Journal of Chromatography, 256 (1983) 201–212
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,429

NEW SPLIT INJECTION TECHNIQUE IN CAPILLARY COLUMN GAS CHROMATOGRAPHY

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(Received September 17th, 1982)

SUMMARY

The main sources of discrimination in split injection arise from the change in the splitting ratio caused by variation in the composition of the gas phase and non-uniform distribution of the solvent in the total gaseous sample plug formed during evaporation. Taking this into account, a new split injection technique, characterized by interruption of the carrier gas flow during the sample evaporation period, has been developed whereby the formation of a sample plug with uniform solvent distribution is enhanced. The applicability of the method is discussed and results obtained on two common kinds of sample and under different injection conditions are given.

INTRODUCTION

Split injection is a simple, convenient and widely used sampling method in capillary column gas chromatography (GC). However, difficulties in obtaining quantitative reproducibility and accuracy are often encountered. Numerous reasons for the observed discrimination have been proposed:

(1) Selective evaporation of molecules of different sizes from the syringe needle[1–7],

(2) Changes in splitting ratio caused by pressure waves[6,8,9],

(3) Changes in splitting ratio caused by variations in gas viscosity and by condensation of solvent at the column inlet[1],

(4) Incomplete evaporation and limited speed of evaporation of the sample[6,10–13],

(5) Insufficient mixing of sample vapour with carrier gas[12–15],

(6) Different rates of diffusion of molecules of different sizes[8,13],

(7) Aerosol formation and droplet splitting[1,12],

(8) Adsorption on the liner surface[3,6],

(9) Explosive evaporation and adsorption of less volatile components at cold parts of the carrier gas inlet system[2,16].

The extent to which each of these mechanisms plays a part depends upon the experimental parameters involved. Considering the complexity of the split procedure,

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0021-9673/83/0000–0000/$03.00

some authors believe that it is not possible to construct a non-discriminating split injector[1,8]. Direct column injection has therefore been proposed as the only reliable method for quantitative capillary GC. Although this is undoubtedly the preferred method of sample introduction when accurate quantitative analyses of high boiling and high polarity samples are required, it has certain disadvantages, the most important of which is the accelerated damage to the column, especially at the inlet, caused by solvent plug flushing and by the accumulation of non-volatile contaminants. These difficulties are greater than would appear at first sight —cutting off the damaged column end requires generally that the ends be straightened, thus destroying deactivation at this point of the column. In the split system, on the other hand, only the insert liner has to be changed when contaminated samples are injected. Since split injection has its own advantages, it would seem worthwhile to aim at a quantitatively reliable split injection system.

In a preliminary series of experiments we have attempted to evaluate the relative importance of the factors generally considered to contribute to discrimination in split injection. This work indicated that the change in the viscosity of the gas phase and the recondensation of the solvent in the column are the main causes of discrimination. In this paper we report a split injection technique which yields negligible discrimination when applied to a wide range of samples.

EXPERIMENTAL

Apparatus and procedure

Two sample types have been used in this study: a medium-polarity sample comprising a mixture of C_{10}–C_{20} fatty acid methyl esters and a synthetic mixture of *n*-alkanes ranging from C_{16} to C_{38}. These samples display both a wide boiling range and differing polarities.

Experiments with the ester sample were carried out on a Fractovap Model 2101 gas chromatograph equipped with a hydrogen flame ionization detector. The column was a 20 m × 0.3 mm I.D. glass capillary coated with Carbowax 20M. Temperature programming: 80°C to 245°C at 5°C/min. Carrier gas: hydrogen at 0.9 kg/cm^2. *n*-Alkanes were separated on a 25 m × 0.3 mm I.D. OV-1 column, installed in a Dani Model 3900 gas chromatograph with separate heating controls for the injector and detector block. Temperature programming: 120°C to 330°C at 10°C/min. Carrier gas: hydrogen at 0.5 kg/cm^2. Detector temperature: 340°C. On-column injections for comparison were carried out on a Dani Model 3900 gas chromatograph equipped with a Dani on-column injection device. Temperature programming: 50°C to 80°C at 25°C/min followed by 80°C to 245°C at 5°C/min for esters; 60°C to 120°C at 25°C/min followed by 120°C to 330°C at 10°C/min for *n*-alkanes. For peak area measurement a Spectra-Physics Model System 1 integrator and a HP Model 3390 A computing integrator were used.

Injections were carried out with a Hamilton 10-μl syringe according to the so-called "solvent flushing" procedure[4]: the syringe needle and barrel were wetted with pure solvent, leaving the needle filled with solvent; 0.1 μl of solvent, followed by 0.1 μl air and then the required volume of sample were drawn into the syringe; the whole liquid plug was drawn back into the barrel, the needle inserted quickly into the liner, the plunger depressed and the needle withdrawn immediately. The needle length was

TABLE I

DISCRIMINATION ON AN EMPTY LINER

Solvent: toluene. Sample volume: 0.5 μl. Injection temperature: 200°C. Split flow: 27 ml/min.

Injection no.	*Relative peak area of methyl ester of fatty acid**			
	n-C_{10}	n-C_{12}	n-C_{14}	n-C_{18}
1	0.103	0.380	0.756	1.326
2	0.068	0.263	0.587	1.309
3	0.070	0.271	0.593	1.300
4	0.098	0.356	0.717	1.357
5	0.066	0.256	0.575	1.306
6	0.082	0.309	0.656	1.313
Mean	0.081	0.306	0.647	1.319
On-column	0.061	0.236	0.548	1.283
*D***	1.33	1.30	1.18	1.03

* Peak area of methyl ester on n-C_{19} acid taken as 1.000.

** Discrimination factor, $D = A_R/A'_R$, where A'_R = on-column relative peak area.

about 22–23 mm; it intrudes only a few millimetres into the insert liner. The sample evaporates within the glass injection liner. The liner used with the Carlo Erba gas chromatograph is about 7.3 cm × 2.6 mm I.D.; the Dani apparatus incorporates liners of about 5.8 cm × 3.6 mm I.D. The columns were mounted so that they enter about 4–5 mm into the liner. In different experiments the liner design or carrier gas flow was changed, and the sample injected under the same operating conditions.

RESULTS AND DISCUSSION

Empty liner

The empty liner is the simplest and most commonly used liner. The results obtained are given in Table I and compared with on-column injection. As can be seen, the lower boiling decanoic and dodecanoic acid esters show discrimination (about

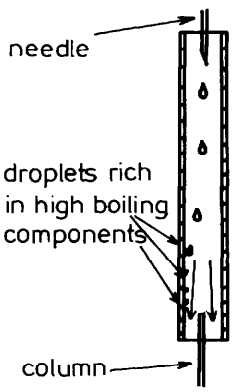

Fig. 1. Empty liner.

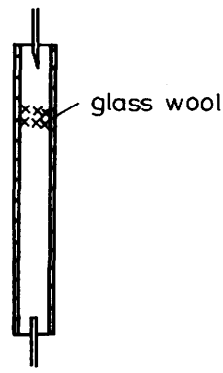

Fig. 2. Glass wool packed liner.

TABLE II

RESULTS OBTAINED WITH THE GLASS WOOL PACKED LINER

Solvent: toluene. Sample volume: 0.5 μl esters.

Glass wool treatment	*Injection temp. (°C)*	*Relative peak area*				D_{10}*
		C_{10}	C_{12}	C_{14}	C_{18}	
Silanization	300	No peak appears				–
Washing with chromic acid, then water	200	Peaks show severe tailing				–
	300	0.084	0.319	0.691	1.335	1.38
Washing with HCl, then water	200	0.081	0.318	0.699	1.381	1.33
	300	0.071	0.275	0.608	1.306	1.16

* The discrimination factor of decanoic acid methyl ester.

TABLE III

RESULTS ON GLASS WOOL PACKED LINER

Solvent: *n*-decane. Sample: 0.1–5 μl esters. Injection temperature: 300°C. Split flow: 23 ml/min. Glass wool washed with HCl, then water.

Sample volume (μl)	*Relative peak area*			
	C_{10}	C_{12}	C_{14}	C_{18}
0.5	0.074	0.272	0.608	1.292
0.5	0.073	0.276	0.617	1.302
0.3	0.073	0.277	0.618	1.302
0.3	0.073	0.280	0.625	1.310
0.1	0.076	0.280	0.637	1.308
0.1	0.073	0.278	0.629	1.302
Mean	0.074 ± 0.0012	0.277 ± 0.003	0.622 ± 0.010	1.303 ± 0.006
D	1.21	1.17	1.14	1.02

TABLE IV

GLASS BEAD PACKED LINER

Solvent: toluene. Sample: 0.5 μl esters. Injection temperature: 200°C.

Split flow-rate (ml/min)	*Relative peak area*				D_{10}
	C_{10}	C_{12}	C_{14}	C_{18}	
65	0.074	0.285	0.632	1.342	1.22
30	0.070	0.265	0.595	1.317	1.15
25	0.069	0.268	0.598	1.321	1.13
20	0.066	0.262	0.591	1.323	1.09
15	0.064	0.249	0.561	1.287	1.04

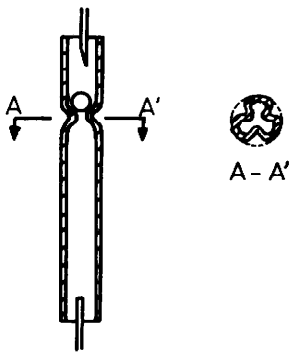

Fig. 3. Glass bead packed liner.

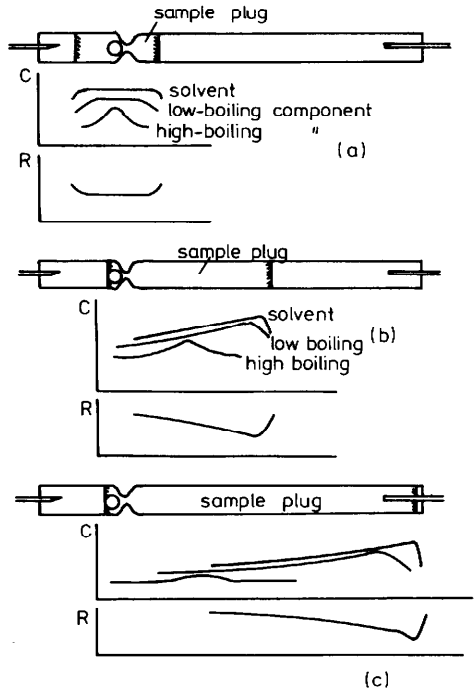

Fig. 4. Sample plug configuration. a, Carrier gas (hydrogen) flow-rate, 0 ml/min; solvent plug, 0.5 μl; sample plug, 0.1 ml; liner volume, 0.5 ml. b, Carrier gas flow-rate, 15 ml/min; sample plug, 0.2 ml; evaporation time, 0.4 sec. c, Carrier gas flow-rate, 45 ml/min; sample plug, 0.4 ml. C = Concentration; R = splitting ratio.

30%) in comparison to the higher boiling acid esters. Also the results of successive injections vary greatly in the case of lower boiling components. This may be explained as follows. As liquid droplets travel along the liner, evaporation takes place continuously; low boiling constituents evaporate quickly, and the droplets become richer in high boiling constituents (Fig. 1). These droplets strike the liner wall at a lower part of the liner where they more or less completely evaporate. Because of the lower diffusion rate of high boiling molecules, however, they will be vented off before they can reach the centre of the liner, and thus the true splitting ratio for these components will be larger than that for low boiling substances.

If we can force these droplets to make contract with a hot surface above the column inlet, discrimination should become less. Thus we must supply an effective evaporative surface in the upper region of the liner.

Glass wool packed liner

In order to avoid discrimination encountered with empty liners, many authors[5,12,13] recommend the use of glass wool both to supply an effective evaporation surface and to ensure sufficient mixing of the sample with the carrier gas. Glass wool however has a very high surface area, and great caution must be exercised in the case

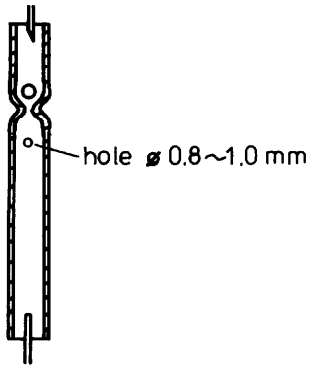

Fig. 5. Two-stream liner.

of polar substances. We inserted a short glass wool plug (pretreated as described in Table II) into the liner at the injection region (Fig. 2). The results obtained with this liner are shown in Tables II and III.

The reproducibility with this liner is reasonable, but discrimination caused by adsorption becomes dominant, especially at lower injector temperatures. While the glass wool provides an effective evaporation surface, the increase in surface also increases adsorption.

Evaporation from glass bead surface

In order to reduce the influence of adsorption, we substituted glass wool with a smooth glass bead (or a number of smaller glass beads, Fig. 3). The results in Table IV show that at lower split flows the relative peak areas are very close to those obtained by on-column injection. This means complete evaporation can be achieved with this device without noticeable adsorption. With increasing split flow-rate, discrimination becomes more evident. To explain this result we assume that evaporation from the surface of the glass bead takes a certain time (the order of a few tenths of a

TABLE V

RESULTS OBTAINED WITH TWO-STREAM LINER

Solvent: toluene. Sample: 0.5 μl esters. Injection temperature: 200°C. Split flow: 27 ml/min.

Injection no.	*Relative peak area*			
	C_{10}	C_{12}	C_{14}	C_{18}
1	0.063	0.246	0.563	1.276
2	0.056	0.232	0.539	1.274
3	0.062	0.247	0.573	1.286
4	0.065	0.251	0.568	1.280
5	0.064	0.252	0.573	1.288
6	0.062	0.242	0.556	1.279
Mean	0.062 ± 0.003	0.245 ± 0.007	0.562 ± 0.013	1.281 ± 0.006
D	1.02	1.04	1.03	1.00

second), depending upon the sample volume and liner temperature. Solvent and low boiling substances are evaporated quickly whereas high boiling compounds lag behind. In the absence of a carrier gas flow the solvent vapour would be distributed uniformly by diffusion in the so formed sample plug (Fig. 4a). When this plug is transported to the column inlet, the splitting ratio remains constant over the length of the plug, resulting in less discrimination. It should be pointed out that in this situation the distribution of individual components in the plug need not be uniform. The actual distribution of sample components is symmetrical rather than uniform (see Fig. 4).

If carrier gas flows during the evaporation step the symmetrical distribution will be destroyed. The carrier gas flushes away sample molecules immediately after they enter the gas phase. Therefore the main part of the solvent exists at the front of the sample plug. Low boiling components, which also appear mainly at the front of the solvent plug, will experience a much lower splitting ratio (Fig. 4b) due to changes in viscosity of the gas phase and condensation of the solvent. When the carrier gas flow is increased further, as in the case of Fig. 4c, the difference in splitting ratio between low boiling and high boiling substances also becomes greater resulting in even greater discrimination.

The sample plug sizes in Fig. 4a, b and c are different. Assuming an evaporation time of 0.4 sec, we can calculate that with no flow the gaseous plug size of 0.5 μl of toluene is *ca.* 0.1 ml, whereas with a flow-rate of 0.25 ml/sec (15 ml/min) the plug size increases to $0.1 + 0.25 \times 0.4 = 0.2$ ml. We therefore must reduce the flow-rate through the evaporation zone during the time of evaporation.

Two-stream liner

The above results indicate that the flow-rate of the carrier gas through the evaporation region is of critical importance. By reducing this flow-rate we can reduce discrimination; but at the same time the splitting ratio is also reduced. In order to reduce the gas flow through the evaporation region while maintaining a larger splitting ratio, we pierced the liner wall behind the evaporation area (Fig. 5). The carrier

TABLE VI

RESULTS OBTAINED WITH STOP-FLOW METHOD

Solvent: toluene. Sample: 0.5 μl esters. Injection temperature: 200°C. Split flow: 27 ml/min.

Injection no.	*Total integration peak area*	*Relative peak area*			
		C_{10}	C_{12}	C_{14}	C_{18}
1	444,000	0.063	0.248	0.570	1.332
2	475,000	0.060	0.240	0.553	1.297
3	530,000	0.059	0.237	0.543	1.263
4	525,000	0.060	0.237	0.548	1.296
5	530,000	0.061	0.240	0.547	1.283
6	510,000	0.062	0.246	0.560	1.264
7	465,000	0.059	0.237	0.547	1.266
Mean	497,000 ± 35,000	0.061 ± 0.0015	0.241 ± 0.0045	0.553 ± 0.009	1.286 ± 0.025
D	–	1.00	1.02	1.01	1.00

TABLE VII

INFLUENCE OF SPLITTING RATIO

Solvent: toluene. Sample: 0.5 μl esters. Injection temperature: 200°C.

Split flow (ml/min)	*Total area*	*Relative peak area*				D_{10}
		C_{10}	C_{12}	C_{14}	C_{18}	
15	850,000	0.062	0.247	0.563	1.288	1.02
27	506,000	0.061	0.241	0.553	1.286	1.00
30	440,000	0.061	0.245	0.558	1.280	1.00
60	215,000	0.063	0.250	0.565	1.276	1.03
65	185,000	0.060	0.243	0.557	1.263	0.98
120	114,000	0.063	0.241	0.553	1.267	1.03

TABLE VIII

INFLUENCE OF LINER TEMPERATURE AND SOLVENT NATURE

Sample: 0.5 μl esters. Split flow: 27 ml/min.

Solvent	*Injection temp. (°C)*	*Relative peak area*				D_{10}
		C_{10}	C_{12}	C_{14}	C_{18}	
Toluene	200	0.061	0.241	0.553	1.286	1.00
	250	0.062	0.244	0.555	1.275	1.02
n-Decane	200	0.065	0.258	0.587	1.290	1.07
	250	0.064	0.255	0.582	1.284	1.05
		0.064	0.256	0.587	1.286	1.05
n-Octane	250	0.071	0.272	0.609	1.297	1.16
n-Octane–toluene (2:1)	250	0.063	0.252	0.574	1.277	1.03

TABLE IX

INFLUENCE OF SAMPLE VOLUME

Injection temperature: 250°C.

Solvent	*Sample volume (μl)*	*Relative peak area*				D_{10}
		C_{10}	C_{12}	C_{14}	C_{18}	
Toluene	0.1	0.064	0.264	0.573	1.264	1.05
	0.5	0.062	0.243	0.555	1.275	1.02
	1.0	0.059	0.239	0.558	1.289	0.97
n-Decane	0.1	0.065	0.260	0.571	1.284	1.06
	0.5	0.064	0.255	0.582	1.284	1.05

gas flow is divided into two streams. The main gas stream flows through the hole into the liner, and only a small part of the carrier gas flows through the evaporation region, resulting in a relatively shorter and uniform sample plug. When this plug encounters the main stream it will become even more uniform through mixing and this should lead to much lower discrimination. The results shown in Table V confirm this.

Although this liner solves most problems, there remains uncertainty in the control of the flow-rate of the two streams. If the flow-rate through the evaporation area is too low increased peak width is observed. If on the other hand we have excessive flow through the evaporation zone, as in the case of too high a splitting ratio (*i.e.*, too high a carrier gas flow-rate), the symmetry of the plug is lost. Acceptable flow conditions for this liner lie within relatively narrow boundaries, and this is difficult to control.

Stop-flow method

This problem can be resolved by a technique in which the carrier gas flow is temporarily stopped during the evaporation period in order to form an ideal sample plug with uniform solvent distribution, and then quickly to sweep the sample plug through the split region.

The injection is then carried out as follows. With a simple glass ball packed liner, the on-off valve behind the split valve is closed to stop the carrier gas flow, the pressure is allowed to stabilize (10 sec), the sample is injected and after 1–2 sec the valve is opened and temperature programming and integration started. The split valve should be kept at the required setting during injection. The whole procedure closely resembles splitless injection, but the concept is nevertheless quite different. In splitless injection one normally closes the vent valve for 30–60 sec in order to flush the total sample into the column. Here column flow is absolutely necessary, while in our method we just stop the split flow for 1–2 sec to allow the formation of an ideal sample plug. Column flow during this 1–2 sec evaporative period is detrimental, but unavoidable (as will be shown below). Results obtained by this split injection method are given in Table VI.

Table VI shows that the stop-flow method gives accurate and reproducible results, and thus that the analysis of the main causes of discrimination is correct. The total integration area in Table VI can serve as a measure of the absolute accuracy of the stop-flow method. The relative standard deviation of the absolute area measurement is about 7%, which is in the range of accuracy of a 10-μl syringe injecting 0.5 μl of sample.

Influence of injection parameters on the results. If an injection technique is reliable, variation within limits of parameters such as liner temperature, splitting ratio, solvent nature and sample volume should not affect the quantitative results. The performance of the stop-flow method under different conditions is documented in Tables VII–IX.

Over a wide range, the splitting ratio has no influence on the quantitative results. This greatly facilitates sample handling. Injecting a concentrated sample solution under a larger splitting ratio eliminates the need for sample dilution or for small volume injection, as is necessary in on-column injection. A change in liner temperature within the normal range has no noticeable influence on the results as shown in

TABLE X

DISCRIMINATION CAUSED BY LONG RETARDING TIME

Injection temperature: 250°C. Solvent: toluene.

Sample (μl)	*Retarding time (sec)*	*Relative peak area*				D_{10}
		C_{10}	C_{12}	C_{14}	C_{18}	
0.5	1–2	0.062	0.244	0.555	1.275	1.02
	5	0.075	0.292	0.643	1.298	1.23
1.0	1	0.059	0.239	0.558	1.289	0.97
	2	0.066	0.263	0.604	1.312	1.09

Table VIII. Solvents of different polarities result in some differences. The more polar solvent toluene gives better results than the non-polar solvent *n*-decane. Poorer results are obtained when a lower boiling non-polar solvent (*e.g.*, *n*-octane) is used. This can be explained by slight adsorption of the esters on the glass surfaces. The addition of *ca.* 30% (v/v) toluene to *n*-octane is sufficient to compensate for this effect.

With toluene as solvent at a liner temperature of 250°C, the discrimination factor of decanoic acid methyl ester, D_{10}, can rise to 1.21 for a sample volume of 0.1 μl. This is caused by a larger relative proportion of the sample adhering to the wall of the needle. When the needle is inserted into the hot evaporative zone this part of the sample is evaporated but with severe discrimination[4]. The effect can be counteracted by drawing a further 0.1 μl of solvent into the barrel after the sample, thus washing the needle.

Limitation of the method. As has been stated above, the on-off valve must be opened 1–2 sec after injection. A longer delay will lead to noticeable discrimination (see Table X). This may be explained by the fact that during the period when the valve is closed a small flow of carrier gas equal to the flow-rate through the column still exists in the injection liner. If the valve is closed for too long a period the front of the sample plug, which is richer in low boiling components (see Fig. 4a), will reach the column inlet by diffusion and be swept into the column with carrier gas. Low boiling components thus experience an average splitting ratio significantly different to that of high boiling components. With increasing sample volume the front edge of the sample

TABLE XI

DISCRIMINATION CAUSED BY LONG STOP-FLOW TIME IN THE INLET VALVE-CLOSING VERSION

Solvent: toluene. Injection temperature: 250°C.

Sample volume (μl)	*Retarding time (sec)*	*Relative peak area*				D_{10}
		C_{10}	C_{12}	C_{14}	C_{18}	
0.5	2	0.061	0.243	0.558	1.291	1.00
0.5	5	0.057	0.230	0.544	1.272	0.93
1.0	5	0.053	0.215	0.511	1.270	0.87

TABLE XII

ANALYSIS OF *n*-ALKANE SAMPLES

Solvent: *n*-decane. Sample: 0.5 μl A. Injection temperature: 250°C. Split flow: 50 ml/min.

	n-C_{16}	n-C_{18}	n-C_{24}	n-C_{26}	n-C_{34}	n-C_{36}
Peak area relative to n-C_{36}*	0.804 ± 0.024	0.700 ± 0.021	1.257 ± 0.052	1.218 ± 0.054	0.773 ± 0.022	1.000
Known value	0.821	0.679	1.191	1.189	0.802	1.000
D	0.98	1.03	1.06	1.02	0.96	–

* Average from five injections.

plug reaches the column inlet earlier, therefore a shorter stop-flow time must be used with increasing sample volumes. This is confirmed by the results obtained with another version of the stop-flow method.

In this version, instead of closing the split valve, the carrier gas inlet valve on the carrier gas line ahead of the injector block is closed. The other operations are the same as described above. In this mode of operation, with excessive stop-flow time the front part of the sample plug will now enter the split line rather than the column, causing a discrimination towards low boiling substances (Table XI).

It is suggested, therefore, that the time of stopping the flow in each mode should be about 1–2 sec. This has been found to be sufficient for complete evaporation.

Samples with wide boiling range. In order to check the applicability of the stop-flow technique to samples having a wide boiling range, we analyzed mixtures of *n*-alkanes from hexadecane to octatriacontane. For sample A, the known values of relative peak area (see Table XII) were calculated from the weights of the samples, whereas for sample B (Table XIII), the known values were obtained by on-column injection. The somewhat large standard deviations found arise at least in part from the fact that we have used samples with a concentration of *ca.* 0.01 % and the large splitting ratio. This results in larger errors on integration than for a more concentrated sample. Taking account of this, the agreement between the known and experimental values is satisfactory.

TABLE XIII

ANALYSIS OF *n*-ALKANE SAMPLES

Solvent: toluene. Sample: 0.5 μl B.

	n-C_{16}	n-C_{18}	n-C_{24}	n-C_{26}	n-C_{32}	n-C_{34}	n-C_{36}	n-C_{38}
Peak area relative to n-C_{38}*	1.87 ± 0.006	3.41 ± 0.17	3.11 ± 0.15	1.55 ± 0.174	1.52 ± 0.044	1.37 ± 0.03	1.19 ± 0.017	1.00 –
Known value	1.95	3.56	3.04	1.47	1.47	1.33	1.19	1.00
D	0.96	0.96	1.02	1.05	1.03	1.03	1.00	–

* Average from ten injections.

CONCLUSION

Within reasonable limits of variation of the operating parameters such as injection temperature, splitting ratio, solvent nature and sample volume, the stop-flow injection technique can produce accurate and reproducible results with samples of high boiling range. It has the advantage of being extremely cheap, and can be implemented with almost every capillary column gas chromatograph without any need for instrument modification. The liners used with the stop-flow technique are very simply constructed and can easily be replaced or cleaned when non-volatile materials accumulate. The operation is simple enough to be carried out by every laboratory worker.

ACKNOWLEDGEMENT

We thank Mr. G. Nicholson in this institute for providing the capillary columns and for valuable discussion.

REFERENCES

1 K. Grob, Jr., in R. E. Kaiser (Editor), *Capillary Chromatography, Fourth International Symposium, Hindelang*, Institute of Chromatography, Bad Dürkheim, 1981, p. 185.
2 G. Schomburg, in R. E. Kaiser (Editor), *Capillary Chromatography, Fourth International Symposium, Hindelang*, Institute of Chromatography, Bad Dürkheim, 1981, p. 371.
3 K. Grob and K. Grob, Jr., *J. Chromatogr.*, 151 (1978) 311.
4 K. Grob, Jr. and H. P. Neukom, *High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 15.
5 G. Schomburg, H. Husmann and R. Rittmann, *J. Chromatogr.*, 204 (1981) 85.
6 F. Munari and S. Trestianu, in R. E. Kaiser (Editor), *Capillary Chromatography, Fourth International Symposium, Hindelang*, Institute of Chromatography, Bad Dürkheim, 1981, p. 849.
7 F. Poy, S. Visani and F. Terrosi, *J. Chromatogr.*, 217 (1981) 81.
8 H. Bruderreck, W. Schneider and I. Halász, *J. Gas Chromatogr.*, 5 (1967) 217.
9 K. Grob, Jr. and H. P. Neukom, *High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 563.
10 A. L. German and E. C. Horning, *Anal. Lett.*, 5 (1972) 619.
11 W. G. Jennings, *J. Chromatogr. Sci.*, 13 (1975) 185.
12 G. Schomburg, H. Behlau, R. Dielmann, F. Weeke and H. Husmann, *J. Chromatogr.*, 142 (1977) 87.
13 C. Watanabe, H. Tomita and N. Sato, in R. E. Kaiser (Editor), *Capillary Chromatography, Third International Symposium, Hindelang*, Institute of Chromatography, Bad Dürkheim, 1981, p. 499.
14 M. J. Hartigan and L. S. Ettre, *J. Chromatogr.*, 119 (1976) 187.
15 L. S. Ettre, *Introduction to Open Tubular Columns*, Perkin-Elmer, Norwalk, CT, 1979.
16 J. Eyem, *J. Chromatogr.*, 217 (1981) 99.