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Note

Selectivity comparisons of polystyrene-divinylbenzene columns*

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Because the pH of the mobile phase that can be used with conventional silica-based alkyl-bonded reversed-phase columns is restricted, there has been considerable interest in alternative column materials, including organic polymers. However, in early studies using XAD-2 columns the efficiency of the separations was often low and the softness of the materials made them difficult to handle^{1,2}. As a consequence polymer columns have not gained wide acceptance, despite their high chemical stability in extremes of pH. Recently more rigid microparticulate polystyrene-divinylbenzene beads (PS-DVB) have become available as stationary phases^{3,4}.

Although a wide range of compounds has been examined on polystyrene-divinylbenzene columns there has been an emphasis on the separation of relatively polar samples, including phenols⁵, carboxylic acids⁶, organic anions⁷ and nucleosides⁸. These separations were of particular interest because the surface of the polymer is free from silanophilic interactions, and tailing with polar samples, especially amines, is greatly reduced. Polymer columns are also applicable to the separation of less polar samples. However, only a few direct comparisons have been made with ODS-silica columns, including the separations of giberellins⁹ and aromatic compounds^{10,11}.

The present paper uses the retention indexes of a set of test compounds to compare the selectivity of the polymer columns to conventional bonded-phase ODS columns.

EXPERIMENTAL

Materials

High-performance liquid chromatography (HPLC). The separations were carried out using a Pye Unicam PU 4010 pump, an Altex 153 fixed-wavelength detector at 254 nm and a Hewlett Packard 3390 integrator. The samples were injected using a Rheodyne 7125 valve with a 10- μ l loop. The columns were 15 cm \times 4.1 mm I.D. packed with Hamilton PRP-1 (Hamilton, Reno, NV, U.S.A.) and PL-Gel PLRP-S 5 μ m (Polymer Laboratories, Church Stretton, U.K.). Methanol and acetonitrile (Fisons Scientific, Loughborough, U.K.) were HPLC grade and AR potassium dihydrogen phosphate was used to prepare 0.02 M buffer solutions (pH 7.0).

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Retention indexes

The retention indexes of the test compounds toluene, 2-phenylethanol, nitrobenzene, *p*-cresol and *N*-methylaniline were determined by comparison of their retentions to the alkylarylketones acetophenone–valerophenone as described^{12,13}.

RESULTS AND DISCUSSION

In order to be able to compare the retention power and selectivity of different HPLC systems, a common scale of reporting retention is required in which the relative retentions of a set of standard test compounds can be determined. However, although HPLC is a very widely applied technique, it still lacks an accepted method for the reporting of retentions. The widely used method of capacity factors (k') is very unreliable as it is highly dependent on the measurement of an absolute value for the column dead volume. In order to overcome this problem the use of retention indexes based on a homologous series of alkylarylketones has been investigated¹² and it has been shown that the indexes of samples are virtually independent of the exact value of the dead volume¹⁴.

In order to compare the selectivity of different columns, a set of test compounds (toluene, nitrobenzene, *p*-cresol and 2-phenylethanol) has been selected to reflect the effect of electron-donation, electron-acceptance, dipole-interaction and charge-transfer interactions. Their retention indexes characterize the eluent–column combination in a similar manner to the use of Rohrschneider's constants in gas-liquid chromatography (GLC)¹⁴.

Using this concept, the retentions of the alkylarylketones, acetophenone–valerophenone, and the selectivity test compounds were measured on two commercially available PS–DVB columns using methanol–buffer (90:10) and acetonitrile–buffer (70:30) (Table I). The PS–DVB columns had a much higher retentive power than Spherisorb–ODS and it was therefore necessary to use a high proportion of organic modifier to give similar retention times to those used earlier¹⁴. As well as the four test compounds used previously, *N*-methylaniline was also examined as ion-exchange effects which can often cause tailing on ODS-silica should be absent from polymer columns.

Using the alkylarylketones as an index scale, the retention indexes of the test compounds were calculated (Table II). It was found that, unlike the studies on silica based columns, the four alkylarylketones showed a poor linear relationship between $\log k'$ and carbon number (Cn). However, if acetophenone was excluded, a much better correlation was obtained. The reason for the anomalous behavior of acetophenone is unclear unless a minimum specific length of alkyl side chain is necessary for systematic interaction with the polymer stationary phase. The results therefore were based on only three alkylarylketones. For *p*-cresol and phenylethanol this meant a considerable extrapolation and the indexes may not be accurate. In each mobile phase the retention properties of the two PS–DVB polymer columns were very similar, but as expected, the two mobile phases produced different relative retentions.

If the indexes are compared with the indexes (based on all four ketones) for the test compounds measured on a Spherisorb–ODS column with methanol–buffer (60:40) and acetonitrile–buffer (50:50) (Table II), clearly the more polar standards, 2-phenylethanol and *p*-cresol, are much less retained on the polymer columns com-

TABLE I
CAPACITY FACTORS OF RETENTION INDEX KETONES AND SELECTIVITY TEST COMPOUNDS ON POLYSTYRENE COPOLYMER COL-
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PhMe = toluene; PhNO₂ = nitrobenzene; PhEtOH = 2-phenylethanol; PhNHMe = N-methylamine; MeCOPh = acetophenone; EtCOPh = propiophenone;
PrCOPh = butyrophenone; BuCOPh = valerophenone. Buffer = 0.02 M phosphate (pH 7.0).

Mobile phase	Column	Capacity factors									
		PhMe	PhNO ₂	PhEtOH	p-Cresol	PhNHMe	MeCOPh	EtCOPh	PrCOPh	BuCOPh	
Methanol-Buffer (90:10)	PL-Gel	7.19	5.97	1.34	1.41	4.09	4.04	6.47	9.16	13.67	
	Hamilton	5.24	4.01	0.76	0.84	2.92	2.77	4.72	6.67	9.88	
Acetonitrile-Buffer (70:30)	PL-Gel	7.41	4.16	1.19	1.52	3.99	2.79	4.55	6.52	9.38	
	Hamilton	4.38	2.30	0.64	0.81	2.20	1.53	2.55	3.66	5.26	
Methanol	PL-Gel	2.52	2.43	0.65	0.64	1.75	1.99	2.65	3.19	4.04	

TABLE II
RETENTION INDEXES OF TEST COMPOUNDS ON PS-DVB COLUMNS AND ODS-SPHERISORB

Test compounds as in Table I. Buffer = 0.02 M phosphate (pH 7.0).

Mobile phase	Column	Retention index										Slope* ($\times 1000$)
		PhMe	PhNO ₂	PhEtOH	p-Cresol	PhNHMe	MeCOPh	EtCOPh	PrCOPh	BuCOPh	Corr.*	
Methanol Buffer (90:10)	PL-Gel	937	881	481	494	779	776	902	994	1102	0.9949	1.60
	Hamilton	930	858	409	438	773	759	902	996	1102	0.9975	1.60
Acetonitrile Buffer (70:30)	PL-Gel	1034	875	529	596	864	765	900	1000	1100	0.9999	1.57
	Hamilton	1050	871	515	584	860	759	900	1000	1100	0.9998	1.56
Methanol	PL-Gel	879	862	234	227	706	767	903	991	1104	0.9961	0.91
Methanol Buffer (60:40)	Spherisorb- ODS	999	851	737	746	788						
Acetonitrile Buffer (50:50)	Spherisorb- ODS	1014	880	688	731	847						

* Slope and correlation for $C_n \times 100$ against $\log k'$ for EtCOPh to BuCOPh.

pared to the other compounds or the alkylarylketones. From earlier studies using ODS-Hypersil the effect of high proportions of methanol in the eluent was to increase the indexes of almost all the test compounds¹². Thus in 90% methanol the predicted indexes on the Spherisorb-ODS column would be even higher so that the shorter retentions of the polar compounds on the polymer column is even more marked. Of particular note is that at 100% methanol this difference between the polar and non-polar test compounds is even greater.

N-Methylaniline showed a much smaller effect than the hydroxyl compounds and gave sharp symmetrical peaks in both systems. Although nitrobenzene has been reported to show some charge transfer activity with phenyl bonded phases, there is no evidence of any specific interaction with the phenyl groups of the column in these studies¹⁵.

The use of retention-based indexes in the present study is of particular interest as one of the few comparable studies on PS-DVB columns used Popl's aromatic retention index scale although in that case no comparison was made with the ODS-silicas^{10,11}. Unfortunately, insufficient of the sample compounds were common between the two studies for a direct comparison to be carried out.

The retention indexes of the test compounds on the polymer columns thus enable the retention properties of these columns to be directly compared between manufacturers or to conventional silica-based alkyl-bonded columns.

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