe (without make-up gas); (c) with 40 ml/min make-up gas to the lightpipe. Temperature, 40°C for 17 min then 5°C/min up to 130°C. Peaks: 1 = *n*-pentane solvent; 2 = decane; 3 = dodecane.

TABLE I

AVERAGE CHROMATOGRAPHIC FRACTION HALF-PEAK WIDTH VOLUMES AT DIFFERENT MAKE-UP GAS FLOW-RATES THROUGH THE LIGHTPIPE

V_L = 0.117 ml; Carrier gas flow-rate = 2.4 ml/min.

Make-up carrier gas flow-rate (ml/min)	Total carrier volume flow-rate (ml/min) (F)	Experimental average half-peak width ($\bar{Y}_{1/2}$) (min)	$\bar{V}_{1/2} = F\bar{Y}_{1/2}$ (ml)
0	2.4	0.160	0.38
10	12.4	0.155	1.92
20	22.4	0.152	3.40
30	32.4	0.151	4.89
40	42.4	0.149	6.32

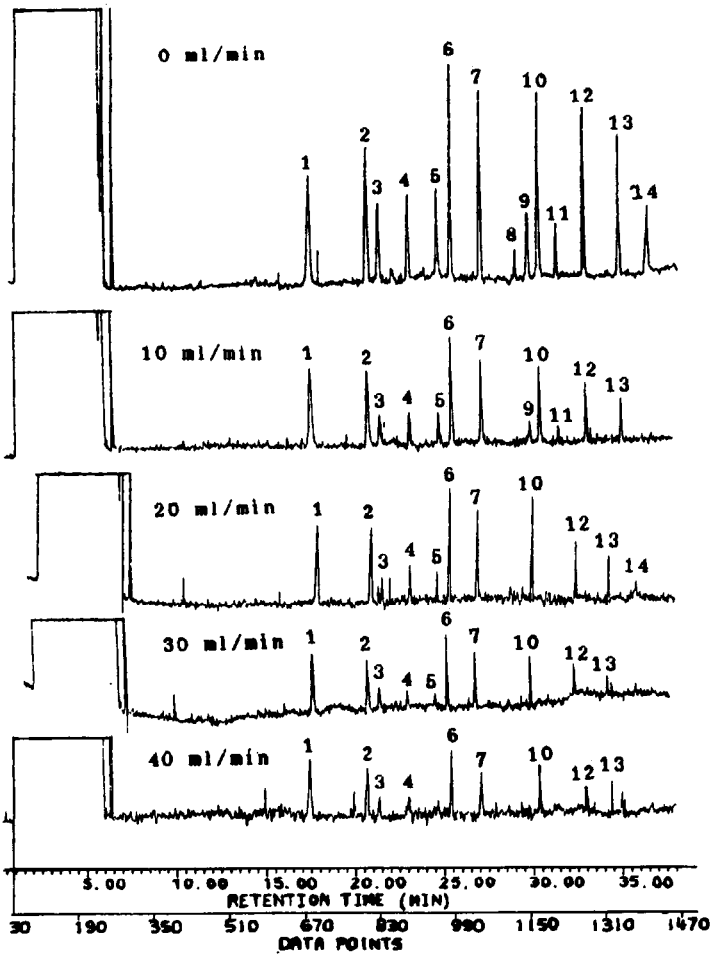

Fig. 6. Gram–Schmidt reconstruction chromatogram with make-up gas flow-rates to the lightpipe. *n*-Pentane solution, 100 μl; 38°C for 17 min then 6°C/min up to 170°C; carrier gas flow-rate, 2.4 ml/min. Peak identification as in Fig. 3.

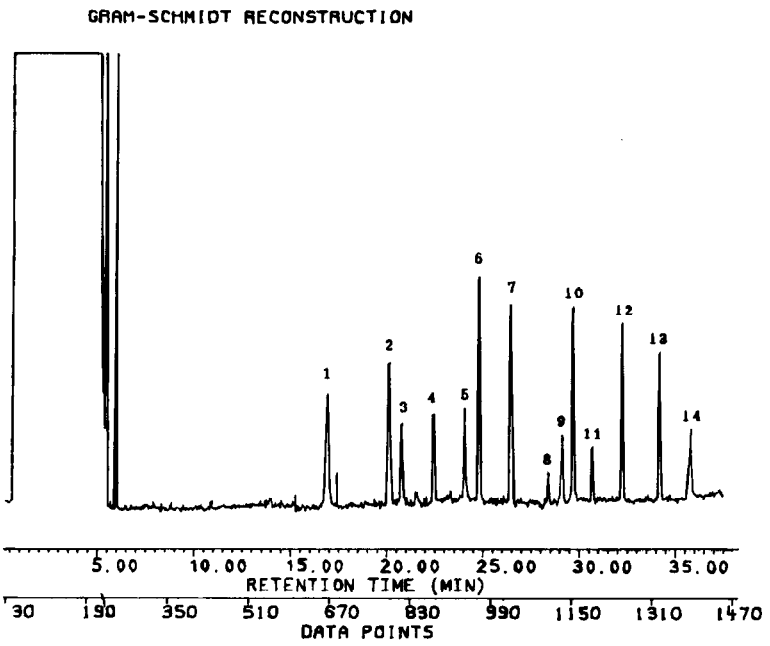

Fig. 7. Gram–Schmidt reconstruction chromatogram for *n*-pentane solution. Chromatographic conditions as in Fig. 6; on-column injection of 100 μl of the *n*-pentane solution. Lightpipe make-up gas flow-rate, 40 ml/min for 12.5 min, then closed. Peak identification as in Fig. 3.

equal to that of the lightpipe *i.e.* $\bar{V}_{1/2} \geqslant \bar{V}_L$, is the best resolution and sensitivity achieved. This may require the introduction of a make-up gas. Table I shows the average value of the half-peak width of the sample volume ($\bar{V}_{1/2}$) obtained by fourteen chromatographic fractions with different make-up gas flow-rates to the lightpipe.

It can be seen from Table I that when the make-up gas flow-rate to the lightpipe is zero, the calculated value $\bar{V}_{1/2}$ is closest to V_L, where the system has the best sensitivity. The experimental results confirmed this. Fig. 6 shows the Gram–Schmidt reconstruction chromatograms for samples obtained at various make-up gas flow-rates into the lightpipe. In fact, with increasing make-up gas flow-rates into the lightpipe, the sensitivity of the system decreases. To obtain well shaped solvent peaks and the optimum sensitivity, a make-up gas flow-rate of 40 ml/min is required during the elution of the solvent. This additional gas flow must be stopped during the analysis. Fig. 7 shows the Gram-Schmidt chromatogram for a 100-μl *n*-pentane solution using the retention gap technique.

Good results were also obtained using solvents of various boiling points and polarity, such as diethyl ether, acetone, dichloromethane, chloroform and *n*-hexane.

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