CHROM. 15,137

EFFECT OF HIGH-TEMPERATURE AGEING ON THE GAS CHROMATOGRAPHIC PROPERTIES OF POROUS POLYMER BEADS

G. CASTELLO* and G. D'AMATO

Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, 16132 Genova (Italy)

(Received June 22nd, 1982)

SUMMARY

   The effect of column ageing at 200°C under a flow of carrier gas on the gas chromatographic behaviour of porous polymer bead (PPB) stationary phases was investigated by analysing standard mixtures of linear alkanes and polarity "probes": ethanol, butanol, pyridine, nitromethane, 1-nitropropane, benzene, methylethyl ketone and methylpropyl ketones.

   A linear dependence of the logarithm of the adjusted retention times ($\log t'_R$) on the time of ageing was observed for many PPBs, but some of them showed non-linear relationships (Chromosorb 103, 107 and 108). The PPBs showing linear behaviour can be divided into four classes: (1) no variation of $\log t'_R$ with ageing (Porapak N, Q and R and Chromosorb 106); (2) linear increase in $\log t'_R$ (Porapak P and S and Chromosorb 101, 102 and 104); (3) linear decrease in $\log t'_R$ (Porapak T); (4) horizontal, increasing or decreasing $\log t'_R$ values depending on the chemical composition of the polarity probes (Chromosorb 105).

   The variation of retention times and elution order with thermal ageing of the PPBs can explain the differences between retention data reported in the literature and must be taken into account in the determination of the high-temperature polarity of these stationary phases.

INTRODUCTION

   The effect of various parameters on the reproducibility of gas chromatographic (GC) retention data obtained by using porous polymer beads (PPBs) in the analysis of light hydrocarbons and inorganic gases has been previously examined at low temperatures[1-3] and a general classification based on retention index (I) values of ethylene, acetylene and carbon dioxide was suggested[4]. Preliminary investigations intended to verify if the low-temperature characterization could be extended to analytical conditions near the temperature limits of the beads showed that some of the discrepancies previously observed between retention times and I values of reference substances[5,6] may depend on the variation of the GC behaviour of the PPBs with the length of the high-temperature conditioning (ageing) of the columns.

   Columns filled with various PPBs (Porapak and Chromosorb "Century

TABLE I

PHYSICAL PROPERTIES OF ROHRSCHNEIDER AND OF SOME McREYNOLDS' PROBES

Probe	Symbol	Reference system*	Molecular weight	Boiling point (°C at 760 torr)
Ethanol	ETA	R	46.07	78.5
Methyl ethyl ketone	MEK	R	72.12	79.6
Benzene	BE	R–M	78.12	80.1
Nitromethane	NM	R	61.04	100.8
Methyl propyl ketone	MPK	M	86.14	102
Pyridine	Py	R–M	79.10	115.5
Butanol	BUA	M	74.12	117.25
1-Nitropropane	1NP	M	89.09	130.5

* R = Rohrschneider; M = McReynolds.

Series") were therefore submitted to continuous ageing at 200°C for 25–30 days under a flow of helium and analyses of reference polarity probes were carried out at suitable intervals. Standard mixtures containing linear alkanes (5–10°C) and variable amounts of the polarity probes suggested by Rohrschneider[7,8] and McReynolds[9] were used (see Table I). GC behaviour of these compounds, selected in order to characterize the "polarity" of the GLC stationary phases, differs widely and their use was therefore useful for measuring the changes in the interactions of different types of solute molecules with the various PPBs.

EXPERIMENTAL

Stainless-steel columns (3 m × 2.4 mm I.D.) packed with known amounts of Porapak or Chromosorb "Century Series" PPBs (80–100 mesh) were installed in a Varian 3760 gas chromatograph equipped with a thermal conductivity detector and heated at 200 ± 1°C. A flow of helium of 20 ml min⁻¹ was used as the carrier gas and was maintained continuously for the entire ageing time of the column (25–30 days). The analyses were accomplished by injecting the reference mixtures directly into the column inlet, with the injector temperature at 200°C in order to avoid overheating of the initial section of the column. The flow of carrier gas was measured before and after analysis.

For each PPB tested, the samples were prepared by mixing equal amounts of some probes and linear alkanes, in order to avoid interferences between adjacent peaks. Several mixtures were therefore injected at regular time intervals (from 1 to 5 days), depending on the behaviour of the column: more frequent analyses were carried out when a rapid initial change in the retention times showed a greater dependence of the column characteristics on the ageing time. Very small amounts of sample were injected, in order to obtain symmetrical peaks. When necessary, a larger amount of a probe or of a linear alkane was added to the mixture in order to act as a solvent and to permit greater and reproducible amounts of sample to be handled without increasing the widths of the peaks to be measured. Of course, the retention times of the compounds used as the solvents were not taken into account in the evaluation of the run.

Retention times were measured with a Varian CDS-111 C data system. The dead time was taken as being equal to the retention time of air, corresponding at 200°C to that of helium within the accuracy limits of the retention time measurements (±0.01 min).

RESULTS AND DISCUSSION

Some of the PPBs tested showed no appreciable variation of the retention times of the probes with ageing time. The left-hand plot in Fig. 1 shows the typical behaviour of Porapak R which, together with Porapak N and Chromosorb 106, was not affected by thermal deterioration of the column. Least-squares calculations permitted the intercept, a, and slope, b, of the following equation to be measured:

$$\log t'_R = a + bt \tag{1}$$

where t'_R is the adjusted retention time (min) calculated by subtracting the air dead time from the retention time of each compound and t is the ageing time (days). Table II shows the values of a and b for all the polarity probes and two linear alkanes. A horizontal trend of eqn. 1 is shown, for Porapak N and R and Chromosorb 106, by the small values of the slope, b.

A horizontal trend of eqn. 1 was also shown by Porapak Q, but on this stationary phase the peaks of alcohols and pyridine tailed severely, with retention times values depending on the amount injected. The correlation coefficients of eqn. 1
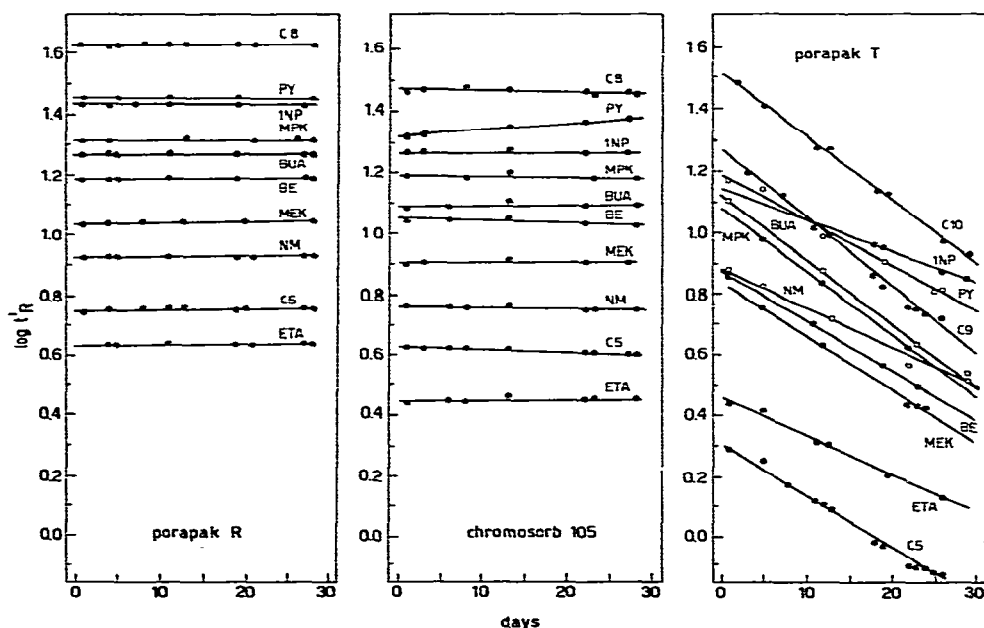

Fig. 1. Variation of log t'_R as a function of ageing time at 200° and a carrier gas flow-rate of 20 cm³/min for some PPB columns, showing constant values or linear changes of log t'_R. Symbols as in Table I.

TABLE II

INTERCEPTS (a) AND SLOPES (b) OF CORRELATIONS BETWEEN THE LOG t_R VALUES OF VARIOUS PROBES AND ALKANES ANALYSED AT 200°C ON PPB COLUMNS THAT SHOW LINEAR VARIATION OF LOG t_R AS A FUNCTION OF AGEING TIME (t) AT 200°C AND A CARRIER GAS FLOW-RATE OF 20 cm³/min

Probe*	Porapak N		Porapak P		Porapak Q		Porapak R		Porapak S	
	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$
ETA	0.678	0.95	-2.243**	12.6		(0.420)***	0.637	0.52		(0.406)***
MEK	1.112	0.85	0.125	3.78	0.905	3.04	1.038	1.92	0.800	2.75
NM	1.047	2.52	0.134	0.38	0.687[1]	3.23	0.928	0.95	-"	
BE	1.201	1.60	0.364	-1.43	1.099	9.04	1.183	1.30	0.949	6.58
BUA	1.328	-3.68	0.247**	10.25		(1.069)***	1.270	-0.53		(1.003)***
MPK	1.393	-0.90	0.325	3.78	1.190	4.07	1.318	-0.09	1.083	7.82
Py	1.505	0.95	0.594**	8.30		(1.301)***	1.455	-0.51		(1.193)***
INP	1.546	1.71	0.489	7.54	1.211	9.42	1.433	-1.28	-"	
n-Pentane	0.713	-2.75	-0.181	1.32	0.742	4.23	0.750	2.27	0.547	5.13
n-Octane	1.602	-4.66	0.477	2.54	1.626	6.50	1.628	0.42	1.444	14.0

Porapak T		Chromosorb 101		Chromosorb 102		Chromosorb 104		Chromosorb 105		Chromosorb 106	
a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$
0.462	−128	−0.079	9.0	0.159	6.8	0.295	4.6	0.447	3.47	0.605	3.61
0.847	−182	0.315	12.5	0.629	9.9	0.626	5.8	0.904	−0.35	1.156	6.46
0.882	−127	0.296	6.4	0.478	6.9	0.803	6.5	0.760	−4.97	0.888	4.02
0.882	−167	0.556	9.3	0.843	8.1	0.597	11.6	1.051	−9.14	1.361	8.31
1.021	−169	0.440	14.4	0.774	10.6	0.720	6.9	1.089	0.87	1.302	7.42
1.088	−211	0.535	15.6	0.898	11.2	0.796	7.0	1.192	−4.60	1.456	9.70
1.195	−151	0.781	11.0	1.050	10.3	1.014	1.4	1.321	20.9	1.537	7.22
1.153	−106	0.687	13.1	0.975	12.0	1.106	6.4	1.272	−2.64	1.493	7.72
0.310	−173	0.0002	11.2	0.417	8.1	−0.132	4.2	0.630	−11.6	0.995	8.11
1.048	−213	0.742	22.2	1.266	14.4	0.483	8.14	1.476	−5.69	1.931	11.4

* For abbreviations, see Table 1.

** Tailing peaks.

*** Very tailing peaks, scattered results, average log t_R shown in parentheses.

§ Partially reacts with stationary phase.

§§ Reacts with stationary phase, multiple or very broad peaks.

were therefore low on this stationary phase, and a suitable calculation of a and b was not possible. The average values over the entire ageing time are therefore shown in Table II for these polar probes. Scattering area values of the nitromethane peak (without a change in the retention time) seem to show that this compound reacts with the stationary phases and is therefore decomposed in the column. The trend of log t'_R on Porapak P was near to horizontal for linear alkanes, nitroalkanes, benzene and ketones and showed a significant slope for alcohols and pyridine, whose peaks were non-symmetrical but with reproducible t'_R values which permit the calculation of a and b.

Another group of PPBs (Porapak S and Chromosorb 101, 102 and 104) show a slight and linear increase in log t'_R with t. The slopes, b, are very similar for all of the probes and n-alkanes, and the plots of log t'_R versus t therefore show parallel straight lines. As with Porapak Q, severe tailing of the alcohol and pyridine peaks was observed on Porapak S. Linear log t'_R plots with positive (for pyridine), negative (for alkanes and benzene) and near zero slopes (for the other probes) were shown by Chromosorb 105 (see central plot in Fig. 1), while rapidly decreasing log t'_R values were obtained on Porapak T (right-hand plot in Fig. 1), which shows changes in the elution order also (Fig. 2).

Only three PPBs (Chromosorb 103, 107 and 108) showed non-linear plots of log t'_R values (Table III and Fig. 3). After ageing for about 5 days, near linear variations were again observed for Chromosorb 103 and 107.

The observed behaviour of the PPBs can hardly be correlated with the polymer composition given by the producers. Tailing peaks for alcohols and pyridine were shown by ethylvinylbenzene–divinylbenzene, styrene–divinylbenzene and vinylpyridine polymers (Porapak Q, P and S, respectively) but, on the other hand, other styrene–divinylbenzene polymers (Chromosorb 101 and 102) did not show excessive
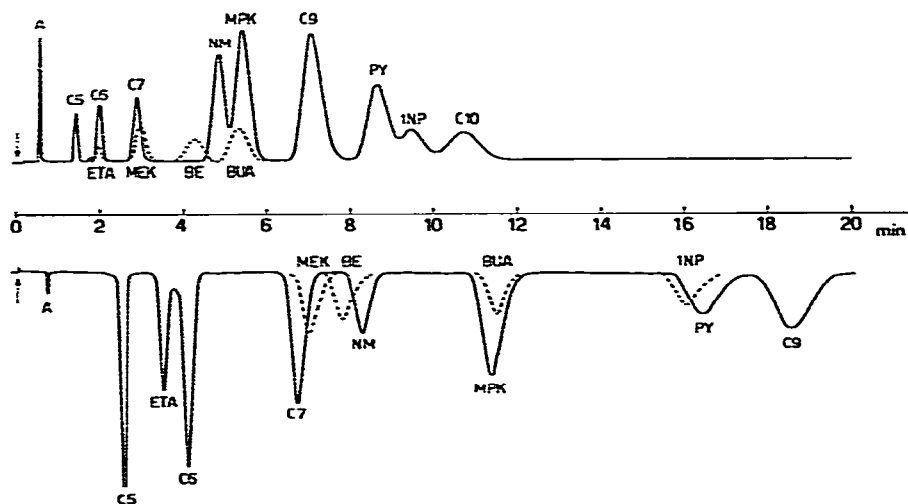

Fig. 2. Variation of the retention times and elution order of linear alkanes and polarity probes on a 3 m × 1/8 in. I.D. column filled with Porapak T (80–100 mesh) as a function of ageing time at 200°C. Below, after 3 days; above, after 25 days. Symbols as in Table I. Broken peaks were taken from other chromatograms, in order to avoid interference.

TABLE III

VALUES OF t_R' (min) AS A FUNCTION OF AGEING AT 200°C AND A CARRIER GAS FLOW-RATE OF 20 cm³/min FOR PPB COLUMNS SHOWING A NON-LINEAR DEPENDENCE OF LOG t_R' ON TIME

Probe*	Chromosorb 103			Chromosorb 107			Chromosorb 108		
	Initial t_R'	t_R' after 8 days	t_R' after 22 days	Initial t_R'	t_R' after 10 days	t_R' after 22 days	Initial t_R'	t_R' after 10 days	t_R' after 22 days
ETA	0.78	0.86	0.92	3.67**	3.08	3.07	2.25**	1.79	1.48
MEK	1.60	1.74	1.79	9.41	8.15	7.91	4.42	3.59	2.94
NM	—***	—	—	8.63	8.02	8.05	5.49	4.54	3.94
BE	2.47	2.60	2.70	1.03	9.20	8.71	5.30	4.14	3.52
BUA	2.32	2.67	2.83	15.93**	12.88	12.53	6.98**	6.01	4.79
MPK	2.51	2.73	2.89	17.65	14.64	14.13	7.31	5.88	4.75
Py	4.61	4.91	5.06	21.26**	19.95	19.67	11.08**	9.25	7.83
1NP	—***	—	—	27.27	23.63	23.17	12.52	10.26	8.74
n-Pentane	0.61	0.64	0.67	3.34	2.66	2.52	1.53	1.03	0.87
n-Octane	2.89	3.23	3.39	23.90	16.57	15.21	7.36	4.97	4.07

* For abbreviations, see Table I.
** Tailing peaks.
*** Reacts with stationary phase.

tailing of polar compounds. Decomposition of nitromethane and 1-nitropropane, probably by reaction with the stationary phase, was so high on Porapak S and Chromosorb 103 (polystyrene type) that it impaired the determination of retention times. Acrylic ester polymer showed both linear (Chromosorb 105) and non-linear (Chro-
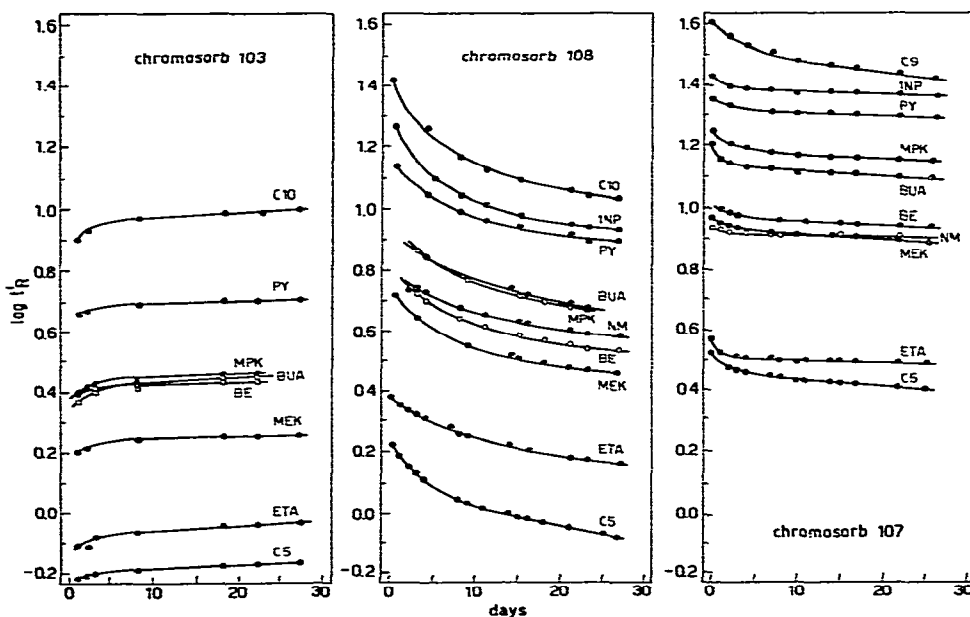

Fig. 3. Values of log t_R' as a function of ageing time at 200°C, and a carrier gas flow-rate of 20 cm³/min for some PPBs columns, showing non-linear variation of log t_R'. Symbols as in Table I.

mosorb 107 and 108) variations of log t'_R values. A strong and linear decrease in log t'_R values with ageing time was observed only with Porapak T [ethylene glycol dimethacrylate polymer (EGDMA)] and may be due to the fact that the temperature limit for this phase given by the producer for continuous isothermal use is 190°C, but, on the other hand, horizontal trends were shown by Porapak N (vinylpyrrolidone) that theoretically has the same temperature limit. All other PPBs were tested largely below their temperature limits (225°C for Chromosorb 106, 107 and 108; 250°C for Porapak P, Q, R and S and Chromosorb 102, 104 and 105; 275°C for Chromosorb 101 and 103) and therefore their behaviour cannot be correlated with thermal decomposition. In general, vinylpyrrolidone, styrene–divinylbenzene, polystyrene and acrylonitrile–divinylbenzene (Chromosorb 104) polymers showed no variation of the retention times with ageing or a small and linear change of log t'_R values (Chromosorb 103 also shows a linear trend after the first 5 days of ageing). Acrylic esters, EGDMA and vinylpyridine polymers show great changes in their behaviour with ageing time (Porapak T, Chromosorb 107 and 108) or react with probes and show tailing peaks (Porapak S).

At low temperatures, the effect of ageing on retention times is expected to be very small, owing to the reduced kinetics of the various chemical and physical modifications responsible for the observed changes. This was confirmed by the repeatability of the retention data obtained with PPB columns that which have been in use in our laboratory for many years. Fig. 3 shows the value of the retention index (with respect to methane and ethane) of acetylene and carbon dioxide measured on two Porapak P columns that were continuously maintained under a flow of helium in order to keep metastable helium detectors free from contamination for immediate use and maximum sensitivity. Taking into account the fact that the I values in Fig. 3 were calculated from chromatograms obtained during routine analyses, at various flow-rates, with different sampling volumes and at temperatures ranging between 20 and 35°C,
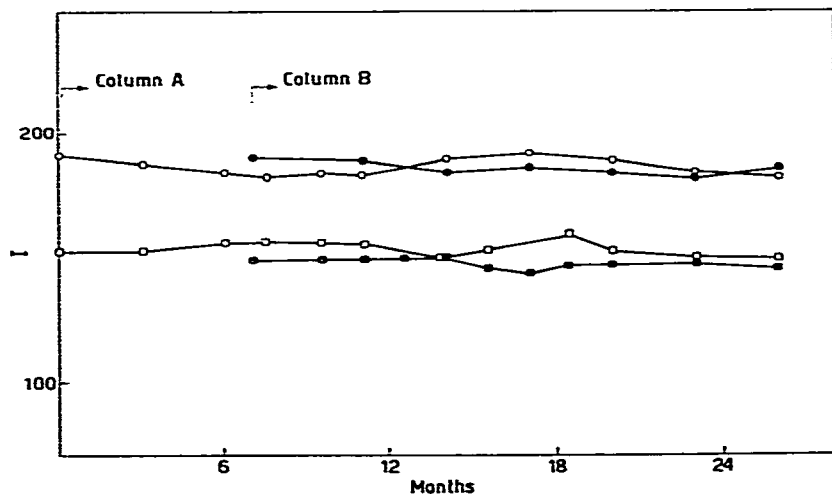

Fig. 4. Ageing of Porapak P at low temperature (20–40°C). The retention index values of acetylene (above) and carbon dioxide (below) were measured at intervals on columns maintained continuously under a flow of carrier gas.

the results show that the ageing of PPBs at low temperature has a negligible effect on the performance of the columns.

In contrast, the variation of the characteristics of some PPBs with ageing at high temperature is significant and may explain many of the differences between retention values reported in the literature, especially when the changes in retention times for products having different polarities reverse the order of elution of some peaks (Porapak T and Chromosorb 103, 105, 107 and 108). PPBs of the same type belonging to similar batches could show the same initial behaviour in different laboratories, but slowly change their characteristics as a function of ageing time and temperature. Polymers that show a horizontal dependence of log t'_R on ageing time (Porapak N, Q and R and Chromosorb 106) yield constant and reproducible values of both absolute and relative retention data, while near parallel changes in log t'_R values of the various probes and linear alkanes still permit comparable values of relative retention to be obtained (Porapak S and Chromosorb 102). All of the other PPBs that show different slopes of the log t'_R plots of various probes or non-linear behaviour will probably cause scattered values of reference data to be obtained in different laboratories. Of course, greater changes in the chemical and physical characteristics of the PPBs, caused by oxidation due to the use of a contaminated carrier gas or by the reaction of some samples with the stationary phase, may have increased the variation between the results reported by various workers. Also, when great care is taken when measuring the retention times of reference compounds in near ideal conditions (fresh stationary phase, pure carrier gas, controlled conditioning and column ageing, use of standards that do not react with the stationary phase, etc.), the reported results show that the unavoidable variation in some retention times during the column life must be taken into account when a classification of the GC properties and polarities of PPBs used at high temperature is attempted.

REFERENCES

1 G. Castello, G. D'Amato and G. Canciani, *Ann. Chim. (Rome)*, 68 (1978) 255.
2 G. Castello and G. D'Amato, *J. Chromatogr.*, 196 (1980) 245.
3 G. Castello and G. D'Amato, *J. Chromatogr.*, 212 (1981) 261.
4 G. Castello and G. D'Amato, *J. Chromatogr.*, 243 (1982) 25.
5 W. R. Supina and L. P. Rose, *J. Chromatogr. Sci.*, 7 (1967) 192.
6 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
7 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
8 W. R. Supina and L. P. Rose, *J. Chromatogr. Sci.*, 8 (1970) 214.
9 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.