Journal of Chromatography, 552 (1991) 353–363
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2084

Gas chromatographic analysis of some glycol ether analytes on a specially packed column

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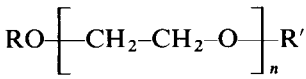
ABSTRACT

The retention behaviour and analysis of some glycol ethers on a specially packed column are reported. A column (0.45 m × 2.0 mm I.D.) packed with a deep acid-washed pink diatomite Chromosorb P, deactivated by a layer of poly(ethylene glycol succinate) additionally coated with a higher content of the same polyester phase was used. Transmission electron microscopic observation of the support surface after the polyester deactivation and the additional coating was carried out. The performance of the proposed short column was compared with that of a wide-bore capillary column (10.0 m × 0.53 mm I.D., 1.2 μm film thickness) and the parameters obtained are given. The glycol ether retentions under linear temperature programming conditions were expressed in terms of relative retention temperatures and retention indices; *n*-alkanols were selected as fixed points on the retention index scale of glycol ethers. The performance of the proposed column with some isomeric oxygen-containing analytes such as xylenols, phenols and ketones is reported. Special attention was given to the main product 2-methoxyethanol and capillary gas chromatography–mass spectrometry with selective detection was employed.

INTRODUCTION

Glycol ethers (GE) have found widespread applications as solvents, emulsifiers and intermediates in various organic syntheses. Hence there is a need for the development of an analytical method for their rapid and reliable determination and gas chromatography (GC) is still the method of choice [1–4].

The glycol ethers considered in this work (Table I) have the general formula



where R is an alkyl group with values 1, 2 or 4, R′ is hydrogen, hydroxy or *n*-alkyl and $n = 1$ or 2.

The polar character of glycol ethers gives rise to problems in their analysis on conventional GC packed columns. Even when using a relatively inert support such as silanized diatomites, coated with polar polyglycol phase, severe peak tailing and loss of

0021-9673/91/$03.50

sample owing to adsorptive effects is still evident [4]. The use of a porous polymer support, *e.g.*, Porapak Q, improves the GE peak shapes but the retention is significant [2].

In the last 15 years, support deactivation with polymers [5–8] has become an effective and indispensable method for obtaining reliable retention data and quantitative results for various polar analytes on packed columns. Using the procedure given in previous papers [6,8], a polyester type instead of a polyglycol type of phase for support deactivation was investigated.

The aim of this work was to develop a specially packed column for the analyses of some glycol ethers as an alternative to a wide-bore (WB) capillary column.

The optimum combination of column dimensions, phase loading, carrier gas, flow-rate and some other aspects, related to polyester deactivated Chromosorb P, contributed to the retention and separation of C_3–C_{18} *n*-alkanols and glycol ethers.

EXPERIMENTAL

Preparation of GC column packing

The iron content of Chromosorb P was reduced to 0.015% by thorough acid washing in a modified Soxhlet apparatus of our design [5,6,9]. The next step in the deactivation of the support was carried out with poly(ethylene glycol succinate) (PEGS) as follows: Chromosorb P was coated with 5.0% (w/w) PEGS, treated at 300°C for 24 h with argon at a flow-rate of 5 ml/min and subjected to methanol extraction as described in detail elsewhere [6–8]. This deactivated support coated with 15% (w/w) PEGS was used for column packing; empty glass columns were deactivated with dimethyldichlorosilane (DMDCS) in advance [5,6]. The packed column was conditioned at 210°C for 24 h with argon at a flow-rate of 20 ml/min.

GC apparatus

The GC measurements were carried out with a Model PU 304 chromatograph (Philips, Cambridge, U.K.), equipped with a dual flame ionization detector and a Model PU 4800 microcomputer with a built-in integrator. Glass packed (0.45 m × 2.0 mm I.D.) and fused-silica (FS) WB capillary (10.0 m × 0.53 mm I.D.) columns were used and their performances were compared. Hydrogen was used as the carrier gas. The samples were introduced with a Hamilton 1.0-μl microsyringe. For the WB column direct injection was used. For the determination of 2-methoxyethanol the internal standard (I.S.) method was used with diethylene dioxide as a standard.

GC measurements were performed with linear temperature programming (LTP). The retention behaviour of GEs under LTP conditions was expressed as relative retention temperature (*RRT*) and retention index (*I*) according to following equations:

$$RRT_{\mathrm{LTP}} = T_{\mathrm{R}(i)}/T_{\mathrm{R(S)}}$$

where $T_{\mathrm{R}(i)}$ is the retention temperature of the analyte *i* (°C) and the $T_{\mathrm{R(S)}}$ is the retention of the standard and

$$I_{\mathrm{LTP}} = 100\left[\frac{T_{\mathrm{R}(i)} - T_{\mathrm{R}(n)}}{T_{\mathrm{R}(n+1)} - T_{\mathrm{R}(n)}} + n\right]$$

where $T_{R(n)}$ and $T_{R(n+1)}$ are the retention temperatures of the *n*-alkanols as fixed points and *n* is the carbon number of the fixed points, as described [9].

The peak asymmetry factor, f_{as}, was determined using the peak width at 10% of the peak height, $W_{0.1}$ [8]; 1-butanol and 1-octanol were used as test asymmetry substances.

Electron microscopy (EM)

For observation of the changes on the diatomite surface during the various treatments, transmission electron microscopy (TEM) was used. The micrographs were obtained with a Model EM 400 instrument (Philips, Eindhoven, The Netherlands). Support samples were prepared by the carbon–platinum (C–Pt) replica technique as described elsewhere [8,9]. A Model 306 vacuum evaporator (Edwards, Crowly, U.K.) was used.

Gas chromatographic–mass spectrometric (GC–MS) apparatus and measurements

GC–MS for identifying impurities in 2-methoxyethanol was carried out on a Hewlett-Packard GC–MS system consisting of an HP 5890 gas chromatograph, an HP 5970 B-UNIX mass-selective detector and an HP 9000 computer. The column was FS HP-1 (cross-linked dimethylsilicone), 0.33 μm film thickness (25.0 m $\times$ 0.2 mm I.D.). The carrier gas was helium at a total flow-rate of 35 ml/min. The temperature programme and other conditions are given in the figure captions. Typical MS conditions were electron impact (EI) ionization, ionization energy 70 eV, vacuum $3 \cdot 10^{-8}$–$8 \cdot 10^{-8}$ bar and ion source temperature 220°C.

Chemicals, reagents and materials

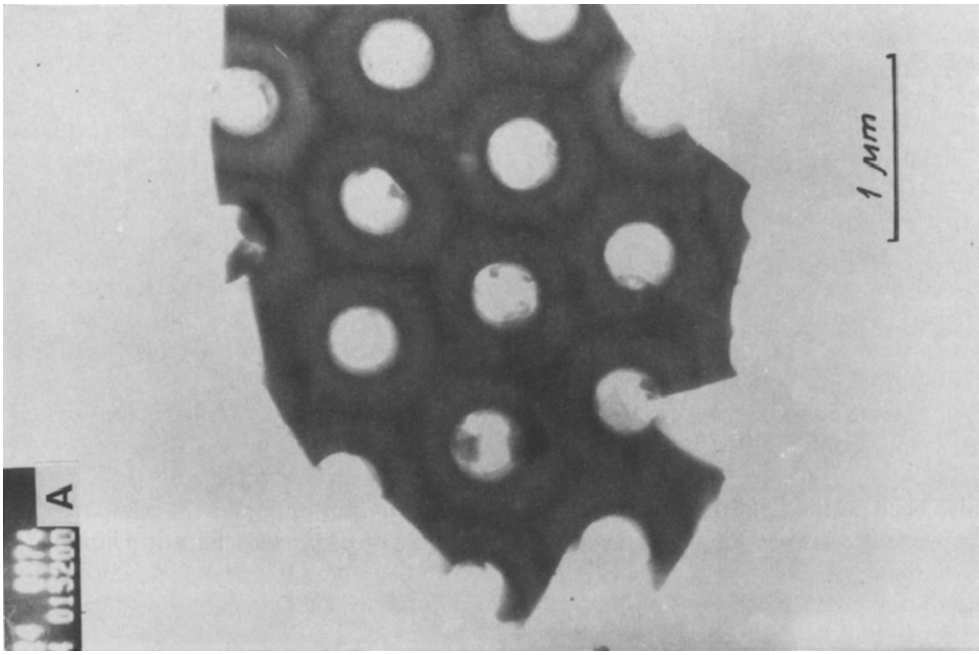
All analytes, solvents and reagents were of analytical or GC quality. The ketones, alkanols, xylenols and phenols were supplied by PolyScience (Evanston, IL, U.S.A.), Supelco (Gland, Switzerland) and Fluka (Buchs, Switzerland). Chromosorb P was supplied by Johns-Menville (Denver, CO, U.S.A.) and PEGS and DMDCS by E. Merck (Darmstadt, Germany). Glycol ethers were supplied by Hoechst (Frankfurt, Germany). The main product 2-methoxyethanol was produced in the Organic Chemistry Department of the Institute of Chemical Industry (Sofia, Bulgaria).

RESULTS AND DISCUSSION

The polar character of the glycol ethers shown in Table I necessitates special attention to the support activity. Most column packings employed for the analysis consist of white diatomites, deactivated with silanes and polyglycols, as liquid stationary phases [1–4].

Some advantages of pink supports deactivated with polymers, and of polyester-type phases, *e.g.*, PEGS, in comparison with white supports and polyglycol-type phases, particularly of poly(ethylene glycol) 20M, were reported recently [6–8]. It has also been pointed out that a polymer used as a deactivator improves the compatibility between the support siliceous surface and the polymer used as a separation liquid [7].

The polyester phase PEGS has been found to be a reasonable choice for analysing polar, closely boiling and/or isomeric analytes [6,8]; it is not only a good tail reducer but also increases selectivity.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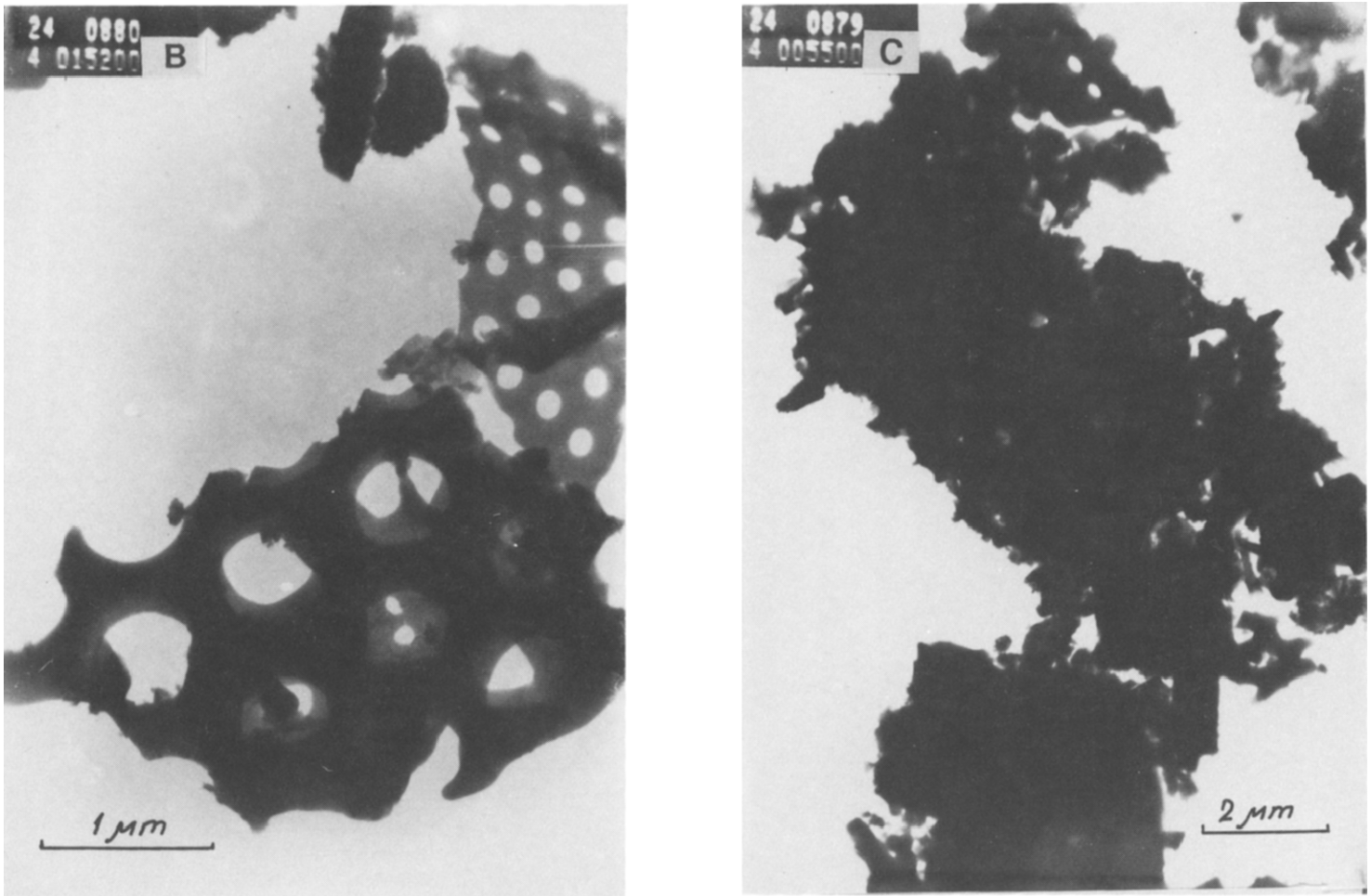

Fig. 1. Electron micrographs of (A) Chromosorb P AW (0.015% iron content) surface deactivated by polymer (PEGS), treated at 300°C and solvent extracted, magnification × 15 200, and (B and C) Chromosorb P AW, polyester deactivated and coated with the same polymer at higher content (15%, w/w), (B) × 15 200 and (C) × 5500.

TABLE I

BOILING POINTS (T_b) AND RETENTION TEMPERATURES (T_R), RELATIVE RETENTION TEMPERATURES (*RRT*) AND RETENTION INDICES (*I*) UNDER LTP CONDITIONS OF GLYCOL ETHERS

Compound[a]	Formula	T_b (°C)	T_R (°C)	RRT_{LTP}	I_{LTP} (i.u.)
2-Methoxyethanol (2)	$CH_3OCH_2CH_2OH$	124.3	61	1.17	477.8
2-Ethoxyethanol (3)	$C_2H_5OCH_2CH_2OH$	135.1	65	1.25	516.7
2-Butoxyethanol (4)	$C_4H_9OCH_2CH_2OH$	171.2	84	1.61	690.0
2-(2-Methoxyethoxy)ethanol (7)	$CH_3O(CH_2CH_2O)_2H$	193.2	125	2.40	995.5
1-Methoxy-2-(2-ethoxyethoxy)methane (5)	$CH_3O(CH_2CH_2O)_2CH_3$	161.0	87	1.67	713.3
1-Ethoxy-2-(2-ethoxyethoxy)ethane (6)	$C_2H_5O(CH_2CH_2O)_2C_2H_5$	188.0	96	1.85	773.3
1-Butoxy-2-(2-ethoxyethoxy)butane (8)	$C_4H_9O(CH_2CH_2O)_2C_4H_9$	256.0	136	2.61	1090.9
Diethylene dioxide (I.S.) (1)	$OCH_2CH_2OCH_2CH_2$	101.3	52	1.00	384.6

[a] Elution peak numbers as shown in Fig. 3 are given in parentheses.

In previous studies it was shown that when observing the changes on the siliceous diatomite surface, TEM is preferable to the scanning mode [7–9]. The electron micrographs (Fig. 1) illustrate the polymer spreading on the surface; the coverage with PEGS used as a deactivator is insufficient (Fig. 1A), while additional coating with PEGS at a higher concentration ensures much greater surface coverage (Fig. 1B and C).

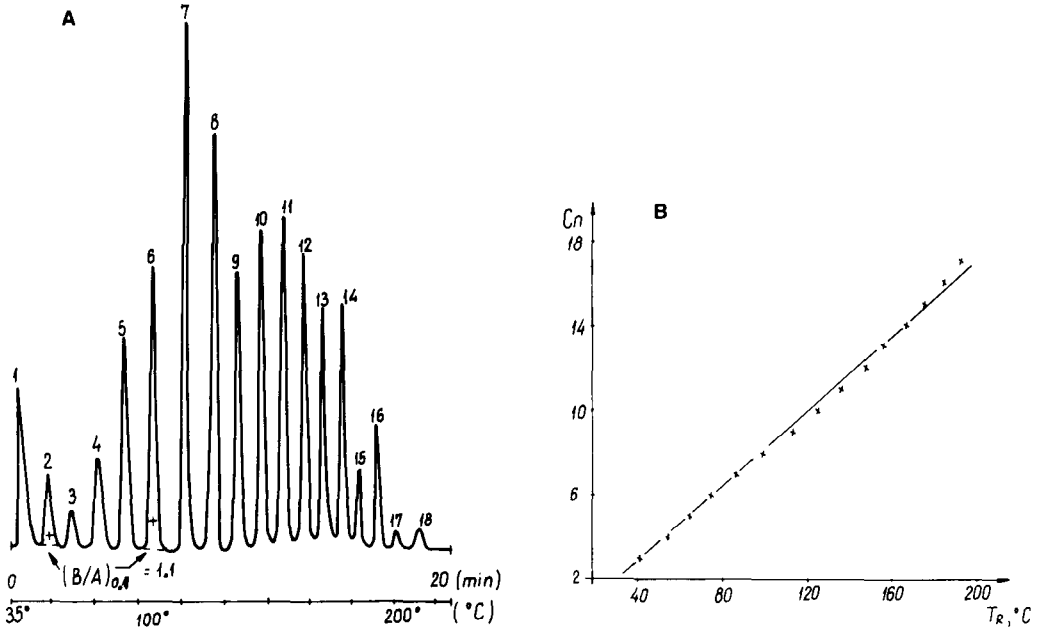

Fig. 2. (A) Chromatogram of a test mixture of C_3–C_{18} *n*-alkanols: 1 = propanol; 2 = butanol; 3 = pentanol; 4 = hexanol; 5 = heptanol; 6 = octanol; 7 = nonanol; 8 = decanol; 9 = undecanol; 10 = dodecanol; 11 = tridecanol; 12 = tetradecanol; 13 = pentadecanol; 14 = hexadecanol; 15 = heptadecanol; 16 = octadecanol; 17 = nonadecanol; 18 = eicosanol. GC conditions as specified in Fig. 3. (B) Plot of the number of carbon atoms (C_n) for *n*-alkanols *versus* the retention temperatures, T_R (°C).

TABLE II

COMPARISON OF THE PROPOSED SHORT PACKED (A) AND THE WIDE-BORE CAPILLARY (B) COLUMNS

Parameter[a]	Column	
	A (0.45 m × 2 mm I.D.)	B (10.0 m × 0.53 mm I.D., 1.2 μm)
K_2	3.5	4.8
$\alpha_{1,2}$	2.0	2.0
$R_{1,2}$	2.75	6.54
$TZ_{1,2}$	1.33	4.5
$N_{eff(2)}$/m	760	986
$H_{eff(2)}$	0.13	0.10
$(B/A)_{0.1(3)}$[b]	1.08	1.15

[a] K = Capacity (or partition ratio); α = selectivity; R = resolution; TZ = separation number; N_{eff} = number of effective plates; H_{eff} = height equivalent to a theoretical plate. Subscripts: 1 = *n*-heptane; 2 = *n*-octane; 3 = *n*-octanol.

[b] Measured with a micrometric magnifying glass (±0.1 mm).

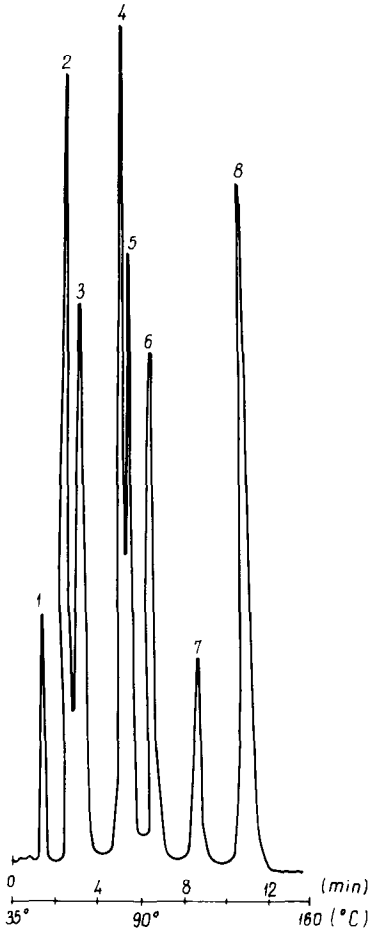

Fig. 3. Chromatogram of glycol ethers: peak numbers as shown in Table I. Conditions: glass column (45.0 cm × 2.0 mm I.D.) packed with Chromosorb P AW (0.015% iron) deactivated with PEGS film and additionally coated with 15% (w/w) PEGS; column temperature, programmed from 35°C to 160°C at 9.5°C/min; injector temperature, 250°C; hydrogen flow-rate, 13.5 ml/min; diethylene dioxide as an internal standard (I.S.); sample volume injected, 0.2–0.3 μl.

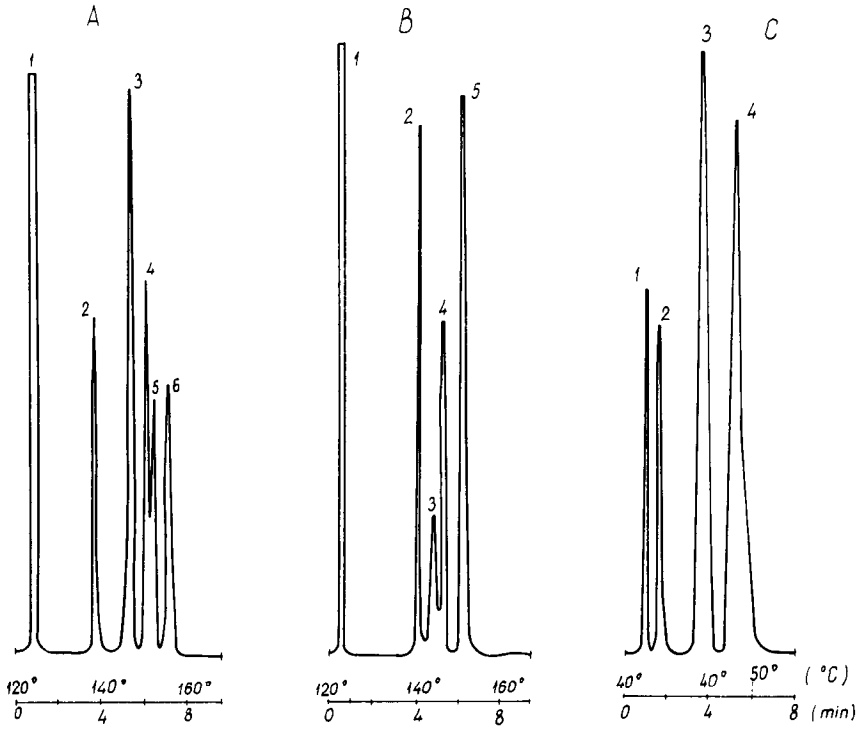

Fig. 4. Chromatograms of oxygen-containing analyte mixtures. (A) Xylenols: 2 = 2,6-, 3 = 2,5-, 4 = 2,3-, 5 = 2,5- and 6 = 3,4-xylenol in benzene (= 1). Column temperature, programmed from 120°C (1 min) to 160°C at 6°C/min; hydrogen flow-rate, 16 ml/min; other conditions as in Fig. 3. (B) Phenols: 2 = phenol, 3 = *m*-cresol, 4 = *o*-ethylphenol and 5 = *p*-ethylphenol in benzene (= 1). (C) Ketones: 1 = 3-pentanone, 2 = 2-methylpentanone, 3 = 4-heptanone and 4 = 2-heptanone. Column temperature, programmed from 40°C (4 min) to 70°C at 6.5°C/min; hydrogen flow-rate, 13.1 ml/min; other conditions as in Fig. 3.

TABLE III

REPEATABILITY OF RETENTION OF GLYCOL ETHERS UNDER LTP CONDITIONS IN TERMS OF RELATIVE RETENTION TEMPERATURES (*RRT*) AND RETENTION INDICES (*I*)

$\bar{x}$ = Average value (n = 6); S.D. = standard deviation; R.S.D. = relative standard deviation.

Glycol ether[a]	RRT_{LTP}			I_{LTP}[b]		
	$\bar{x}$	S.D.	R.S.D. (%)	$\bar{x}$	S.D.	R.S.D. (%)
2	1.17	0.05	4.28	477.8	0.51	0.11
3	1.25	0.06	4.38	516.7	0.45	0.09
4	1.61	0.03	1.64	690.0	0.58	0.08
7	2.40	0.06	2.55	995.5	0.51	0.05
5	1.67	0.05	3.06	713.3	0.37	0.05
6	1.85	0.05	2.59	773.3	0.39	0.05
8	2.61	0.05	2.00	1090.9	0.31	0.03
1	1.00	–	–	384.6	0.46	0.12

[a] Numbers as shown in Table I and Fig. 3.
[b] C_3–C_{11} *n*-alkanols as fixed points (Fig. 2B).

A miniaturized column packed with polyester deactivated Chromosorb P and additionally coated with a higher content of PEGS under LTP conditions give an effective separation of various polar mixtures, as shown in Figs. 2–4. Compounds are eluted with symmetrical peak shapes, relatively low column temperatures and shorter

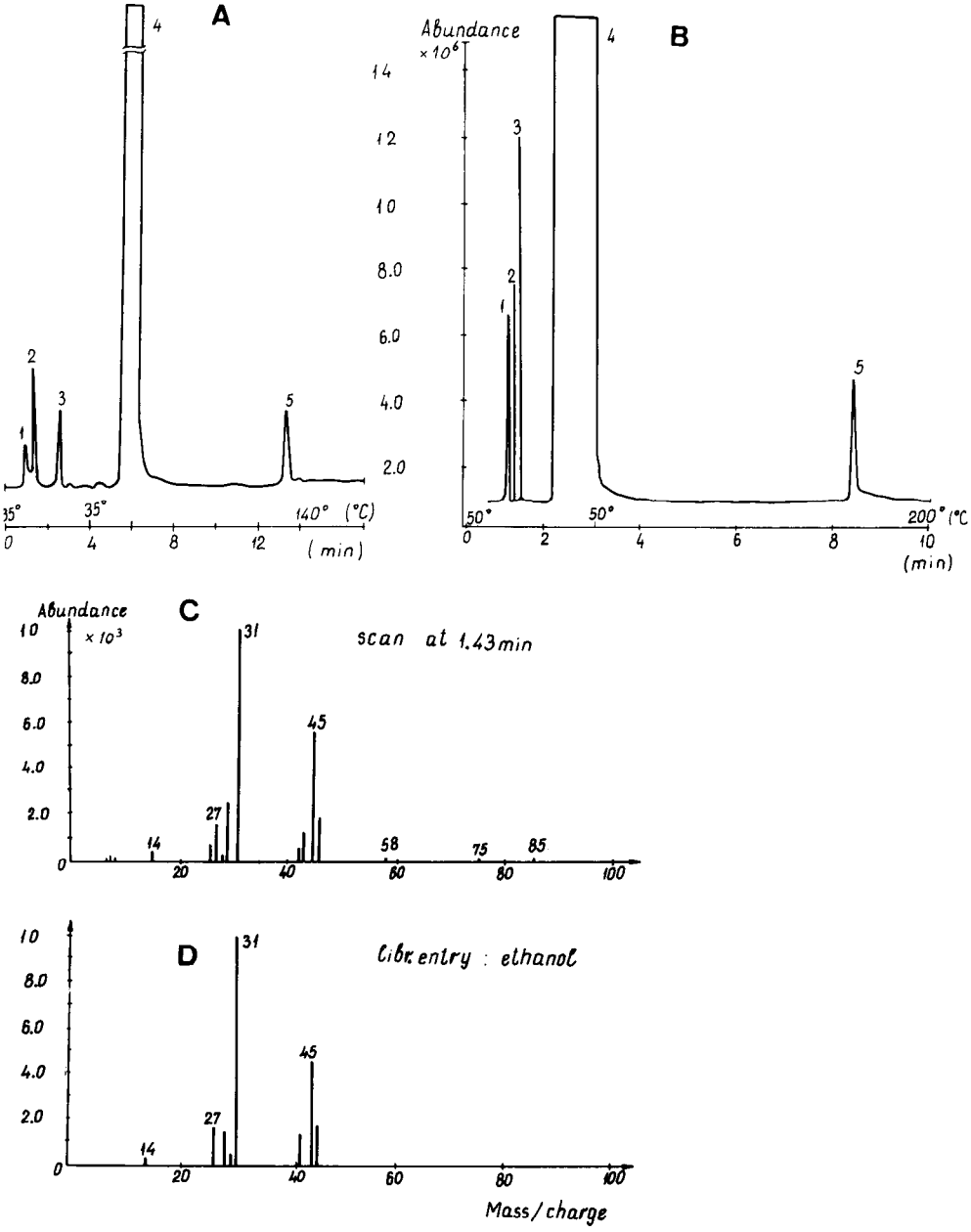

Fig. 5.

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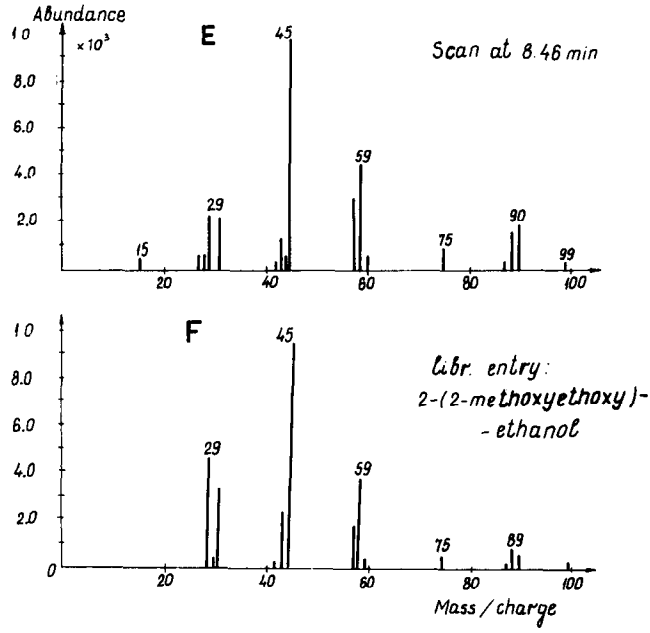

Fig. 5. Chromatograms of 2-methoxyethanol and its impurities (A) on the proposed packed column and (B) on a capillary column. (A) Flame ionization detection. Peaks: 1 = unindentified; 2 = ethanol; 3 = diethylene dioxide (I.S.); 4 = main peak; 5 = 2-(2-methoxyethoxy)ethanol. Column temperature, programmed from 35°C (4 min) to 150°C at 9.5°C/min; hydrogen flow-rate, 13.5 ml/min; other conditions as in Fig. 3. (B) Mass-selective detection total ion chromatogram. Peaks: 1 = air; 2 = water; 3 = ethanol; 4 = main peak; 5 = 2-(2-methoxyethoxy)ethanol. Column, 25.0 m × 0.2 mm I.D., 0.33 μm, HP-1 fused silica; column temperature, programmed from 50°C (3 min) to 200°C (5 min) at 8°C/min; injector temperature, 250°C; detector temperature, 250°C; MS scan, 10–150 u. (C–F) Mass spectra of impurities: C = ethanol, E = 2-(2-methoxyethoxy)ethanol found in 2-methoxyethanol, and D and F = library spectra for comparison.

analysis times. For this miniaturized column only 1.5 cm^3 of packing material is required.

The column performance was evaluated preliminarily with a test mixture of C_3–C_{18} *n*-alkanols. The chromatogram in Fig. 2 illustrates an analysis without baseline noise and with low adsorption activity; the peak asymmetry factor, f_{as}, for 1-butanol and 1-octanol (Fig. 2, Table II) is *ca.* 1.0. Good experimental results and a comparison between the proposed and a wide-bore capillary column (Table II) show that the former could be an alternative to the WB capillary column.

The retention of the glycol ethers (Fig. 3) expressed as retention temperatures, T_R, relative retention temperatures, *RRT*, and retention indices, *I*, under LTP conditions are given in Table III. It is demonstrated that the retention of *n*-alkanols used as fixed points on the retention index scale of the glycol ethers increases linearly with increase in the number of carbon numbers, C_n (Fig. 2B). The retention of the GEs under investigation corresponds better to *n*-alkanols than to *n*-alkanes [9]; the retention of 1-ethoxy-2-(2-ethoxyethoxy)ethane (C_8) is just between those of C_7 and C_9 alkanols, but between C_5 and C_6 *n*-alkanes. The results from the statistical

evaluation of retention data (Table III) indicate that the retention indices, *I*, are to be prefered to *RRT*s and that the S.D. for *I* is 0.31–0.58 index units.

Special attention was paid to the analysis of the main product, 2-methoxyethanol (Fig. 5). Despite the different types columns used, their separation efficiencies are very similar. The identification of impurities with the proposed PEGS column was carried out with standards with confirmation by mass-selective detection data (Fig. 5C–F).

CONCLUSIONS

A miniaturized packed PEGS column was evaluated by analysing selected polar glycol ethers and some other oxygen-containing compounds such as alkanols, phenols, xylenols and ketones.

The effects and benefits of the polyester as a deactivator and a separation phase have been pointed out. The polar compounds are eluted with highly reproducible retention values, symmetrical peak shapes, relatively low column temperatures and shorter analysis time.

A comparison of the performances of the proposed and wide-bore capillary columns showed that the former column is comparable to the latter. Hence a packed PEGS column could be an alternative to wide-bore capillary columns with respect to separation power, resolution, etc.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. E. Kaschieva of the Higher Institute of Chemical Technology, Sofia, for the TEM observations. They thank Hewlett-Packard (Vienna, Austria) for the GC–MS analysis of the 2-methoxyethanol product, and Dipl. Eng. R. Dojkova of the Institute of Chemical Industry, Sofia, for its synthesis.

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