Stationary phase for analysis of the oxidation products of p-xylene by gas—liquid chromatography

[a]M. ŠINGLIAR, [a]V. MACHO, and [b]M. REVÚS

[a]*Research Institute for Petrochemistry,*
972 71 Nováky

[b]*Slovnaft, 823 20 Bratislava*

A new stationary phase for satisfactory separation of the products of oxidation of p-xylene has been proposed. The stationary phase is a mixture of poly(ethylene glycol) 20 M-TPA, sebacic acid, and phosphoric acid. To reduce retention time of acids in the sample, the column temperature was programmed. It was established that the increments of retention indices for equal functional groups of benzene derivatives in *para* position are constant. But in case that one of the groups is carboxyl, the increments of retention indices are different.

Для анализа продуктов окисления p-ксилола газовой хроматографией была предложена новя неподвижная фаза, позволяющая хорошо разделить все присутствующие компоненты. Этой фазой является смесь полиэтиленгликоля 20 M-TPA, себациновой и фосфорной кислот. Было обнаружено, что увеличение показателей элюирования для определенной функциональной группы является постоянным для *пара* положения. Однако, если одной из функциональных групп является карбоксильная группа, ход изменения показателей элюирования изменяется.

In our previous paper [1] we established that the oxidation products of p-xylene could be successfully analyzed by gas chromatography on a stationary phase which consisted of poly(ethylene glycol adipate) polyester (5%) and phosphoric acid (2%). The separation of all components present in the sample could be achieved. But if dimethyl terephthalate was present in an increased amount, its peak overlapped the peak of dimethyl isophthalate. We tried to solve this problem with a new stationary phase.

The problem of gas chromatographic analysis of benzene carboxylic acids and their methyl esters was solved by several authors.

The dimethyl esters of phthalic acids can be very well separated on various stationary phases [2—6], but the benzene carboxylic acids eluate too late.

Other stationary phases [7—14] were used for separation of methyl esters of benzene carboxylic acids only.

On other stationary phases the peaks of dimethyl isophthalate and dimethyl phthalate are overlapped [15—17].

Pomazanov et al. [18] determined small amounts of benzoic and *p*-methylben-zoic acid in terephthalic acid on a packing consisting of Chromosorb W and phosphoric acid. The carrier gas was saturated with vapour of formic acid for the chromatographic peaks to be symmetrical.

New stationary phases, prepared by authors were used for analysis of the oxidation products of *p*-xylene [19] and *m*-xylene [20].

Benzene carboxylic acids were analyzed as trimethyl silyl derivatives [21, 22].

As it was convenient to determine the content of acids in the oxidized products directly and not in form of their methyl esters, we tried to find a phase which fulfilled these criteria:

a) good separation of the dimethyl terephthalate from dimethyl isophthalate and from benzoic acid,

b) the monomethyl ester of terephthalic acid must not be eluated too late.

Experimental

The measurements were carried out on a Hewlett—Packard chromatograph, model 5830A with a flame ionization detector. The columns were made of stainless steel, their length being 0.5 m and I.D. 0.3 cm.

Nitrogen was used as a carrier gas, the flows are quoted in the legends to chromatograms. The flow of hydrogen was $28 \, cm^3 \, min^{-1}$. The temperature of column was raised in compliance with the programme according to need. The temperature of vaporizer was 270°C while the temperature of detector was 300°C.

The following packings of chromatographic column were prepared and tested:

Packing *A*: 3.7 wt % of poly(ethylene glycol) 20 M-TPA and 1.5 wt % of phosphoric acid (conc. 80 wt %) were applied to silanized Chromosorb W, size 0.144—0.177 mm.

Packing *B*: 3.7 wt % of poly(ethylene glycol) 20 M-TPA on equal support.

Packing *C*: 5.0 wt % of poly(ethylene glycol) 20 M-TPA + 2.0 wt % of sebacic acid on equal support.

Packing *D*: 5.0 wt % of poly(ethylene glycol) 20 M-TPA + 2.0 wt % of sebacic acid + 2.4 wt % of phosphoric acid (conc. 80 wt %) on equal support.

We also tested phosphoric acid alone as a stationary phase, 10 wt % Igepal CO-880, 10% UCON 50 HB 280 X, 5% poly(diethylene glycol) adipate) + 2 wt % phosphoric acid. But none of these packings had the required properties.

Chemicals

The following substances were available for measuring the separating properties of the prepared packings of chromatographic columns and the retention values: *p*-xylene (*p*X), benzaldehyde (BD), methyl benzoate (MB), *p*-methyl toluylate (*p*MT), *p*-tolualdehyde (*p*TA), terephthalaldehyde (TPA), isophthalaldehyde (IPA), *p*-formyl methyl benzoate (*p*FMB), dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), dimethyl phthalate

(DMO), benzoic acid (BAC), *p*-toluic acid (*p*TAC), *p*-formylbenzoic acid (*p*FBA), trimethyl ester of trimellitic acid (TTA), monomethyl ester of terephthalic acid (MTA), benzyl alcohol (BAL), *p*-tolylmethanol (*p*TM), and n-amyl benzoate (nAB) as internal standard for quantitative determination. All substances were commercial products of Aldrich — Europe Div. Janssen Pharmaceutica, B-2340, Beerse, Belgium. Poly(ethylene glycol) 20 M-TPA was delivered by C. Erba, Milan. Sebacic acid was a product of BDH-Chemicals Ltd.

Results and discussion

The chromatograms obtained with a model mixture of oxidized products on poly(ethylene glycol) 20 M-TPA (chromatogram *B*) and on equal poly(ethylene glycol) with an addition of phosphoric acid (chromatogram *A*) are represented in Fig. 1. As obvious from that figure and Table 1, an addition of phosphoric acid brought about a reduction in retention time of all components of the analyzed sample, in particular, of acids. Moreover, the peaks of acids became symmetrical.

The chromatograms also show that the DMT/DMI separation was not complete. The resolution of the two substances did not improve even by a change of temperature programme (Table 2). The DMT/DMI resolution got better by extending the column from 0.5 to 1.2 m, but MTA was not eluted from the column at all.
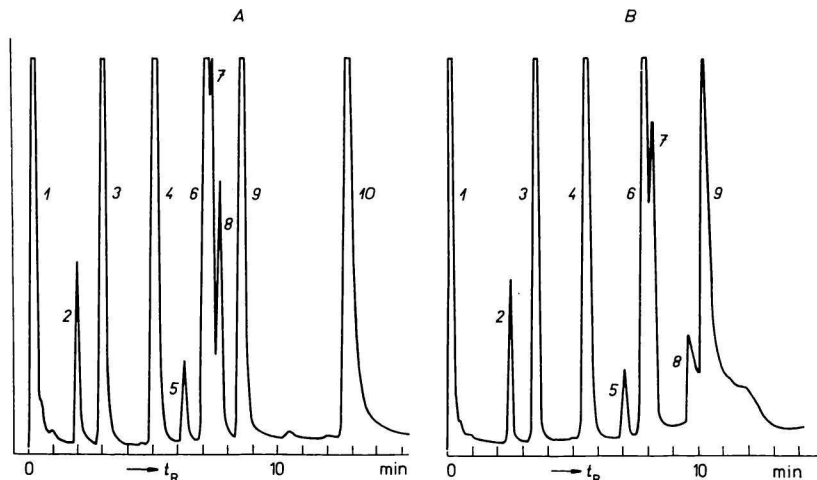

Fig. 1. Chromatogram of a model mixture of the oxidation products of *p*-xylene obtained with the stationary phase.

A. Poly(ethylene glycol) 20 M-TPA (3.7%) + H_3PO_4 (1.5%); *B*. poly(ethylene glycol) 20 M-TPA (3.7%).

Temperature programme: initial temperature 80°C, final temperature 200°C, gradient 10°C min^{-1}. Flow of the carrier gas 24 cm^3 min^{-1}.

1. Solvent; *2.* MB; *3.* *p*MT; *4.* nAB; *5.* *p*FMB; *6.* DMT; *7.* DMI; *8.* BAC; *9.* *p*TAC; *10.* MTA.

Table 1

Retention times [min] of the substances of the model mixture of oxidized product

Substance	A_1	A_2	B
Air	0.05	0.22	0.05
MB	1.97	8.13	2.57
*p*MT	2.97	9.47	3.59
nAB	5.06	11.58	5.63
*p*FMB	6.26	14.11	7.12
DMT	7.09	15.15	7.93
DMI	7.33	15.98	8.23
BAC	7.67	19.39	9.68
*p*TAC	8.53	22.51	20.25
MTA	12.79	—	—

Conditions:
A_1: 3.7% PEG 20 M-TPA + 1.7% H_3PO_4, column length 0.5 m;
A_2: equal packing, column length 1.2 m;
B: 3.7% PEG 20 M-TPA, column length 0.5 m.
Flow of the carrier gas 24 cm^3 min^{-1}.
Temperature programme: 80→200°C, 10°C min^{-1}.

The elution temperatures of particular substances at different temperature programmes are given in Table 2.

We examined the possibility of replacing phosphoric acid by other acid which would shorten the elution time of acids but would not impair the DMT/DMI resolution too much. Thus we prepared a packing which consisted of poly(ethylene glycol) 20 M-TPA and sebacic acid (packing C). The separation of the three investigated substances is better on this packing than it is on packing A, but the elution of MTA is late and the peak is not symmetrical.

We ascertained the influence of temperature programme and initial temperature on resolution of DMT/DMI and on retention time. As evident from the data in Table 3, the resolution $R_{DMT/DMI}$ does not practically change at the tested temperature programmes. The retention times decrease with increasing initial temperature especially for those substances which are eluated later. On the other hand, the elution temperatures for these substances almost do not change (Fig. 2).

Furthermore, we prepared packing D which consisted of 5.8 wt % of poly(ethylene glycol) 20 M-TPA, 1.9 wt % of sebacic acid, and 2.4 wt % of phosphoric acid. A mixture of nAB, DMT, DMI, and DMO was separated on a column of 0.5 m length. The DMT/DMI pair was separated reasonably and DMO was eluated together with DMI. If the amount of poly(ethylene glycol) 20 M-TPA was

Table 2

Retention times (t_R) and retention temperatures (T_R) of the substances of the model mixture
Stationary phase A. Flow of the carrier gas 24 cm³ min⁻¹

Substance	Temperature programme, °C							
	5 80→200		10 80→200		10 110→200		10 125→200	
	t_R/min	T_R/°C	t_R/min	T_R/°C	t_R/min	T_R/°C	t_R/min	T_R/°C
MB	2.29	91.5	3.01	110.0	1.24	122.4	0.75	132.5
pMT	5.65	108.3	4.10	121.0	1.91	129.1	1.19	136.9
nAB	9.25	126.2	6.10	141.0	3.43	144.3	2.32	148.2
pFMB	12.43	142.3	7.79	157.9	4.92	159.2	3.61	161.1
DMT	13.93	149.7	8.51	165.1	5.61	166.1	4.24	167.4
DMI	14.55	152.6	8.61	166.1	5.81	168.1	4.49	169.9
BAC	17.41	167.4	10.29	182.9	7.29	182.9	5.78	183.3
pTAC	18.9	174.5	11.05	190.5	8.03	190.3	6.55	190.5
MTA	29.08	—	19.15	—	15.98	—	14.43	—
$R_{DMT/DMI}$	0.53		0.52		0.49		0.47	

$$R = \frac{2(t_{R(DMI)} - t_{R(DMT)})}{w_{(DMT)} + w_{(DMI)}}$$

Fig. 2. Variation of retention time (t_R) and retention temperature (T_R) with initial temperature at a programmed temperature increase of the column. Column packing C.
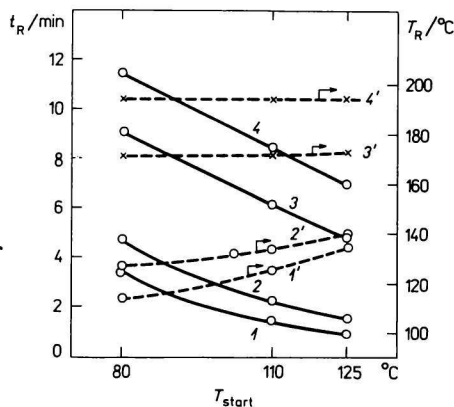*1, 1′.* MB; *2, 2′.* pMT; *3, 3′.* DMT; *4, 4′.* pTAC.

Table 3

Retention times (t_R) and retention temperatures (T_R) of the substances of the model mixture
Stationary phase *C*. Flow of the carrier gas 21 cm³ min⁻¹

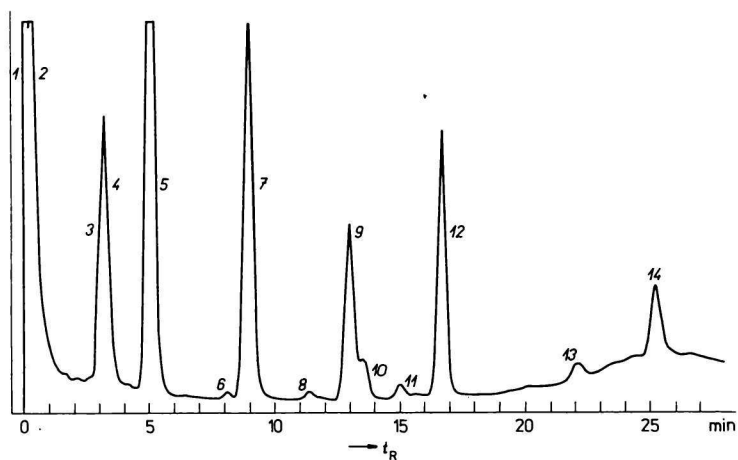| Substance	Temperature programme, °C					
	10 80→200		10 110→200		10 125→200	
	t_R/min	T_R/°C	t_R/min	T_R/°C	t_R/min	T_R/°C
MB	3.43	114.3	1.51	125.1	0.96	134.6
*p*MT	4.68	126.8	2.33	133.3	1.53	140.3
nAB	6.89	148.9	4.12	151.2	2.95	154.5
*p*FMB	8.18	161.8	5.30	163.0	4.02	165.2
DMT	9.11	171.1	6.17	171.7	4.82	173.2
DMI	9.40	174.0	6.45	174.5	5.08	175.8
BAC	10.95	189.5	7.94	189.4	6.56	190.6
*p*TAC	11.44	194.4	8.45	194.5	7.01	195.1
MTA	22.16	—	19.43	—	18.40	—
$R_{DMT/DMI}$	0.50		0.47		0.45	

Fig. 3. Chromatogram of the oxidation products of *p*-xylene.
Column packing *D*. Temperature programme: initial temperature 80°C, final temperature 200°C, gradient 5°C min⁻¹.
1. Solvent; *2. p*X; *3. p*TA; *4.* MB; *5. p*MT; *6.* not identified; *7.* nAB; *8. p*FMB; *9.* DMT; *10.* DMI; *11.* BAC; *12. p*TAC; *13. p*FBA; *14.* MTA.

increased to 10 wt %, the separation of DMT/DMI was quite satisfying also in case when concentration of DMT was increased.

The chromatogram of a real sample of oxidized product obtained with packing D is represented in Fig. 3. It is to be seen that the separation of all substances present in the product is good. The presence of phosphoric acid in the stationary phase manifested itself especially in the reduction of retention time of p-methylbenzoic acid and of the monomethyl ester of terephthalic acid. The retention values of all standards obtained with this packing are given in Table 4.

Table 4

Elution values of the standards

Substance	t_R/min	T_R/°C	I
pX	0.35	81.8	1100
BD	1.71	88.6	1367
MB	2.80	94.0	1432
pTA	3.01	95.0	1475
pMT	4.46	102.3	1543
BAL	5.68	108.4	1628
pTM	7.50	117.5	1724
nAB	9.21	121.0	1767
TPA	9.30	126.5	1827
IPA	9.73	128.7	1848
pFMB	10.55	132.8	1889
DMT	12.24	141.2	2003
DMI	12.77	143.9	2038
BAC	13.90	149.5	2111
pTAC	15.57	157.9	2223
TTA	21.19	186.0	2609
pFBA	23.20	195.0	2741
MTA	23.88	197.0	2772

$$I = 100 \frac{T_{R(X)} - T_{R(C_z)}}{T_{R(C_{z+1})} - T_{R(C_z)}} + 100 \, z$$

Packing of chromatographic column: D.
Temperature programme: 80→200°C, 5°C min⁻¹.
Flow of nitrogen 27 cm³ min⁻¹.

Relationships between the increment in retention index and the kind of substituent

Many papers were concerned with the relationships between retention index and substance structure [23]. *Cook* and *Raushell* [24] revealed such relationships for

the derivatives of toluene. *West* and *Hall* [25] completed the mathematical relationship between the retention index and the type of substituent with the position factor. The authors of that paper measured the values of increments of retention indices for different substituents at 100°C.

We tried to find out similar relationships for the programmed increase of temperature.

The increments of retention indices for individual kinds of substituents are given in Table 5. The best agreement of results appears in case of the methyl group and the value of increment is 109 ± 3 I.u.

Table 5

Increments of retention indices for the functional groups of the substituted derivatives of benzene

| $I_X - I_Y$	ΔI/group
$I_{pMT} - I_{MB} = 1543 - 1432$	111/CH_3
$I_{pTA} - I_{BD} = 1475 - 1367$	108/CH_3
$I_{pTM} - I_{BA} = 1724 - 1618$	106/CH_3
$I_{pTAC} - I_{BAC} = 2223 - 2111$	112/CH_3
$I_{TPA} - I_{BD} = 1827 - 1367$	460/CHO
$I_{pFMB} - I_{MB} = 1889 - 1432$	457/CHO
$I_{pFBA} - I_{BAC} = 2749 - 2111$	638/CHO
$I_{pFMB} - I_{BD} = 1889 - 1339$	550/$COOCH_3$
$I_{DMT} - I_{MB} = 2003 - 1432$	571/$COOCH_3$
$I_{MTA} - I_{BAC} = 3772 - 2111$	661/$COOCH_3$
$I_{TTA} - I_{DMI} = 2609 - 2038$	571/$COOCH_3$

The increment for carbonyl group is 458 I.u. But if a carboxy group occurs in *para* position, the increment is as much as 683 I.u.

Similar situation arises with the increments in retention index for the ester group. If an aldehyde or ester group occurs in *para* position, the increment in retention index is 564 ± 7 I.u. If a carboxy group is in *para* position, the value of increment is 661 I.u.

It is known that the aldehyde, ester, and carboxy groups produce a negative induction and mesomeric effect on the aromatic ring [26]. Owing to the induction effect, fractional charges occur on the atoms of carbon in the benzene ring as well as on the other carbon atoms. As evident from the structure formulae, both groups affect each other.

Thus the polar carbonyl group also influences the activity of the carboxy group and *vice versa*. According to the values of increment in retention index, it may be stated that the carboxy group affects the polarity of the carbonyl group more than the ester group because of its stronger induction effect.

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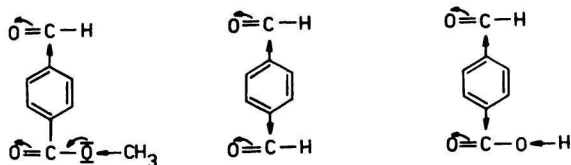
Conclusion

The analysis of the oxidation products of *p*-xylene which contain aromatic acids necessitates the presence of a strong (mineral) acid which prevents sorption of aromatic acids on the support, accelerates their elution and the arising peaks are symmetrical. Phosphoric acid is most frequently used for this purpose. However, it simultaneously impairs the separation effect of the proper stationary phase. It appears that sebacic acid conveniently completes the effect of phosphoric acid and does not impair the separation of DMT and DMI too much. The separation of all other components in the oxidized product may be achieved by a convenient choice of the temperature programme.

The relationship between the increment of retention index and type of substituent can be used in qualitative identification of unknown substances of the sample.

References

1. Šingliar, M., *Petrochémia* (Nováky) *18*, 54 (1978).
2. Šingliar, M., Rendková, I., Revús, M., and Remeň, J., *Petrochémia* (Nováky) *17*, 121 (1977).
3. Komers, R., *Collect. Czech. Chem. Commun. 28*, 1549 (1963).
4. Mori, S. and Takeuchi, T., *J. Chromatogr. 46*, 137 (1970).
5. Kukharenko, T. A. and Grigorieva, E. A., *Neftekhimiya 10*, 303 (1970).
6. Mlejnek, O. and Cvečková, L., *J. Chromatogr. 82*, 377 (1973).
7. Turanov, E. D., Khodyaev, G. Kh., and Kukharenko, T. A., *Dokl. Akad. Nauk Uzb. SSR 30*, 44 (1973).
8. Salbut, P. D. and Wielopolski, A., *Chem. Anal.* (Warsaw) *20*, 303 (1975).
9. Pieš, R., Švihran, S., and Sulik, V., *Fresenius' Z. Anal. Chem. 286*, 253 (1977).
10. Pieš, R., *Fresenius' Z. Anal. Chem. 292*, 236 (1978).
11. Petkevich, T. S., Kovalev, V. I., Mitskevich, N. I., Zernov, P. N., Kenigsberg, T. P., Kovalkov, M. D., Kudryavtsev, I. V., Babkin, V. V., Kudryasheva, N. D., and Chemodanova, T. P., *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, No. 2, 62 (1973).
12. Petkevich, T. S., Kovalev, V. I., Mitskevich, N. I., Zernov, P. N., Kenigsberg, T. P., Kovalkov, M. D., Kudryavtsev, I. V., Babkin, V. V., Kudryasheva, N. D., and Chemodanova, T. P., *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, No. 3, 69 (1973).
13. Nadin, B. E., Zelenkov, M. N., and Mitskevich, N. I., *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, No. 5, 63 (1975).
14. Jirák, J. and Dvořák, J., *Chem. Listy 64*, 75 (1970).

15. Daemen, J. M. H., Daukelman, W., and Hendricks, M. E., *J. Chromatogr. Sci. 13,* 79 (1975).
16. Hicks, J. E. and Jessee, R. S., *Anal. Chim. Acta 58,* 167 (1972).
17. Mlejnek, O. and Cvečková, L., *J. Chromatogr. 94,* 135 (1974).
18. Pomazanov, V. V., Pantaeva, N. M., Mikhaylov, G. D., and Bogatskii, B. F., *Faserforsch. Textiltech.* 27, 147 (1976).
19. Nadin, B. E., Zelenkov, M. M., and Mitskevich, N. I., *Zavod. Lab. 44,* 20 (1978).
20. Drahokoupilová, M., Matoušek, P., and Horská, J., *Chem. Prům. 26,* 638 (1976).
21. Horii, Z., Makita, M., and Tamura, Y., *Chem. Ind.* (London) *1965,* 1494.
22. Kaufman, M. L., Friedman, S., and Wender, I., *Anal. Chem. 39,* 1011 (1967).
23. Haken, J. K., *J. Chromatogr. Sci. 11,* 144 (1973).
24. Cook, L. E. and Raushell, F. M., *J. Chromatogr. 65,* 556 (1972).
25. West, S. H. and Hall, R. C., *J. Chromatogr. Sci. 13,* 5 (1975).
26. Červinka, O., Dědek, V., and Ferles, M., *Organická chemie.* (Organic Chemistry.) P. 272. Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1969.

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