Journal of Chromatography, 446 (1988) 31–38
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1400

POLYESTER DEACTIVATION OF PINK SUPPORTS AND ITS EFFECT ON THE GAS CHROMATOGRAPHY OF SOME POLAR, CLOSELY BOILING AND ISOMERIC ANALYTES

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SUMMARY

Some advantages of pink supports, *e.g.*, Chromosorb P in comparison with white ones, as well as of polyester phases, *e.g.*, poly(ethylene glycol succinate) (PEGS) in comparison with polyglycol ones, with respect to support deactivation are summarized. A polyester layer of PEGS was used for deactivation and as a stationary liquid phase. The polyester deactivation of the surface of Chromosorb P was carried out either (1) by thermal treatment at 300°C and solvent extraction or (2) by thermal treatment at 300°C without solvent extraction. The polyester-deactivated supports obtained by both procedures have similar effects on the gas chromatography of polar analytes with respect to the reproducibility of retention, asymmetry factor, etc. An electron microscopic investigation showed that the deactivated Chromosorb P surface obtained without solvent extraction looks like the support surface extracted for 5 days. Analyses of some closely boiling multicomponent and/or isomeric mixtures containing polar groups (–OH, $-NH_2$, $-NO_2$, etc.) were performed with a glass column (1.0 m × 2 mm I.D.) packed with Chromosorb P that had been thoroughly acid washed and PEGS treated, and additionally coated with 3.0% (w/w) of the same polymer.

INTRODUCTION

An important advantage of polymer-deactivated supports for both packed and capillary gas–liquid chromatographic (GLC) columns[1–9] is that they are much less active than those prepared by conventional methods. The majority of column packings currently employed consist of white diatomites, deactivated with a bonded (or non-extractable[3]) polymer layer, usually a polyglycol, such as poly(ethylene glycol) 20M (PEG 20M)[3–6,8,10].

Recently, some disadvantages of the white supports[7,8,11] and polyglycol phases, particularly of PEG 20M[11], in the analysis of some polar compounds have been reported.

The pink support, *e.g.*, Chromosorb P deactivated by thorough acid washing and a polyester layer of poly(ethylene glycol succinate) (PEGS) is an alternative packing with acceptable inertness. We have prepared it[7] and applied it to the analysis

0021-9673/88/$03.50

of some polar compounds; PEGS serves both as a deactivator and as a stationary liquid phase.

The aims of the present work were: (1) to devise a shorter procedure for the deactivation of the Chromosorb P with a PEGS layer, (2) to compare the polyester-deactivated support obtained by both procedures using electron microscopy (EM) and (3) to examine the performance of a column, packed with Chromosorb P deactivated by PEGS using the described procedure, and additionally coated with the same polymer.

We have examined the possibilities of this column for the analysis of some polar, closely boiling, multicomponent and isomeric mixtures and also of other compounds such as N-(1-ethylpropyl)-3,4-dimethylaniline, 4-nitro-*o*-xylene and naphthalene.

(a) During reductive alkylation of 3,4-dimethylaniline (DMA) with diethyl ketone (DEK), N-(1-ethylpropyl)-3,4-DMA is obtained, which is used in the synthesis of the herbicidal compound Pendimethaline. Analytical control of the different production stages for both the intermediate and end products is also needed.

(b) *o*-Xylene is used as a starting material in the synthesis of dyes, plant protection agents, etc. During its nitration to nitro and then amino derivatives, isomeric mixtures are produced, containing 3- and 4-nitro-*o*-xylene. Depending on the nitration conditions, the contents of these two isomers varies greatly. The isolation of one of the isomers in pure form requires fractional vacuum distillation and crystallization. The numerous stages of *o*-xylene nitration, both on laboratory and semi-industrial scales, require rapid monitoring to determine the contents of 3- and 4-nitro-*o*-xylene, as well as of impurities in the 4-nitro-*o*-xylene product.

(c) During the preparation of 1-amino-8-naphthol-3,6-disulphonic acid (H-acid), analytical control of the thionaphthene content is necessary, since thionaphthene is one of the most undesirable impurities in naphthalene.

EXPERIMENTAL

Column packing procedure

The iron content of Chromosorb P (80–100 mesh) was reduced to 0.015% by thorough acid washing[5–7] in a modified Soxhlet apparatus[6]. For the determination of the iron content, an atomic absorption spectrophotometer, Model SP 191 (Pye Unicam, Cambridge, U.K.) and an electron paramagnetic resonance spectrometer, Model B-ER-420 (Bruker, Karlsruhe, F.R.G.) were used.

The next step in the deactivation of Chromosorb P was carried out with PEGS at 300°C as follows.

(a) One portion of the support was coated with 5.0% (w/w) PEGS, heated at 300°C for 24 h at an argon (or nitrogen) flow-rate of 5 ml/min and subjected to methanol extraction for 5 days, as described in detail[7] elsewhere.

(b) Another portion was coated with 0.5% (w/w) PEGS, conditioned at an argon flow-rate of 200 ml/min at ambient temperature for 1 h, programmed from 4 to 300°C at a rate of 2°C/min at a flow-rate of 5 ml/min for 24 h and heated for 24 h at 10 ml/min argon. The methanol extraction was omitted. This support, coated with 3.0% (w/w) PEGS, was used for packing a glass column (1.0 m × 2 mm I.D.)* and conditioned at 210°C for 6 h at an argon flow-rate of 30 ml/min.

* Empty glass columns were deactivated with dimethyldichlorosilane (DMDCS).

Transmission electron microscopy (TEM)

All steps and procedures in the support deactivation were monitored by TEM. Support samples were prepared by the carbon–platinum (C/Pt) replica technique. This consisted of the evaporation of carbon and platinum onto the diatomite (siliceous) surface, followed by treatment with a solution of 40% hydrofluoric acid. A Model 306 vacuum evaporator was used (Edwards, Crawley, Sussex, U.K.). The micrographs and electron diffraction patterns (Fig. 1A–C) were obtained with a Model EM400 apparatus (Philips, Eindhoven, The Netherlands). A Philips X-ray diffractometer was used for measurements of the interplanar distance of pure PEGS.

GLC

GLC was performed either isothermally or with linear temperature programming (LTP) at argon flow-rates between 16 and 18 ml/min. The chromatographic parameters of a wide range of polar analytes were determined: (1) peak retention as retention times, t_R, and retention temperatures, T_R (Table I and II), and (2) peak asymmetry factor, B/A (Table III). The column performance expressed in theoretical plates per metre, N, for some isomeric alcohols (Table III) was calculated according to both the conventional equation using the peak width at half peak height, $w_{0.5}$, and the Foley and Dorsey equation[12]

$$N_{0.1} = \frac{41.7 + (t_R/w_{0.1})^2}{(B/A)_{0.1} + 1.25}$$

where $w_{0.1}$ = peak width at 10% peak height and $(B/A)_{0.1}$ = peak asymmetry factor with $w_{0.1}$.

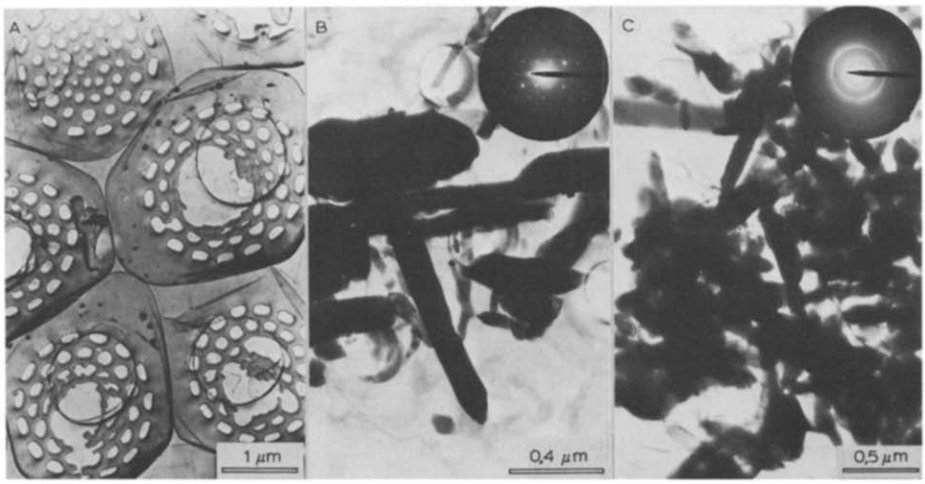

Fig. 1. Electron micrographs of (A) acid washed (AW) Chromosorb P, iron content 0.015%; (B) Chromosorb P-AW, coated with 5.0% (w/w) PEGS, heated at 300°C and extracted; electron diffraction pattern from the crystalline areas of PEGS is shown; (C) Chromosorb P-AW, coated with 0.5%(w/w) PEGS, heated at 30°C, but not extracted; electron diffraction pattern from the crystalline areas of PEGS is shown.

A micrometric magnifying glass (± 0.1 mm) (Carl Zeiss, Jena, G.D.R.) was used for the peak-width measurements; peaks were recorded by a conventional Pye Unicam recorder, Model PM 8 220.

Analyses of some polar closely boiling multicomponent and isomeric model mixtures (Figs. 2 and 3A–C) as well as of industrial mixtures (Fig. 4A–C) were performed with a Pye Unicam gas chromatograph, Model 304, equipped with a dual flame ionization detector and a microcomputer, Model PU 4 800, with a built-in integrator.

Reagents, chemicals and products

All test analytes, solvents and reagents were of analytical or gas chromatographic quality.

Chromosorb P(80–100 mesh) was supplied by Johns-Manville (Denver, CO, U.S.A.), PEGS, DMDCS and hydrofluoric acid by E. Merck (Darmstadt, F.R.G.). Some test analytes were supplied by Poly Science (Evanston, IL, U.S.A.) and Supelco (Gland, Switzerland), some solvents and reagents by Fluka (Buchs, Switzerland). Compounds such as 3,4-DMA, N-(1-ethylpropyl)-3,4-DMA and 4-nitro-*o*-xylene were synthesized in the laboratories and pilot plants of our Institute. The isomeric butyl phenol mixture was synthesized in an organic chemistry laboratory of the Chemical Faculty (Sofia University).

RESULTS AND DISCUSSION

Although the white diatomites, such as Chromosorb W, are currently employed in GLC practice and more frequently recommended for the analysis of polar analytes than the pink diatomites, such as Chromosorb P, in the preparation of polymer-deactivated supports, Chromosorb P has some advantages over Chromosorb W[5–8,10]. Briefly, they are as follows: first, iron impurities are more readily extracted from the Chromosorb P surface, since, *e.g.*, iron(III) oxide is not in a complex form as it is in Chromosorb W[6]; secondly, during prolonged deactivation, Chromosorb P does not give fines because it is less fragile[5,6]; thirdly, Chromosorb P is more suitable for modifications with polar liquids (deactivators and/or stationary liquid phases) and for the analysis of polar analytes[6–8].

Condor *et al.*[11] pointed out that the choice of the support had a significant effect on the degradation of liquid phases and solutes. Thus, acid-washed pink supports with a minimum presence of metal impurities on the surface were preferred over insufficiently washed or silanized supports. Some disadvantages of polyglycol phases, *e.g.*, PEG 20M have been reported[11], mainly its decomposition above *ca.* 160°C. Polyester phases, such as PEGS, do not behave in this way, therefore the latter was a reasonable choice and has been used in our previous study[7]. Chromosorb P, deactivated with this polymer, showed higher thermostability (up to 300°C)[7] than with PEG 20M (up to 270°C)[4–6,9], hence many more stationary liquid phases could be used for additional coating.

PEGS was used as a deactivator and a stationary liquid phase since improved compatability is expected when one and the same polymer is employed for both deactivation and coating[5–8]. As a stationary liquid phase, it showed good selectivity towards nitroanilines[7], closely boiling polar analytes, including positional and optical

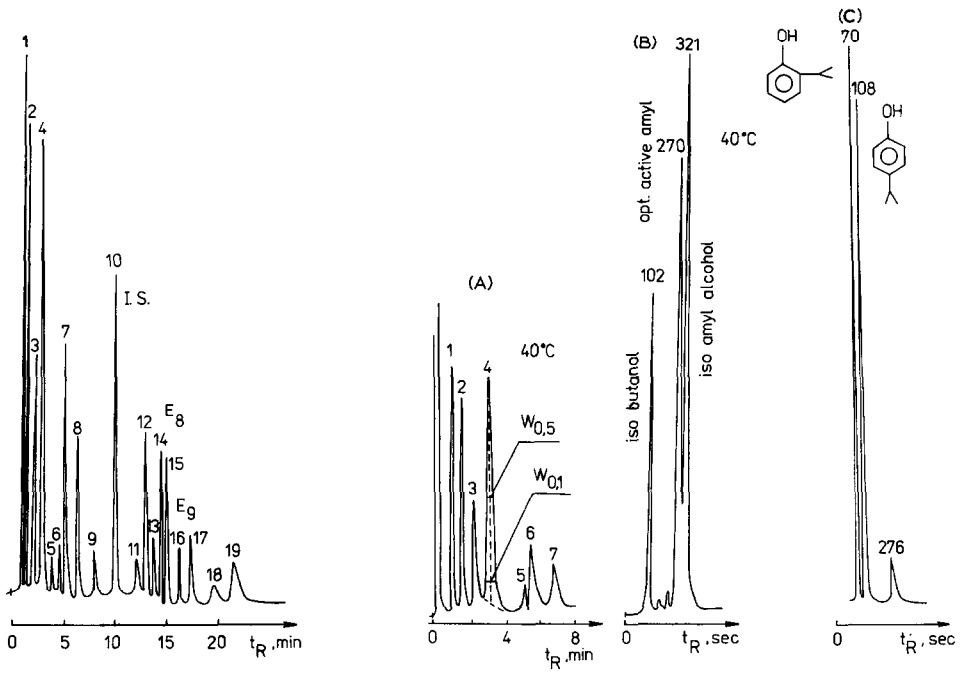

Fig. 2. Chromatogram of a mixture of closely boiling polar compounds with a glass column (1.0 m × 2 mm I.D.) packed with Chromosorb P, thoroughly acid washed and PEGS-treated, and additionally coated with 3.0% (w/w) of the same polymer. Peak numbers as in Table I. LTP conditions: 6 min at 40°C, than raised to 150°C at 7.5°C/min; argon flow-rate 16.6 ml/min; 1-heptanol as internal standard (I.S.).

Fig. 3. Chromatograms of (A) an isomeric alcohol mixture with the column described in Fig. 2; peak numbers as in Table III; column temperature, 40°C isothermal; (B) a mixture of isobutanol and amyl alcohol isomers (optically active and isoamyl alcohol); column temperature as in (A); (C) butyl phenol isomers, 2-*sec.*- and 4-*sec.*-butylphenol; column temperature, 160°C isothermal.

isomers (Figs. 2 and 3A–C), and no degradation of PEGS was observed. The time for deactivation of the support was significantly reduced when the methanol extraction was omitted.

For observation of the changes on the diatomite surface during the various treatments, we used electron microscopy. In recent years much progress has been made in understanding the rôle of the polymer layer on support surfaces (sorbent or capillary[1–3]) and special attention was given to EM[1,10,13,14]. When observing the changes on the siliceous diatomite surface, EM by transmission, TEM, is preferable to EM by scanning (SEM). One reason is the greater resolving ability of TEM; another is the specificity of the diatomites themselves. Chromosorb P has a larger pore size (2–3 μm) then those of other sorbents, *e.g.*, Chromosorb 101 (0.2–0.4 μm)[14]. This means that it is impossible to observe by SEM any surface changes during various treatments. The electron micrographs illustrate the important rôle of iron removal for surface homogeneity (Fig. 1A). Micrographs of Chromosorb P surface-deactivated by polyester thermal treatment and solvent extraction and without such extraction are much alike (Fig. 1B and C). By a combination of X-ray- and electron diffraction, the

TABLE I

REPRODUCIBILITY OF THE RETENTION TIMES t_R, AND RELATIVE PEAK AREAS, A_i/A_{IS}, OF CLOSELY BOILING POLAR COMPOUNDS

S.D. = Standard deviation; R.S.D. = relative standard deviation; $\bar{x}$ = average value (n = 5).

Peak number	*Compound*	t_R			A_i/A_{IS}		
		$\bar{x}$	*S.D.*	*R.S.D. (%)*	$\bar{x}$	*S.D.*	*R.S.D. (%)*
1	tert.-Butanol	71.44	2.93	4.09	0.96	0.02	2.25
2	Isobutanol	103.60	4.56	4.40	1.08	0.04	3.97
3	1-Butanol	144.80	4.60	3.18	0.91	0.01	1.26
4	2-Pentanol	176.00	4.00	2.27	2.04	0.05	2.70
5	*o*-Xylene	189.00	2.00	1.06	0.21	0.01	4.18
6	2-Methyl-1-butanol	288.00	4.69	1.63	0.17	0.01	5.39
7	2-Methyl-2-butanol	313.20	5.40	1.72	1.54	0.02	1.40
8	1-Pentanol	368.00	6.48	1.68	1.05	0.05	4.16
9	1-Hexanol	482.30	4.76	0.99	0.20	0.01	5.42
10	1-Heptanol	604.00	5.80	0.96	1.00	–	–
11	Ethyl carbamate	746.80	7.56	1.01	0.27	0.01	3.07
12	1-Octanol	785.60	7.10	0.91	0.73	0.04	5.58
13	Nitrobenzene	824.40	10.50	1.28	0.22	0.01	4.54
14	Methyl caprilate	874.40	4.56	0.52	0.65	0.02	2.89
15	Ethyl caprilate	903.60	4.11	0.53	0.60	0.02	3.48
16	Methyl pelargonate	958.00	5.70	0.60	0.21	0.01	4.34
17	β-Phenylethanol	1026.00	3.10	0.30	0.29	0.02	6.60
18	3,4-Dimethylaniline (DMA)	1158.00	12.00	1.04	0.10	0.005	5.23
19	N-(1-Ethylpropyl)-3,4-DMA	1238.80	6.70	0.54	0.24	0.01	5.50

crystalline character of the deactivated polyester layer has been examined. Thus, the existence of the polyester layer after methanol extraction was demonstrated (Fig. 1B) and the polyester spreading on the support surface in both cases has been compared, as mentioned above.

GLC analyses of polar analytes with sharp and symmetrical peaks and considerably reduced retention times show that the column is efficient. Figs. 2 and 3A illustrate the resolution of closely boiling compounds (Table I) with retention

TABLE II

RETENTION TIMES, t_R, RETENTION TEMPERATURES, T_R, AND BOILING TEMPERATURES, T_b, OF SOME POLAR COMPOUNDS

Peak numbers as shown in Table I.

	Peak number											
	8	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*
t_R (min)	6.4	8.0	10.0	12.4	13.1	13.7	14.6	15.1	16.0	17.1	19.3	20.6
T_R (°C)	43.6	55.2	70.5	88.4	93.2	98	104.2	108	114.7	123.2	139.7	149.9
T_b(°C)	138	157	176.3	183	195	210.9	192.9	208	214	221	226	260

TABLE III

COLUMN PERFORMANCE FOR C_4–C_5 ISOMERIC ALCOHOLS

$(B/A)_{0.1}$ = Peak asymmetry factor with peak width at 10% peak height, $w_{0.1}$; $N_{0.1}$ = theoretical plates per metre with $w_{0.1}$.

Peak number	*Alcohol*	$(B/A)_{0.1}$			$N_{0.1}$
		$\bar{x}$	*S.D.*	*R.S.D. (%)*	
1	*tert.*-Butanol	1.08	0.04	4.1	500
2	Isobutanol	1.06	0.05	5.2	510
3	*n*-Butanol	1.56	0.09	5.73	560
4	Opt. act. *sec.*-amyl alcohol	2.12*	0.13	6.15	450
5	Opt. act. *n*-amyl alcohol	1.76	0.05	3.11	520
6	Isoamyl alcohol	2.04	0.09	4.38	810
7	*n*-Amyl alcohol	1.8	0.07	3.93	980

* When measured with $w_{0.5}$ the value is 1.1 (see Fig. 3A).

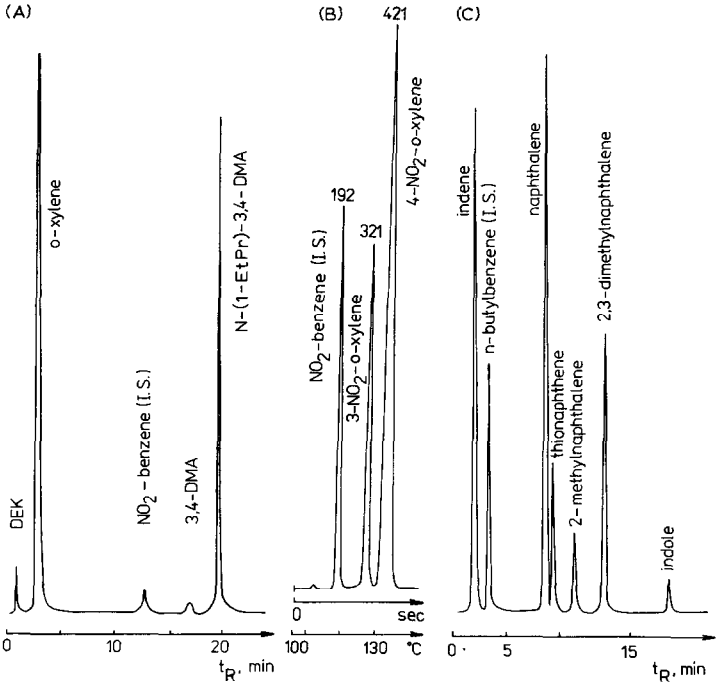

Fig. 4. Chromatograms of (A) a mixture of intermediates in N-(1-ethylpropyl)-3,4-dimethylaniline production with the column described in Fig. 2; LTP conditions, 6 min at 40°C then raised to 200°C at 7.5°C/min; nitrobenzene as I.S. (B) nitro-*o*-xylene isomers: 3- and 4-nitro-*o*-xylene; LTP conditions, 2 min at 50°C then raised to 205°C at 6.5°C/min; nitrobenzene as I.S.; (C) an intermediate naphthalene mixture; LTP conditions 2 min at 50°C then raised to 205°C at 6.5°C/min; *n*-butylbenzene as I.S.

temperatures, T_R, of 100–115°C lower than their boiling points, T_b (Table II). Further evidence of the specificity of the column proposed is given by Fig. 3A–C. Good peak symmetry was achieved (Table III), as well as resolution at low temperatures and in short analysis times. The small-diameter (2 mm I.D.) column required injection volumes of only 0.1–0.5 μl. This also contributed to the symmetrical peaks obtained. The efficiency, N, was determined according to the Foley and Dorsey equation[12], as N at 10% peak height,$w_{0.1}$, was more accurate for Gaussian or near Gaussian peaks in comparison with N at 50 or 30% peak height, $w_{0.5}$, $w_{0.3}$, respectively. As shown in Table III, the $(B/A)_{0.1}$ value of 2.12 for the optically active *sec.*-amyl alcohol peak corresponded to its asymmetrical shape (Fig. 3A), while $(B/A)_{0.5}$ was 1.1. The efficiency with $w_{0.1}$, $N_{0.1}$ for alcohols was 450–980 per metre and the R.S.D. for asymmetry factor measurements was 3.1–6.15% (Table III). The short, small-diameter glass column, packed with polyester-deactivated pink support and additionally coated with the same polymer, under LTP conditions gave an highly effective separation of various polar mixtures, including mixtures of industrial origin (Fig. 4A–C) with low adsorption activity and without baseline noise.

CONCLUSIONS

A column packed with an highly deactivated pink support prepared by thorough acid washing and polyester thermal treatment, additionally coated with the same polymer, ensures a good GLC performance for a wide range of polar, closely boiling and isomeric analytes. The time for the support deactivation is significantly reduced by omitting the methanol extraction procedure.

ACKNOWLEDGEMENT

We are grateful to Professor N. Petsev from the Chemical Faculty of Sofia University for the isomeric butyl phenol mixture, synthesized in his laboratory.

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