Journal of Chromatography, 388 (1987) 325–333
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 162

MICROPACKED COLUMNS: A SUITABLE ALTERNATIVE TO VERY THICK CAPILLARY COLUMNS

TOMAS HERRAIZ, GUILLERMO REGLERO*, MARTA HERRAIZ, ROSARIO ALONSO and MARIA DOLORES CABEZUDO

Instituto de Fermentaciones Industriales, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006 Madrid (Spain)

(First received August 28th, 1986; revised manuscript received October 22nd, 1986)

SUMMARY

A comparative study has been made between micropacked and thick film capillary columns, based on the specific column efficiency (theoretical plate number per metre of column length), peak resolution and sample capacity. Data were obtained for six columns with similar phase ratios: three micropacked columns and three capillary columns, whose thickness ranged from 0.84 to 2.62 μm. The column length and analysis time required to achieve a given resolution are also included.

INTRODUCTION

Thick film capillary columns require fewer plates to achieve the same resolution than thin film columns; therefore they are particularly suitable for the analysis of low-boiling compounds[1,2]. Moreover, the thicker the film, the higher is the capacity and also the less pronounced is the superficial activity of the column. On the other hand, thick films have some disadvantages such as lower efficiency and longer analysis time[3].

Grob and Grob[4] pointed out as early as 1977 that a narrow range of film thickness drastically reduces the range of applications and stressed the importance of carefully selecting the most suitable film thickness for the analysis of a specific sample. At that time, however, it was possible to make high-performance capillary columns with film thicknesses up to only 1.85 μm.

In the last few years several authors[5–8] have carried out extensive studies on the imobilization of the liquid phase. As a result it is now possible to prepare excellent capillary columns with film thicknesses ranging from 1 to 8 μm[9].

Ettre *et al.*[10] studied the performance of several columns with film thicknesses up to 5 μm. Ingraham *et al.*[11] studied some interrelated chromatographic parameters such as column length, internal diameter and phase film thickness (exclusively from 0.1 to 1 μm). Recently, Ettre[12,13] evaluated the effect of the column internal diameter and also of the film thickness on column efficiency. Comparative studies of packed *versus* capillary columns were carried out and the concept of relative sample capacity

0021-9673/87/$03.50

was introduced. David *et al.*[14] considered the influence of the liquid phase polarity on the efficiency of a thick film capillary column. Leclerq *et al.*[15] studied the advantages of a thick film capillary column in the so-called hyphenated techniques (capillary gas chromatography in combination with a spectroscopic technique). Moreover, the use of chromatographic columns wiht high sample capacities has been used to advantage in olfactive analysis of column effluents[16].

In spite of all the advances made in this field during the last few years, high-performance thick film capillary columns containing certain liquid phases are difficult to obtain. Columns made from polar phases such as poly(cyanopropylsiloxanes) and poly(ethylene glycols) are presently being developed. Moreover, it is very difficult to prepare good thick film capillary columns comprised of mixed phases. Therefore, thick film capillary columns can be made only with a limited number of liquid phases, thereby reducing the applicability of the technique.

Micropacked columns[17] might be a suitable alternative to the use of thick film capillary columns because they have high capacities and can withstand carrier gas flow-rates that are compatible with standard injection systems.

We have previously published a theoretical study of all of the parameters which influence the specific column efficiency as well as its permeability[18]. Using Volaspher A-2 as a solid support, micropacked columns whose specific efficiencies ranged between 6200 ($k=3$, $d_c=1$ mm; apolar liquid phases) and 2000 theoretical plates per metre ($k=3$, $d_c=1$ mm; polar liquid phase) were prepared with a variety of pure or mixed stationary phases. Because of the versatility and separation power of these columns, we thought that they might be a suitable alternative to thick film capillary columns. In this paper we report a comparison of micropacked columns and thick film capillary columns, including column efficiency (height equivalent to a theoretical plate, HETP), resolution and sample capacity.

EXPERIMENTAL

For the comparative study six columns were made from Pyrex glass tubing; for all columns the stationary phase was OV-1. Columns A–C were micropacked using Volaspher A-2 (100–125 μm). Columns D–F were thick film columns. The dimensions, percentage loading (for columns A–C) or film thickness (for columns D–F) as well as the phase ratios are given in Table I.

An Hewlett-Packard 5830A gas chromatograph with a standard injector and

TABLE I

CHARACTERISTICS OF THE COLUMNS USED

Column	*Type*	*Length (m)*	*I.D. (mm)*	*Loading (%, w/w)*	*Film thickness (μm)*	*Phase ratio*
A	Micropacked	2.01	0.82	0.95	–	154
B	Micropacked	3.43	0.82	2.15	–	67
C	Micropacked	2.74	0.82	2.46	–	58
D	Open capillary	5.47	0.45	–	0.84	133
E	Open capillary	3.60	0.45	–	1.97	57
F	Open capillary	7.55	0.53	–	2.62	50

TABLE II

RESISTANCE-TO-MASS-TRANSFER TERM, C, AND THE RELATIVE CONTRIBUTIONS, C_g AND C_l, FOR THE SOLUTES USED ON THREE MICROPACKED COLUMNS

Column	*Solute*	$10^4 \cdot C$ *(s)*	C_g *(%)*	C_l *(%)*
A	Ethyl heptanoate	41	12	88
	Ethyl octanoate	33	17	83
	Ethyl nonanoate	25	21	79
	Ethyl decanoate	23	25	75
	Ethyl undecanoate	23	27	73
B	Ethyl heptanoate	34	16	84
	Ethyl octanoate	39	16	84
	Ethyl nonanoate	24	23	77
	Ethyl decanoate	26	23	77
	Ethyl undecanoate	22	26	74
C	Ethyl heptanoate	57	11	89
	Ethyl octanoate	50	11	89
	Ethyl nonanoate	42	12	88
	Ethyl decanoate	41	13	87
	Ethyl undecanoate	39	14	86

flame ionization detector linked to an Hewlett-Packard 18850A data station was used.

The analyses were carried out with an homologous series of ethyl esters of C_7–C_{11} linear acids. Helium was used as the carrier gas. In all cases, the analysis temperature was 125°C.

TABLE III

RESISTANCE-TO-MASS-TRANSFER TERM, C, AND RELATIVE CONTRIBUTIONS, C_g AND C_l, FOR THE SOLUTES USED ON THREE THICK FILM CAPILLARY COLUMNS

Column	*Solute*	$10^4 \cdot C$ *(s)*	C_g *(%)*	C_l *(%)*
D	Ethyl heptanoate	40	10	90
	Ethyl octanoate	27	19	81
	Ethyl nonanoate	19	32	68
	Ethyl decanoate	14	50	50
	Ethyl undecanoate	12	63	38
E	Ethyl heptanoate	128	4	96
	Ethyl octanoate	78	8	92
	Ethyl nonanoate	45	15	85
	Ethyl decanoate	27	27	73
	Ethyl undecanoate	20	40	60
F	Ethyl heptanoate	225	3	97
	Ethyl octanoate	120	7	93
	Ethyl nonanoate	70	14	86
	Ethyl decanoate	41	26	74
	Ethyl undecanoate	28	40	60

TABLE IV

PERFORMANCES OF THE COLUMNS USED WITH ETHYL HEPTANOATE AS SOLUTE

Column	*Capacity factor*	*HETP (mm)*	*Theoretical plate number, N*	*N per metre*	*Resolution**
A	1.79	0.664	3009.4	1504.7	0.296
B	3.86	0.576	5893.9	1733.5	0.393
C	4.46	0.715	3775.7	1398.7	0.363
D	2.15	1.040	5278.3	959.7	0.251
E	4.46	1.880	1915.2	532.0	0.224
F	4.87	2.490	3009.7	401.3	0.198

* Calculated by considering as the second peak that with the specified capacity factor. The relative retention is assumed to be 1.05.

RESULTS AND DISCUSSION

Table II and III give the resistance-to-mass-transfer term, C, as well as the relative contributions, C_g and C_l, in the gas and liquid phases respectively. The calculated values of C for micropacked columns are similar or lower (for the compounds with the smallest capacity factors) than those which are obtained for capillary columns with similar phase ratios (see columns C and F or C and E). It should be noted that C and therefore the column efficiency depends on the phase loading or film thickness used.

Tables IV and V list the specific characteristics as well as the values obtained for HETP, the number of theoretical plates, N, the theoretical plate number per metre and the peak resolution, R_s. Table IV shows data calculated using ethyl heptanoate, while in Table V the solute was ethyl undecanoate. Consistently higher specific efficiencies, N per metre, and peak resolution parameters were obtained with the micropacked columns. Column B (Table V) shows the highest specific efficiency and column F gives the lowest value, 42% less than that of column B. However, the peak resolution in column F is only 23% less than that in column B. With regard to the micropacked columns, data were obtained which showed the expected critical influ-

TABLE V

PERFORMANCES OF THE COLUMNS USED WITH ETHYL UNDECANOATE AS THE SOLUTE

Column	*Capacity factor*	*HETP (mm)*	*Theoretical plate number, N*	*N per metre*	*Resolution**
A	17.19	0.460	4339	2169	0.52
B	36.43	0.460	7450	2172	0.54
C	42.20	0.629	4351	1588	0.46
D	19.77	0.527	10377	1897	0.49
E	42.51	0.670	5377	1494	0.45
F	48.87	0.795	9498	1258	0.41

* Calculated as in Table IV.

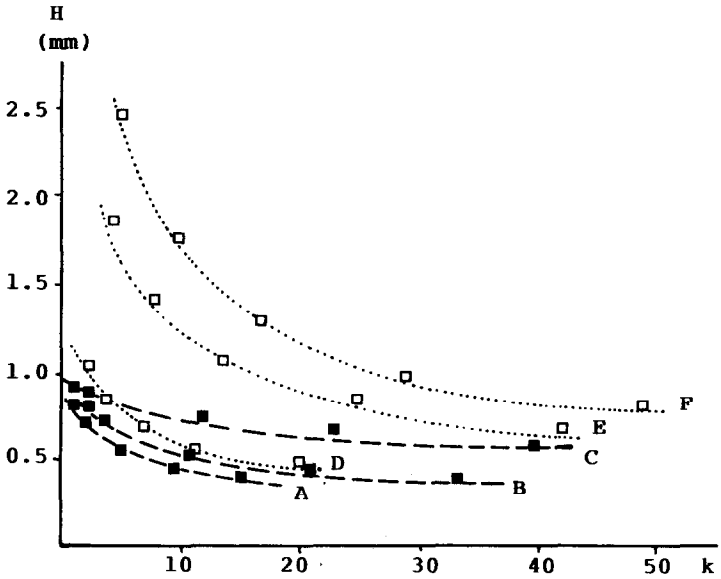

Fig. 1. HETP of micropacked (■) and thick film capillary columns (□) as a function of the capacity factor, k.

TABLE VI

OPTIMUM CARRIER GAS VELOCITY, U_{op}, THE ANALYSIS TIME, t, AND THE ANALYSIS TIME PER METRE OF COLUMN LENGTH, t/L

Parameter	*Column*	*Ethyl heptanoate*	*Ethyl octanoate*	*Ethyl nonanoate*	*Ethyl decanoate*	*Ethyl undecanoate*
U_{op}	A	8.11	8.74	10.11	10.50	10.06
(cm/s)	B	8.40	7.70	10.00	9.40	10.50
	C	6.30	7.20	8.10	7.80	8.00
	D	13.15	15.50	18.00	20.60	21.50
	E	7.32	9.13	11.70	14.70	16.90
	F	5.50	7.40	9.40	12.00	14.30
t	A	1.14	1.60	2.20	3.48	6.00
(min)	B	3.26	5.75	7.28	13.26	20.23
	C	3.91	5.59	8.18	14.50	24.30
	D	2.20	2.80	3.85	5.50	8.80
	E	4.46	5.87	7.74	10.44	15.48
	F	13.27	18.19	23.00	30.60	44.10
t/L	A	0.57	0.80	1.10	1.74	3.00
(min/m)	B	0.96	1.69	2.14	3.90	5.95
	C	1.45	2.07	3.03	5.37	9.00
	D	0.40	0.51	0.70	1.00	1.60
	E	1.24	1.63	2.15	2.90	4.30
	F	1.77	2.41	3.05	4.05	5.84

TABLE VII

NUMBER OF THEORETICAL PLATES, $N_{1.5}$, COLUMN LENGTH, $L_{1.5}$, AND ANALYSIS TIME, $t_{r1.5}$, REQUIRED TO ACHIEVE A RESOLUTION OF 1.5

*Compounds**	*Column*	$N_{1.5}$	$L_{1.5}$ *(cm)*	$t_{r1.5}$ *(min)*
Ethyl heptanoate–ethyl octanoate	A	315	18.1	0.14
	B	249	14.9	0.25
	C	238	17.0	0.53
	D	315	26.5	0.14
	E	237	33.9	0.55
	F	178	31.4	0.76
Ethyl octanoate–ethyl nonanoate	A	262	13.5	0.15
	B	238	11.7	0.27
	C	234	16.0	0.48
	D	216	17.9	0.12
	E	216	22.9	0.49
	F	249	33.0	1.00
Ethyl nonanoate–ethyl decanoate	A	237	11.3	0.20
	B	208	10.3	0.40
	C	206	13.4	0.71
	D	236	13.5	0.14
	E	213	17.1	0.50
	F	210	20.6	0.84
Ethyl decanoate–ethyl undecanoate	A	228	10.5	0.31
	B	211	9.7	0.58
	C	207	13.0	1.18
	D	223	11.7	0.19
	E	214	14.3	0.61
	F	210	17.6	0.97

* Pair of solutes considered in calculating the resolution.

ence of the capacity factor on the resolution. While column A (see Table IV) has a higher specific efficiency than column C, the latter has a resolution which is 22% higher than that of column A.

Fig. 1 shows the column efficiencies expressed in terms of HETP as a function of the capacity factors, k, for the compounds tested. In general, the HETP value are higher for the less strongly retained (low k) compounds, but this effect is more pronounced for the thick film columns than for the micropacked ones.

The optimum carrier gas velocities and the analysis times for all of the compounds used are listed in Table VI. The analysis time per metre of column, t/L, is presented to compare each column's practical utility. Similar values for t/L are obtained for columns with similar phase ratios (A and D, C and E) for compounds having low k values, but the thick film columns give lower t/L values than those of their micropacked counterparts when compounds such as ethyl undecanoate and ethyl decanoate are tested.

This fact should not be regarded as an important disadvantage of the micropacked columns since higher column temperatures would reduce the analysis time. In our case, the resolutions between ethyl decanoate and ethyl undecanoate obtained

TABLE VIII

RELATIVE SAMPLE CAPACITIES

Solute	*Column*	*Relative sample capacity*	*Column*	*Relative sample capacity*
Ethyl heptanoate	A	20.6	D	6.9
	B	25.2	E	19.6
	C	34.8	F	23.1
Ethyl octanoate	A	29.0	D	9.3
	B	41.4	E	27.9
	C	56.9	F	35.4
Ethyl nonanoate	A	43.5	D	13.4
	B	61.3	E	40.7
	C	91.0	F	49.5
Ethyl decanoate	A	68.7	D	20.2
	B	105.2	E	60.2
	C	153.0	F	72.9
Ethyl undecanoate	A	112.0	D	32.3
	B	173.4	E	93.1
	C	258.5	F	112.0

on the micropacked columns A, B and C were respectively 5.6, 8.9 and 6.9 at 125°C. Consequently, it is possible to work at higher temperature without much loss of resolution.

Table VII lists the number of theoretical plates, the column length and the analysis time required to achieve a resolution of 1.5 between various solute pairs. Again comparing columns of similar phase ratios (A and D, C and E), the desired resolution can be achieved with micropacked columns of shorter length for all the solute pairs tried.

The analysis times, $t_{r1.5}$, required to achieve a resolution of 1.5 between solute pairs can also be compared for columns having similar phase ratios; lower values of $t_{r1.5}$ are obtained on the micropacked columns for solutes with high k values, but shorter analysis times for solutes with high k values are achieved on the thick film columns.

The relative sample capacities of columns A–F for all of the compounds considered were calculated according to Ettre[12]. The values per metre of column length are listed in Table VIII. For the micropacked and capillary columns with similar phase ratios, the former have consistently higher values.

Fig. 2 illustrates the variation of the relative sample capacity per one metre of column length with the phase ratio for all of the columns used. Higher relative sample capacities are obtained for micropacked columns. In addition, for each solute, steeper slopes are obtained for such columns.

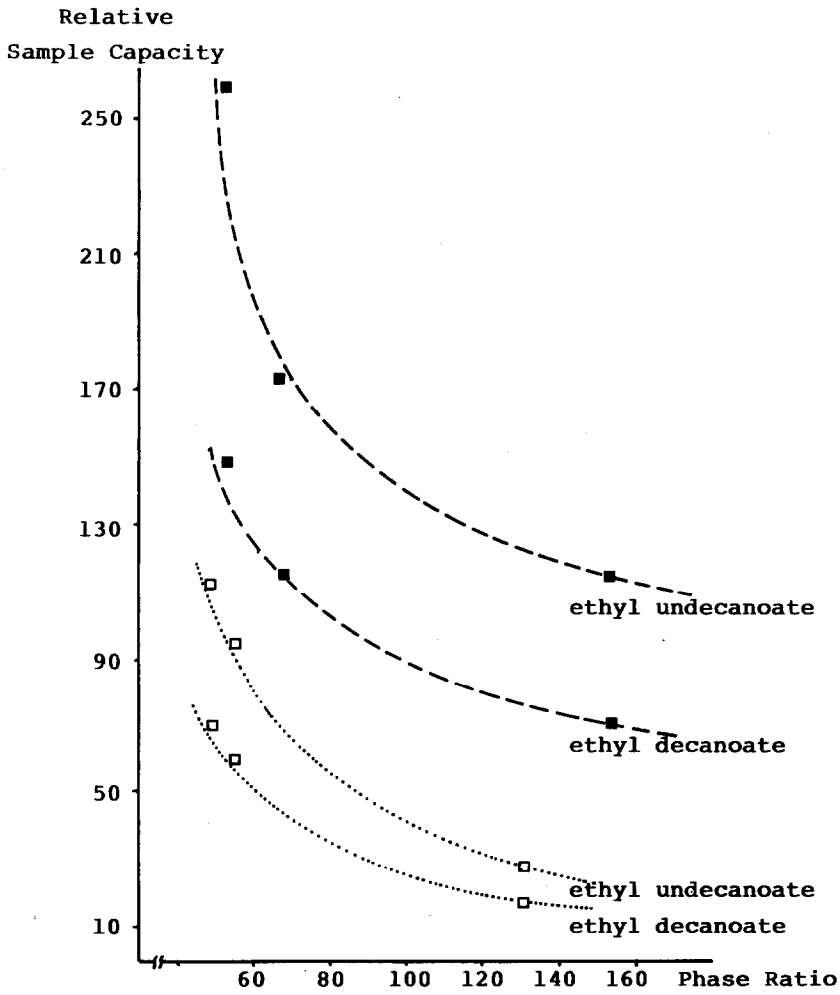

Fig. 2. Variation of the relative sample capacity per metre of column length with the phase ratio. Symbols as in Fig. 1.

CONCLUSIONS

The comparative study between micropacked and thick film capillary columns demonstrates the advantages of both types of columns for analyzing mixtures of medium complexity.

In particular, micropacked columns seem to be good because of their high specific efficiencies and sample capacities. They can also be made from a wide range of stationary liquid phases as well as mixed phases.

ACKNOWLEDGEMENTS

This work was made possible by financial assistance from the Comision Ase-

sora de Investigación Científica y Técnica, Proyect 237/84. One of us (G.R.) is also grateful to the Consejo Superior de Investigaciones Científicas for a grant. We thank Dr. J. Almy, California State University, Stanislaus, for his critical review.

REFERENCES

1 W. Averill and E. W. March, *Chromatogr. Newsl.*, 4 (1976) 20.
2 N. G. Johansen, L. S. Ettre and R. Miller, *J. Chromatogr.*, 256 (1983) 393.
3 L. S. Ettre, *Chromatographia*, 17 (1983) 553.
4 K. Grob, Jr. and K. Grob, *Chromatographia*, 10 (1977) 250.
5 L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 203 (1981) 217.
6 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 13.
7 I. Benecke and G. Schomburg, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 191.
8 G. Schomburg, H. Husmann, S. Ruthe and M. Herraiz, *Chromatographia*, 15 (1982) 599.
9 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 133.
10 L. S. Ettre, G. L. McLure and J. D. Walters, *Chromatographia*, 17 (1983) 560.
11 D. F. Ingraham, C. F. Shoemaker and W. Jennings, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 227.
12 L. S. Ettre, *Chromatographia*, 18 (1984) 477.
13 L. S. Ettre, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 497.
14 F. David, M. Proot and P. Sandra, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 551.
15 P. A. Leclerq, G. J. Scherpenzeel, E. A. A. Vermeer and C. A. Cramers, *J. Chromatogr.*, 241 (1982) 61.
16 A. C. Noble, in G. Charalambous (Editor), *Analysis of Foods and Beverages. Head Space Techniques*, Vol. 2, Academic Press, New York, 1978, p. 203.
17 C. A. Cramers and J. E. Rijks, *Adv. Chromatogr. (N.Y.)*, 17 (1979) 101.
18 G. Reglero, M. Herraiz, M. D. Cabezudo, E. Fernández-Sánchez and J. A. García-Domínguez, *J. Chromatogr.*, 348 (1985) 327.