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Short communication

Specific retention volumes in gas chromatography from low-quality capillary columns

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Abstract

Specific retention volumes obtained from capillary columns of very low quality (column efficiencies about 100 theoretical plates/m), with a commercial polycyanopropylmethylsiloxane (50% substitution) as stationary phase, are compared with those obtained from the same type of columns and stationary phase, but exhibiting higher efficiencies. The statistical study shows that low-quality columns are as appropriate for measuring specific retention volumes as the better-quality columns. The same conclusion may be drawn for Kováts' retention indices or McReynolds' constants, if the aim of the study is the characterization of new stationary phases. © 1998 Elsevier Science B.V.

Keywords: Stationary phases, GC; Retention volume, specific

1. Introduction

Stationary phases (SPs) used in gas chromatography (GC) are characterized in different ways, one of them being the use of the values of the McReynolds constants [1]. A deeper characterization should include specific retention volumes (V_g) of a number of selected compounds, interaction parameters, enthalpy, entropy and Gibbs free energy of solution and mixing, SP's Hildebrand's solubility parameter, etc. This type of characterization is carried out by inverse gas chromatography (IGC), introduced in 1967 by Kiselev [2] and developed in theory and methods, mainly by Smidsrod and Guillet [3]. Many polymers have been studied by IGC [4–17].

The maximum expected error in the value of V_g ,

when obtained by the classical equation [18], has been evaluated as 2% for packed columns [19], and close to 7% for capillary columns [20]. A new equation, derived from the original one has been presented for capillary columns [21]:

$$V_g = \frac{k}{C} \cdot \left(1 - \frac{C}{2\rho}\right)^2 \cdot \frac{273.15}{T_c} \quad (1)$$

where k is the retention factor; C is the concentration of the SP in the solution used to fill the capillary tube during the preparation of the chromatographic column by the static method (g/ml) and ρ is the density of the SP at the column temperature (g/ml). The maximum error expected for V_g with Eq. (1) has been evaluated as 1% [20]. The only additional parameter needed is the density of the SP at the temperature of the column. It has been proven that a value of 1 for ρ will produce a maximum error in V_g , lower than 0.25%, although normally it will be in the order of 0.1% [20].

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Good capillary columns are not always easy to obtain, particularly with polymers of low viscosity or high polarity, even by experienced chromatographers [22,23]. In what follows, we present a statistical study of a few examples of V_g and retention index (I) values obtained on capillary columns which showed both low and high efficiencies. The SP chosen does not form a stable film on the column walls [22,24–28]. Increasing the viscosity of the SP during the process of synthesis [29–31] or once finished [32], would have produced undesirable changes in the characteristics of the SP, and has not been carried out.

2. Experimental

2.1. Instrumentation

Two HP-5890A and a Varian 3300 gas chromatograph, all fitted with a split type injection system and flame ionization detector (FID), were used. Inlet pressures were checked with pressure transducers (Wika Tronic 891.13.500, Alexander Wiegand, Klingenberg, Germany) and numeric displays (Félix Mateo Mod, PM-2900, Barcelona, Spain). The pressure readings had a precision of ± 67 Pa (1 Torr = 133.32 Pa).

2.2. Capillary columns

Seven glass wall-coated open tubular columns

(WCOT) prepared in our laboratories from borosilicate glass tubes, were used. The tube walls were leached, washed and dehydrated following the method described by Grob [33]. The tube was then silanized according to well established methods [25,33–36] and our own experience, and coated by the static method [33]. Columns were conditioned at 200°C for 125 min, except columns 3 and 4 which were conditioned at 160°C for 60 min. The characteristics of the columns are gathered in Table 1. The cyanopropyl group substitution of the SP was shown to be 46% by NMR. The SP was mixed, in all cases, with about 1% of OV-101 to improve the stability of the SP film. Column tubes were prepared in different ways, as described in Table 2. An example of two chromatograms of the same sample on two of the columns used is offered in Fig. 1.

2.3. Chromatograms

Chromatograms were obtained isothermally at 60, 80, 100 and 120°C, with nitrogen as carrier gas, at inlet pressures ranging from about 21.2 to 46.8 kPa. Grob's test was carried out with hydrogen as carrier gas. Electronic integrators were used to compute retention times. Hold-up times were calculated according to the LQG procedure [37,38]. Except for a few experiments, clearly indicated below, all chromatograms corresponding to the same column were carried out at the same carrier gas linear velocity, independent of temperature, ranging from 9.5 to 17 cm/s.

Table 1
Characteristics of the chromatographic columns

	Column						
	1	2	3	4	5	6	7
SP	PS-206	PS-906	PS-906	PS-906	PS-906	PS-906	PS-906
Type	WCOT	WCOT	WCOT	WCOT	WCOT	WCOT	WCOT
L (m)	20.8	19.6	17.7	20.5	19.7	20.1	20.1
I.D. (mm)	0.217	0.247	0.204	0.204	0.243	0.243	0.204
C (mg/ml)	4.40	4.06	4.82	4.82	4.08	4.06	4.92
Film (μm)	0.222	0.233	0.228	0.228	0.230	0.229	0.233
N/m	2930	2400	2841	3308	114	245	92
Aspect	Good	Good	Good	Good	Droplets	Droplets	Droplets

SP, stationary phase; PS-906, polycyanopropylmethylsiloxane (ABCR); WCOT, wall-coated open tubular column; L , length; I.D., internal diameter; C , concentration of the solution of SP used to prepare the capillary column; Film, film thickness at 25°C; N , plate number.

Table 2
Silylating processes of the different columns

	Silylating agent	Process
Columns 1, 3 and 4	A, 20% in CH ₂ Cl ₂	300°C, 15 h
Column 2	A, 50% in CH ₂ Cl ₂	300°C, 15 h
Column 5	(a) B, 100% (b) PS-906, 1% + DCUP, 0.5% in toluene	(a) 380°C, 15 h (b) programmed: 150°C to 170°C at 0.5 °C/min, followed by 1 h at 170°C
Column 6	(a) A, 50% in CH ₂ Cl ₂ (b) A, 50% + DCUP, 0.5% in toluene	380°C, 15 h (b) programmed: 50°C to 150°C, 2 °C/min kept 1 h; then 150°C to 170°C, 1 °C/min kept 1 h
Column 7	(a) PS-906, 20% + DCUP, 0.5% in CH ₂ Cl ₂ (b) PS-906, 20% + DCUP, 0.5% in CH ₂ Cl ₂	(a) the same as process (a) for column 6 (b) the same as process (b) for column 6

A: (Cyanopropyl)methylcyclodisiloxane (ABCR); B: 1,3-bis(3-cyanopropyl)-tetramethyldisiloxane (Petrarch Systems); DCUP: dicumyl peroxide.

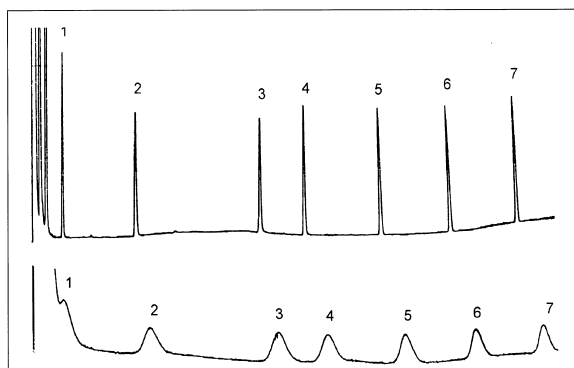


Fig. 1. Chromatograms of a Grob's test in column 1 (high efficiency) and in column 7 (low efficiency). Programmed temperature from 40 to 130°C, at 2.5°C/min with hydrogen as carrier gas. Identification of peaks: 1: *n*-decane; 2: *n*-dodecane; 3: nonanal; 4: 1-octanol; 5, 6 and 7: C₁₀–C₁₂ fatty acid methyl esters. Chromatograms have been run with the same attenuation of the signal. A larger amount of sample has been injected in the case of the low-quality column in order to increase peak height without changing detector conditions.

3. Results and discussion

3.1. Specific retention volumes

3.1.1. Effect of the carrier gas linear velocity

V_g values do not depend on experimental con-

ditions, with the exception of temperature and the nature of the solute and SP. But in very-low-quality columns an effect of the carrier gas velocity might be expected. Table 3 presents the variations between V_g values. The average values of V_g from about 40 injections carried out in high-efficiency columns are also shown. It may be observed that the gas velocity has no appreciable effect on V_g , with a few exceptions in the case of column 7 (92 plates/m), clearly indicating that in difficult cases (drops could be observed in the column with the naked eye) small flow-rates are preferable. Only four values of the table are above 1%, all in column 7, corresponding to very short retention times.

3.1.2. Variability of the values of V_g

Repeated injections in all seven columns at 60, 80 and 120°C (six *n*-alkanes plus the ten McReynolds' probes), and at 100°C (six *n*-alkanes, five methylketones, four alkylbenzenes and five *n*-alcohols) were carried out, totalling about 50 injections of *n*-alkanes and 40 injections of other solutes at each temperature for any one column. Individual relative standard deviation values (R.S.D.s) showed the distribution presented in Table 4. Values at 120°C are higher, due to the short retention times. Lower flow-rates at 120°C would had improved results [20]. Considering the other three temperatures, Table 4

Table 3
Percentage variation of specific retention volumes, at 100°C at two flow-rates

	V_g (see text)	Column 1	Column 3	Column 7
	Column efficiency (N/m):	2930	2841	92
	\bar{u}_{low} (cm/s)/ \bar{u}_{high} (cm/s):	8.8/16.7	8.3/12.2	7.8/13.6
<i>n</i> -Decane	48.43	0.00	0.04	-1.83
<i>n</i> -Undecane	83.43	-0.01	0.08	-0.78
<i>n</i> -Dodecane	144.4	0.00	0.07	-0.53
<i>n</i> -Tridecane	249.0	0.16	0.00	0.00
<i>n</i> -Tetradecane	431.8	0.09	0.09	0.18
<i>n</i> -Pentadecane	721.2	0.11	0.16	0.15
2-Butanone	38.97	-0.24	0.36	-1.52
2-Pentanone	61.77	-0.12	0.29	-1.06
2-Hexanone	109.9	-0.09	0.36	-0.46
2-Heptanone	189.5	-0.11	0.37	-0.21
2-Octanone	325.6	-0.03	0.40	-0.06
Benzene	33.97	1.00	-0.50	-1.44
Ethylbenzene	97.80	0.53	0.14	-0.29
<i>n</i> -Propylbenzene	153.6	0.35	0.26	-0.26
<i>n</i> -Butylbenzene	264.4	0.28	0.27	-0.08
1-Butanol	73.85	-0.11	-0.70	-0.96
1-Pentanol	132.3	-0.16	-0.53	-0.89
1-Hexanol	231.6	-0.14	-0.47	-0.34
1-Heptanol	402.3	-0.13	-0.35	-0.27
1-Octanol	693.5	-0.20	-0.33	-0.32

Average of ten runs at each flow-rate. A negative figure indicates a lower value of V_g at the high flow-rate.

shows that only 2% of the values corresponding to the set of better columns, and 7% of those of the worse columns are higher than 1%. If the experiments at 60°C are excluded because this temperature is too low for some of the solutes injected, then all values are below 1% (87% below 0.5%) in the group of better columns, and 95% of the values corresponding to columns 5 to 7 are below 1%.

3.1.3. Statistical analysis

For statistical purposes, results from columns 1 to 4 (high-efficiency columns) form the sample of population 1, while those from columns 5 to 7 (low-efficiency columns) form the sample of population 2. The aim of the study is to find out if the average value of V_g of population 1 is not different from that of population 2. The comparison is made

Table 4
Relative number of R.S.D. values (% of the total) of V_g , for different levels of error

Temperature (°C):	60	80	100	120
Number of solutes:	15	16	20	16
Type of column ^a	HQ	LQ	HQ	LQ
Number of columns	4	3	4	3
Number of R.S.D. values	60	45	64	48
Value of R.S.D.				
<0.5%	80	48	85	68
0.5–1.0%	13	42	15	23
1.0–1.5%	7	7	0	9
1.5–2.0%	0	3	0	0

^a HQ: High-quality columns; LQ: low-quality columns. No R.S.D. value above 2.0% was found.

with the Snedecor's distribution parameter F for a confidence level of 95%, and the experimental Student's or Cochran's t -test [39].

The statistical study was carried out with the results at 100°C (20 solutes, 40 to 50 injections). The set of values is the same as that used to produce the figures of 100°C of Table 4. The F values of the Snedecor distribution show that, with the exception of n -decane, all substances fulfill the condition that the standard deviations of the two populations are not significantly different ($F_{\text{exp}} \leq F_{\text{tab}}$). For n -decane, it was found that $F_{\text{exp}} > F_{\text{tab}}$, therefore, Cochran's t was calculated instead of Student's t [39]. Mean values of V_g (\bar{X}_i) as well as the value of Student's t are presented in Table 5. The value of t_{exp} should be equal to, or lower than t_{tab} . Table 5 shows that the average values from high quality columns are not significantly different from the average values from the low-quality columns. Differences of V_g , are also presented in Table 5. It may be observed that except

for n -alkanes, the differences between the two sets of columns are smaller for the high values of V_g , confirming that low flow-rates are preferred for low-quality columns [20].

3.1.4. Reproducibility of specific retention volumes with time and use

Table 6 shows an example of the effect of a number of injections (under the heading 'history') at 60, 80, 100 and 120°C, plus a few Grob's tests.

3.2. Retention indices

Table 7 shows average values of retention indices of the ten McReynolds probes [1] at different temperatures. The R.S.D.s are also presented in the table. The overall result is that 60% of the values differ by one or zero retention index units (i.u.), 20% show differences of ± 2 i.u., 12.5% present variations of ± 3 , and only in three cases the difference is 4 or

Table 5
Mean values of V_g at 100°C obtained for columns 1 to 4 (high efficiency) and 5 to 7 (low efficiency)

	High-efficiency columns		Low-efficiency columns		ΔV_g %	t_{exp}
	V_g	R.S.D.	V_g	R.S.D.		
n -Decane	48.43	0.60	48.52	4.64	0.19	0.069 ^a
n -Undecane	83.43	1.05	84.51	4.40	1.29	0.337
n -Dodecane	144.4	1.40	146.0	4.42	1.10	0.280
n -Tridecane	249.0	1.65	252.6	4.47	1.44	0.352
n -Tetradecane	431.8	1.75	435.0	4.73	0.74	0.171
n -Pentadecane	721.2	1.84	727.5	4.18	0.87	0.221
2-Butanone	38.97	2.93	38.36	3.44	-1.58	0.383
2-Pentanone	61.77	3.33	60.70	3.66	-1.75	0.384
2-Hexanone	109.9	3.60	108.5	3.63	-1.28	0.271
2-Heptanone	189.5	3.80	187.6	3.48	-1.00	0.209
2-Octanone	325.6	3.90	323.0	3.37	-0.80	0.165
Benzene	33.97	3.94	33.00	4.27	-2.90	2.216
Ethylbenzene	97.80	4.18	96.20	3.61	-1.64	0.317
n -Propylbenzene	153.6	4.32	151.8	3.48	-1.17	0.224
n -Butylbenzene	264.4	4.84	261.7	3.37	-1.02	0.181
1-Butanol	73.85	4.01	73.00	4.12	-1.16	0.218
1-Pentanol	132.3	4.27	131.2	4.26	-0.83	0.149
1-Hexanol	231.6	4.40	230.5	4.23	-0.48	0.084
1-Heptanol	402.3	4.52	401.7	4.16	-0.15	0.026
1-Octanol	693.5	4.69	695.7	4.17	0.32	0.054

50 Runs for n -alkanes and 40 runs for other substances in each column. (Student's $t_{\text{tab}} = 2.571$; Cochran's $t_{\text{tab}} = 4.303$).

ΔV_g % = $[(V_g \text{ low-efficiency columns} / V_g \text{ high-efficiency columns}) - 1] * 100$. t_{exp} , experimental Student's t . t_{tab} , values from the tables.

^a t_{exp} , experimental Cochran's t .

Table 6
Errors in average V_g values at 100°C deduced after repeated injections at different temperatures

	Column			
	3	4	6	7
'History' (injections)	258	268	260	250
Initial efficiency (N/m)	2841	3308	245	92
Final efficiency (N/m)	1115	1855	242	93
<i>Error in the specific retention volumes (%)</i>				
<i>n</i> -Decane	-0.53	0.23	1.41	2.02
<i>n</i> -Undecane	-0.53	-0.85	0.40	1.59
<i>n</i> -Dodecane	-0.62	-0.41	0.07	-0.13
<i>n</i> -Tridecane	0.16	0.96	0.08	-0.19
<i>n</i> -Tetradecane	0.87	0.86	0.16	0.33
2-Butanone	0.38	-0.05	0.08	1.89
2-Pentanone	-1.08	-0.34	0.85	1.20
2-Hexanone	-0.36	-0.55	0.09	1.19
2-Heptanone	-0.26	-0.59	0.00	0.27
2-Octanone	0.22	-0.09	0.09	-0.12
Benzene	-0.21	0.30	0.78	1.93
<i>n</i> -Ethylbenzene	-0.16	-0.29	0.50	0.82
<i>n</i> -Propylbenzene	0.00	-0.66	-0.19	1.31
<i>n</i> -Butylbenzene	-0.08	-0.77	0.04	0.91
1-Butanol	0.20	-0.14	0.01	0.08
1-Pentanol	0.15	0.38	-0.07	-0.07
1-Hexanol	0.52	0.83	-0.13	0.04
1-Heptanol	0.72	0.96	0.12	0.07
1-Octanol	1.79	1.05	0.47	-

The figures corresponding to the various solutes represent percentage variation. A negative value indicates a lower V_g value after repeated use.

Table 7
Average values of the Kováts' retention indices, and relative standard deviations, of the ten McReynolds' probes at different temperatures

	<i>I</i> (R.S.D.)							
	60°C		80°C		100°C		120°C	
	H	L	H	L	H	L	H	L
Benzene	899 (0.07)	899 (0.24)	915 (0.15)	916 (0.18)	935 (0.08)	935 (0.27)	953 (0.12)	955 (0.55)
1-Butanol	1054 (0.10)	1054 (0.33)	1066 (0.22)	1063 (0.36)	1081 (0.11)	1075 (0.31)	1089 (0.35)	1088 (0.46)
2-Pentanone	1007 (0.07)	1007 (0.33)	1025 (0.08)	1025 (0.31)	1044 (0.01)	1044 (0.26)	1057 (0.48)	1061 (0.58)
1-Nitropropane	1193 (0.14)	1191 (0.36)	1223 (0.10)	1221 (0.35)	1254 (0.12)	1253 (0.29)	1281 (0.49)	1282 (0.57)
Pyridine	1035 (0.11)	1034 (0.48)	1057 (0.31)	1056 (0.33)	1079 (0.11)	1079 (0.54)	1099 (0.52)	1100 (0.63)
2-Methyl-2-pentanol	1116 (0.09)	1120 (0.53)	1145 (0.06)	1146 (0.49)	1176 (0.15)	1174 (0.44)	1200 (0.40)	1199 (0.28)
1-Iodobutane	1060 (0.13)	1057 (0.62)	1064 (0.08)	1061 (0.26)	1071 (0.06)	1068 (0.37)	1071 (0.37)	1072 (0.23)
2-Octyne	1009 (0.04)	1009 (0.24)	1013 (0.04)	1012 (0.25)	1016 (0.17)	1016 (0.36)	1016 (0.50)	1018 (0.55)
1,4-Dioxane	1035 (0.05)	1033 (0.26)	1055 (0.06)	1055 (0.31)	1076 (0.05)	1076 (0.39)	1094 (0.66)	1097 (1026)
<i>cis</i> -Hidrandane	1083 (0.12)	1082 (0.23)	1103 (0.06)	1101 (0.25)	1126 (0.13)	1124 (0.33)	1144 (0.32)	1144 (0.30)

H: High-efficiency columns; L: low-efficiency columns.

more. One reason for this is that in the case of very-low-quality columns, the amount of sample injected was larger than in the case of high-efficiency columns, in order to maintain a reasonable detector response under identical conditions. Even if some of the differences observed might seem high for accurate peak identification, they are nevertheless sufficient for a preliminary SP characterization. Figures of Table 7 have all been obtained from chromatograms run at similar carrier gas linear velocities. It has been mentioned, however, that in the case of low-quality columns, lower flow-rates tend to increase the precision of the results.

4. Conclusions

In view of the results presented in this paper, we may come to the conclusion that low-quality capillary columns (even columns with droplets of stationary phase) are as appropriate for measuring specific retention volumes, as higher-quality columns, with a high number of plates per metre and good coating efficiency. This conclusion is particularly important for those researchers wishing to carry out thermodynamic characterization of new polymer materials, often unsuitable for the preparation of capillary columns of high quality, by IGC. The variability among columns is somewhat higher with very low-quality columns, so in these cases two or three

columns should be prepared to improve precision. Results also show that Kováts' retention indices or the McReynolds' constants for a preliminary characterization of stationary phases, may be obtained equally well from low-quality capillary columns.

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