Journal of Chromatography, 365 (1986) 375–382
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 846

EVALUATION AND APPLICATION OF FUSED-SILICA CAPILLARY COLUMNS WITH IMMOBILIZED LIQUID STATIONARY PHASES FOR THE ANALYSIS OF PETROCHEMICAL PRODUCTS

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SUMMARY

The efficiencies of fused-silica capillary columns with immobilized liquid stationary phases produced by different companies and by the U.S.S.R. Institute of Petrochemical Synthesis were compared. The applicability of such columns to the analysis of petrochemical products was studied. It was found that the commercial fused-silica capillary columns with immobilized liquid stationary phases have similar resolution parameters and have the efficiency of 3000–5000 theoretical plates with separation numbers of 25–40. Highly effective columns (4000–5500 theoretical plates) of this type can be used for the analysis of complex mixtures of petrochemical products.

INTRODUCTION

Recently, thin-walled fused-silica capillary columns have found broad applications. These columns have inner diameters of 50–530 μm, the thickness of the walls is about 40–70 μm and the thickness of the protective coating is about 15–30 μm[1–6]. Fused-silica capillary columns combine a low residual adsorption activity with extremely high flexibility. Owing to difficulties connected with the coating of the walls of the capillary columns with the liquid stationary phase (LSP) and their ageing and taking into account the special requirements for columns for on-column sample injection, methods of LSP film immobilization in capillary columns have been developed for practical use[7–9]. Capillary columns with immobilized phases possess the advantages of high activity, long life, low background current and possibilities for the direct introduction of liquid samples into the column and of removing contaminants from the columns by means of solvents. LSPs of the silicone type are the most widely used immobilization reagents which are cross-linked using, *e.g.*, dibenzoyl, dicumenyl and *tert.*-butyl peroxides[10].

Fused-silica capillary columns with immobilized LSPs are produced by many companies, *e.g.*, Supelco, Hewlett-Packard (U.S.A.), Scientific Glass Ingineering (Australia) and Nordion Instruments (Finland). Capillary columns made from the quartz glass (fused silica) have been developed and produced in the U.S.S.R.[4–6,11].

It is of great interest to evaluate the efficiency of fused-silica capillary columns

0021-9673/86/$03.50

TABLE I

SEPARATION CHARACTERISTICS OF THE INVESTIGATED FUSED-SILICA CAPILLARY COLUMNS

Column No.	*Manufacturer*	*Column dimensions (length × I.D.)*	*LSP**	*Plate number (plates/m)*	*Plate height (mm)*	*k*	*TZ*	*C***
1	Scientific Glass Ingineering (Australia)	12 m × 0.22 mm	PB-1	3800	0.26	6.5	25	$2.6 \cdot 10^{-3}$
2	Supelco (U.S.A.)	15 m × 0.25 mm	SPB-5	3650	0.27	3.7	25	$2.0 \cdot 10^{-3}$
3	Nordion Instruments (Finland)	25 m × 0.32 mm	SE-30	2950	0.34	14.5	37	$1.6 \cdot 10^{-3}$
4	Institute of Petrochemical Synthesis, U.S.S.R. Academy of Sciences	25 m × 0.22 mm	SE-30	4500	0.22	5.4	40	$3.5 \cdot 10^{-3}$
5	As 4	25 m × 0.22 mm	OV-101	5500	0.18	2.5	35	$3.0 \cdot 10^{-3}$
6	As 4	20 m × 0.20 mm	SKTFT-	3800	0.26	2.5	—	—

* All columns were coated with the immobilized LSP. PB-1 is equivalent to SE-30, SPB-5 to SE-54 and SKTFT-50 to polydimethylsiloxane with 25% trifluoropropyl content.

** Coefficient of resistance to mass transfer in the Van Deemter equation. Hydrogen carrier gas.

with immobilized LSPs produced by different companies and to elucidate the possibilities for their application to the analysis of petrochemical synthesis products.

EXPERIMENTAL

The experiments were carried out using Micromat 412 (Nordion Instruments) and LKhM-8MD (Model 5) (U.S.S.R.) gas chromatographs with flame ionization detectors. The splitting ratio of the carrier-gas flow in the sample injection unit was 1:100 and the sensitivity scale of the electrometer was $1 \cdot 10^{-11}$–$5 \cdot 10^{-11}$ A.

To determine and compare the separation parameters, commercially available fused-silica columns with immobilized polydimethylsiloxane LSPs of the SE-30 type, produced by Supelco, Scientific Glass Ingineering and Nordion Instruments, were used, in addition to columns with different LSPs developed at the Institute of Petrochemical Synthesis (U.S.S.R.).

In our laboratory, fused-silica capillaries of length 20–25 m and I.D. 200–220 μm with a polybenzimidazole protective coating[11] were used for column preparation. The capillary was coated with LSPs of the silicone type: SE-30 and OV-101 (Carlo Erba, Italy) and SKTFT-50 (U.S.S.R.). The coating was ccarried out by dynamic method using a 2% solution of the LSP in hexane (SE-30 and OV-101) or ethyl acetate (SKTFT-50). The LSP solution contained 1% of benzoyl peroxide (with respect to the LSP). After coating with the LSP, the column was dried in a flow of helium at 60°C for 10 min, then the flow of carrier gas was stopped, heating with temperature programming was begun (heating to 200°C at 6°C/min) and when 200°C was reached the column was purged with helium for 10 min. After cooling, the column was washed with chloroform and hexane (5-ml portions). The washed columns were conditioned in a flow of carrier gas at 280°C for 3 h. The characteristics of the various columns, which were determined under optimal conditions of carrier-gas (helium) flow for each column, are listed in Table I.

The efficiency and the capacity factor (k) were defined with respect to n-decane at 70°C and the number of separations with respect to n-nonane and n-decane at 70°C. The background current at 290°C was $1 \cdot 10^{-12}$–$2 \cdot 10^{-12}$ A for columns 1–3 and $2 \cdot 10^{-12}$–$3 \cdot 10^{-12}$ A for columns 4 and 5.

RESULTS AND DISCUSSION

From Table I it is obvious that the main separation characteristics of the columns studied are similar. The specific cfficiency of the columns is sufficiently high and is above 3000–5000 theoretical plates per metre and the separation number (Trennzahl, TZ) reached 40 for a column with a length of 25 m. The lower TZ for columns 1 and 2 is due to their smaller length. The coefficient of resistance to mass transfer, C in the Van Deemter equation varies from $1.6 \cdot 10^{-3}$ for column 3 to $3.5 \cdot 10^{-3}$ for column 4; this fact can be explained by the greater irregularities of the LSP film in column 4.

Fig. 1 shows the chromatogram of Grob's test mixture obtained with column 4. As the surface of the column before coating was not deactivated the peaks of the polar compounds have small adsorption tails. Based on the form of the peaks of 2,6-dimethylphenol, 2,6-dimethylaniline and dicyclohexylamine, it could be conclud-

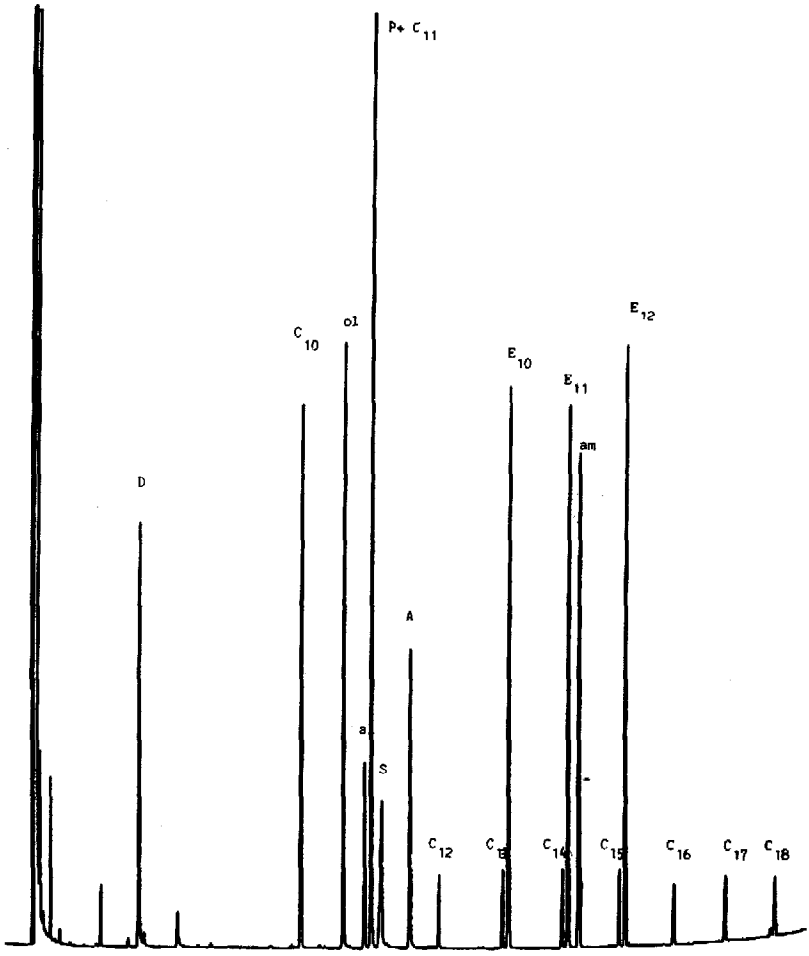

Fig. 1. Chromatogram of modified Grob's test mixture. Column 4 (25 m × 0.22 mm I.D., immobilized SE-30 LSP), Micromat 412 chromatograph. Injector temperature, 225°C; detector temperature, 280°C; column temperature, programmed from 50 to 280°C at 10°C/min; carrier gas, helium; inlet pressure, 1.9 atm. C_{10}–C_{18} = *n*-alkanes; E_{10}–E_{12} = methyl esters of the C_{10}–C_{12} acids. A = 2,6-Dimethylaniline; P = 2,6-dimethylphenol; al = nonanal; am = dicyclohexylamine; D = 2,3-butanediol; ol = 1-octanol; S = ethylhexanoic acid.

ed that the surface of the column possesses slightly acidic properties. This necessitated the activation of the surface of fused-silica capillary columns, especially for the separation of highly polar substances and substances with great sorption properties.

Figs. 2–6 show the chromatograms of kerosene, diesel fuel, a mixture of polyaromatic compounds, a mixture aromatic compounds and a mixture of alkylphenols, respectively. It is clear that fused-silica capillary columns with immobilized LSPs give highly effective separations with a low adsorption activity and a low background current at high temperatures.

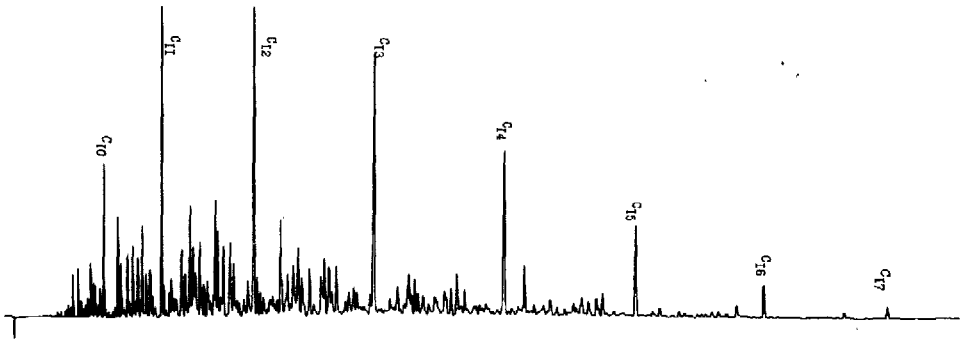

Fig. 2. Chromatogram of kerosene fraction. Column 5 (25 m × 0.22 mm I.D., immobilized OV-101 LSP), Micromat 412 chromatograph. Injector temperature, 300°C; detector temperature, 300°C; column temperature, programmed from 50 to 280°C at 10°C/min; carrier gas, helium; inlet pressure, 1.9 atm.

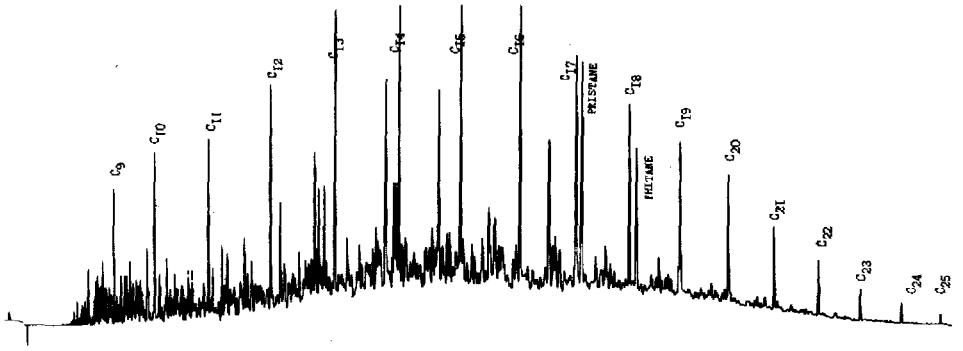

Fig. 3. Chromatogram of diesel fuel. Column 4 (25 m × 0.22 mm I.D., immobilized SE-30 LSP), Micromat 412 chromatograph. Injector temperature, 300°C; detector temperature, 300°C; column temperature, programmed from 50 to 280°C at 10°C/min; carrier gas, helium; inlet pressure, 1.6 atm.

CONCLUSIONS

Commercially available fused-silica capillary columns with the immobilized LSPs are similar in their separation characteristics and show surface efficiencies of 3000–5000 theoretical plates per metre and a separation number of 25–40.

High-performance fused-silica capillary columns with immobilized LSPs can be expediently used for the analysis of complex mixtures of petrochemical synthesis products.

ACKNOWLEDGEMENTS

The authors thank Nordion Instruments (Finland) for providing the Micromat 412 capillary chromatograph and fused-silica capillary columns and Supelco (U.S.A.) and Scientific Glass Engineering (Australia) for supplying fused-silica capillary columns.

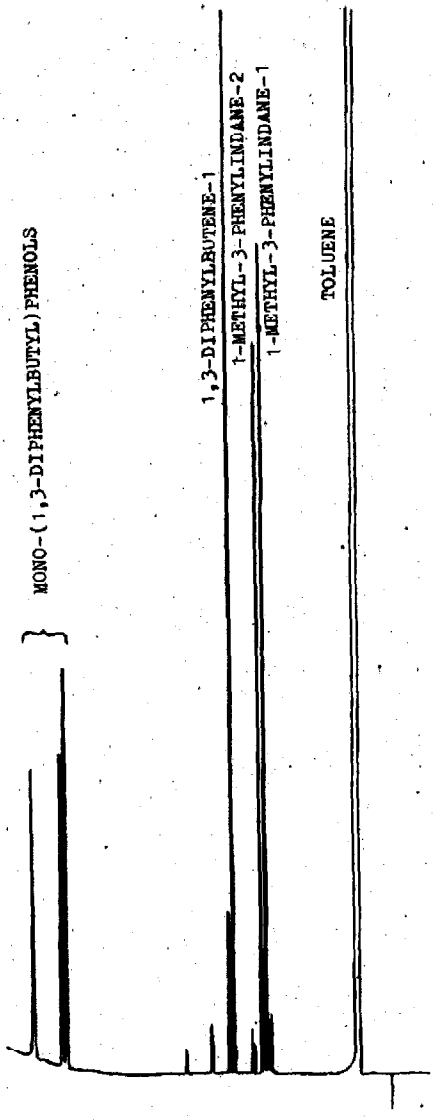

Fig. 4. Chromatogram of a mixture of polyaromatic compounds. Column 5 (25 m × 0.22 mm I.D., immobilized OV-101 LSP), LKhM-8MD (Model 5) chromatograph. Injector temperature, 300°C; column temperature, programmed from 180 to 250°C at 6°C/min; carrier gas, helium; inlet pressure, 1.6 atm.

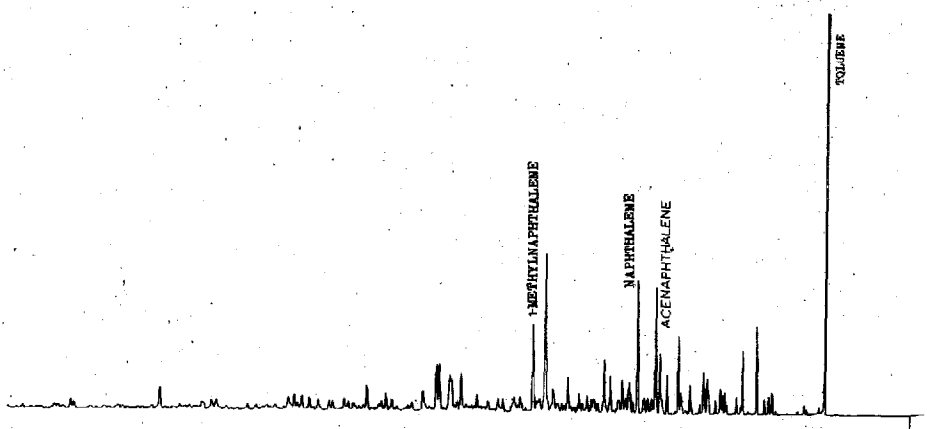

Fig. 5. Chromatogram of a mixture of aromatic compounds (fraction of b.p. 180–320°C). Column 5 (25 m × 0.22 mm I.D., immobilized OV-101 LSP), Micromat 412 chromatograph. Injector temperature, 300°C; detector temperature, 300°C; column temperature, programmed from 70 to 280°C at 5°C/min; carrier gas, helium; inlet pressure, 1.6 atm.

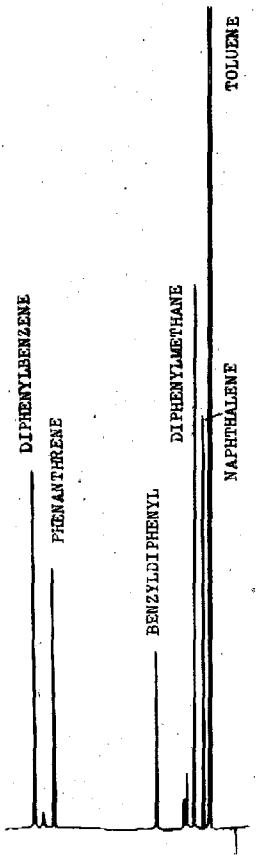

Fig. 6. Chromatogram of phenol alkylation reaction products. Column 6 (20 m × 0.20 mm I.D., immobilized SKTFT-50 LSP), LKhM-8M (Model 5) chromatograph. Injector temperature, 300°C; column temperature, programmed from 130 to 280°C at 8°C/min; carrier gas, helium; inlet pressure, 1.5 atm.

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