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## INDIRECT DETERMINATION OF SPECIFIC RETENTION VOLUMES IN GAS CHROMATOGRAPHY

### USE OF RETENTIONS OF THE McREYNOLDS PROBES RELATIVE TO *n*-DECANE

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#### SUMMARY

Specific retention volumes of *n*-decane on 24 liquid stationary phases of the silicone type have been calculated from retention data relative to *n*-decane, of *n*-dodecane and the ten probes used by McReynolds to characterize stationary phases in gas chromatography. The average error of prediction is 1.2%, with only one error above 3% (5%). Relative retentions of consecutive *n*-alkanes varied from 1.18 to 1.64. The experimental values of the specific retention volumes of *n*-decane varied between 1.39 and 129.2 ml/g.

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#### INTRODUCTION

Specific retention volumes,  $V_g$ , are difficult to obtain with accuracy due to the many experimental parameters which must be controlled. Much attention has been paid to the search for an empirical relationship between this quantity and the relative retention of various substances, as the latter are easily obtained on any gas chromatograph with a reasonable control of the oven temperature. A linear relationship between the specific retention volume of an *n*-alkane and the logarithm of the relative retention of consecutive *n*-alkanes has been found<sup>1</sup>. The accuracy of predictions has considerably improved with the use of more reliable experimental values<sup>2</sup>, leading to the hope that a further improvement will result when a larger number of specific retention volumes of *n*-paraffins becomes available.

The accuracy of prediction has been found to be higher when the relative retentions of other substances are included in the expression<sup>3</sup> and there is no doubt that average errors would have been lower if a better set of  $V_g$  values had been used.

The choice of the standard substances used for the prediction was made following certain criteria which led to the selection of various three-component systems. Care was taken to avoid the inclusion of alcohols (with activity coefficients in the liquid phases very different from those of *n*-hydrocarbons) and substances having retention volumes very different from that of *n*-octane (the *n*-alkane whose specific retention volume was to be calculated).

In this paper we present results obtained using a totally different set of standard substances: the ten probes used by McReynolds<sup>4</sup> to characterize 226 liquids used as stationary phases in gas chromatography. The set includes substances of varied chemical structure, but they were chosen from 68 that could best predict the retention of other solutes in gas chromatography (GC). The apparent advantage of this set of probes is that most reports on stationary liquid phases used in GC state the values of the McReynolds constants which are equivalent to the corresponding retention indices. If the logarithm of the relative retention of two *n*-alkanes is also known for a given stationary phase, and this value is included in McReynolds' publication, then the logarithm of the retention of any of the ten probes relative to an *n*-alkane or to any other substance whose retention index is known can be deduced.

Unfortunately, values of the specific retention volume of *n*-alkanes are not given by McReynolds<sup>4</sup>, and a previous publication by the same author covering fewer stationary phases<sup>5</sup> only lists four of the ten substances used later for the characterization.

In order to test the kind of accuracy which could be obtained with this set of substances, 24 liquid phases of the silicone type which had been characterized in our laboratories were chosen. Full details of the procedure used to measure the percentage loading of the liquid in the packing, the weight of packing in the column and the control of experimental parameters during the analyses are given elsewhere<sup>6</sup>.

## EXPERIMENTAL

Some of the values used were obtained on a Perkin-Elmer F-21 gas chromatograph fitted with a mechanical manometer to measure the column head pressure. Other values were obtained on a Sigma-2 gas chromatograph fitted with a mercury manometer attached to the inlet gas line. The temperature of the column oven was controlled at 120°C, with the help of a thermocouple. The amount of liquid in the column was calculated by careful weighing of the packing during its preparation, and the percentage loading of the stationary phase was deduced with the help of an extraction method<sup>7</sup>. The only exception was the liquid OV-101 whose percentage loading was estimated by ashing three samples of the packing.

## RESULTS AND DISCUSSION

### *The correlation equation*

The expression used in this paper is an extension of that employed earlier<sup>1,3</sup> and can be written as

$$\ln V_{Rn\text{-decane}} = a_0 + \sum_{i=1}^{11} a_i \ln (t'_{Ri}/t'_{R10}) \quad (1)$$

where  $V_{g_{n\text{-decane}}}$  is the specific retention volume of *n*-decane and  $t'_{Ri}/t'_{R10}$  is the retention of the *i*th compound relative to *n*-decane on the same chromatographic column.

The eleven substances used in our calculations are shown in Table I. Experimental values of the specific retention volume of *n*-decane, and retentions of the solutes listed in Table I relative to *n*-decane on 24 stationary phases, produce an overdetermined system of linear equations, with  $a_i$  ( $i = 0, 1, \dots, 11$ ) as unknowns. The system has been solved according to the algorithm of Nash<sup>8</sup>. This method of solving overdetermined systems of linear equations with a least mean squares criterion, when compared with the traditional method for solving normal equations, has the advantage of numerical stability<sup>9</sup>. The starting matrix of data has 13 columns and 24 rows, each row corresponding to one chromatographic column. Data in the matrix are arranged as follows:

Column 1 Coefficient of the unknown,  $a_0$ .

Columns 2–12 The natural logarithms of the retentions of the compounds listed in Table I relative to *n*-decane.

Column 13 The natural logarithms of the experimental specific retention volumes of *n*-decane, as shown in Table IV.

TABLE I  
THE SOLUTES USED

<i>i</i>	Name	<i>i</i>	Name
1	Benzene	6	2-Methyl-2-pentanol
2	<i>n</i> -Butanol	7	Iodobutane
3	2-Pentanone	8	2-Octyne
4	1-Nitropropane	9	1,4-Dioxane
5	Pyridine	10	<i>cis</i> -Hydrindane
		11	<i>n</i> -Dodecane

The relative retentions used are listed in Table II.

The solution of the system produces the values of  $a_i$  in eqn. 1 shown in Table III. The use of eqn. 1 together with the values in Table III allows the prediction of the  $V_g$  values on the 24 liquid phases with the errors shown in Table IV.

It must be emphasized that although there are only 24 liquid phases, the values of the specific retention volumes of *n*-decane range between 1.39 and 129.19, a ratio of 1:93. The "polarities" of the liquid phases considered measured as the sum of the first five McReynolds constants range from 306 for OV-101 to 4202 for OV-275, a range similar to that covered by the 226 liquid phases listed by McReynolds in his classic publication<sup>4</sup>. In the set of liquid phases considered in this paper, there are fourteen commercial stationary phases, five liquids prepared by mixing two components at the time of coating of the solid support (OV-101 and OV-25 or OV-225 with SP-2340) making homogeneous mixed stationary phases, denoted by the symbol M following the name and five mixed heterogeneous liquid phases (mixed packings) represented by the symbol MP.

TABLE II  
RETENTIONS RELATIVE TO *n*-DECANE OF THE SOLUTES LISTED IN TABLE I  
M denotes a homogeneous mixed liquid phase; MP denotes a mixed packing.

Liquid phase	Solute										
	1	2	3	4	5	6	7	8	9	10	11
1	OV-225	0.5116	0.7772	0.5091	2.0118	1.5150	0.8362	1.2125	0.9395	1.8446	2.8564
2	SP-2300	0.8532	1.3855	1.3699	3.8278	3.0098	1.3620	1.8669	1.7926	2.3248	2.7601
3	SP-2310	1.3777	2.6858	1.6022	7.5542	5.3560	2.3452	2.6084	3.2275	2.6548	2.5023
4	SP-2330	1.9435	4.0652	3.2120	11.3174	8.2685	3.2371	2.8858	4.6926	3.1995	2.3852
5	SP-2340	2.3971	5.1521	2.7728	13.1485	10.1789	3.5063	3.5241	5.9750	2.7728	2.4758
6	SP-2300-MP*	0.9883	1.9267	1.1160	5.2138	3.5203	1.5936	1.8157	1.2326	2.2654	2.7079
7	SP-2310-M*	1.7641	3.7554	2.0455	10.7035	7.4892	2.8355	2.9545	4.3182	2.7922	2.4805
8	SP-2330-M*	2.0270	4.3919	2.4730	12.2568	8.8378	3.4189	3.3649	1.7432	5.2568	2.3608
9	OV-101	0.1514	0.1437	0.1632	0.2046	0.2718	0.2184	0.3579	0.4653	0.1980	3.1266
10	OV-3	0.1630	0.1497	0.1804	0.2595	0.2903	0.2235	0.4215	0.5147	0.2134	1.1369
11	OV-3M**	0.1698	0.1601	0.1911	0.2508	0.2862	0.2274	0.4097	0.5044	0.2284	1.1168
12	OV-7	0.1828	0.1687	0.2099	0.3268	0.3538	0.2419	0.4853	0.5554	0.2542	3.2698
13	OV-7-MP**	0.2086	0.1842	0.2240	0.3457	0.4352	0.2611	0.3009	0.5856	0.3012	1.2569
14	OV-11	0.2255	0.2049	0.2580	0.4407	0.4840	0.2808	0.6009	0.6508	0.3280	3.2643
15	OV-11-MP (1)**	0.2350	0.2061	0.2513	0.4091	0.5062	0.2789	0.5659	0.6352	0.3406	3.1225
16	OV-11-MP (2)**	0.2507	0.2188	0.2693	0.4504	0.5597	0.2934	0.6047	0.6697	0.3731	3.0943
17	OV-17	0.2608	0.2426	0.3077	0.5452	0.5999	0.3168	0.6957	0.7323	0.4032	3.2328
18	OV-17-M**	0.2726	0.2335	0.3034	0.5110	0.6063	0.3080	0.6503	0.7065	0.3964	3.0983
19	OV-22	0.3243	0.2851	0.3567	0.6697	0.7870	0.3580	0.8154	0.8410	0.5066	3.1290
20	OV-22-MP**	0.3410	0.2795	0.3679	0.6833	0.8118	0.3556	0.8358	0.8556	0.5383	3.0975
21	OV-61	0.2523	0.2133	0.2668	0.4507	0.4918	0.3401	0.6219	0.6717	0.4055	1.5112
22	OV-61-M**	0.2453	0.2114	0.2583	0.4394	0.5174	0.2837	0.5917	0.6527	0.3485	1.4040
23	OV-25	0.3819	0.3197	0.4088	0.7737	0.9269	0.3914	0.9299	0.9402	0.5960	3.0699
24	OV-275	5.1727	10.6906	7.3741	30.2230	25.4964	5.4892	5.9281	13.7482	4.3022	2.8345

\* Mixture of liquids OV-225 and SP-2340.

\*\* Mixture of liquids OV-101 and OV-25.

TABLE III  
SOLUTION OF EQN. 1

$a_0 = 2.1019$	$a_6 = 0.51504$
$a_1 = -2.8830$	$a_7 = -0.19901$
$a_2 = -0.49885$	$a_8 = 1.9441$
$a_3 = 0.17459$	$a_9 = 0.57415$
$a_4 = 0.57041$	$a_{10} = -1.0916$
$a_5 = -0.19451$	$a_{11} = 0.29843$

TABLE IV  
PREDICTION OF SPECIFIC RETENTION VOLUMES OF *n*-DECANE USING EQN. 1 WITH THE COEFFICIENTS LISTED IN TABLE III

Liquid phase	$V_g$		Error (%)
	Expl.	Calc.	
1 OV-225	40.66	40.53	0.319
2 SP-2300	25.55	25.55	0.0
3 SP-2310	12.92	13.23	2.40
4 SP-2330	7.97	7.94	0.376
5 SP-2340	5.59	5.52	1.25
6 SP-2300-MP	18.01	18.17	0.888
7 SP-2310-M	9.24	9.10	1.51
8 SP-2330-M	7.40	7.41	0.135
9 OV-101	128.64	129.81	0.909
10 OV-3	129.19	132.15	2.29
11 OV-3-M	116.58	115.81	0.660
12 OV-7	119.83	118.54	1.07
13 OV-7-MP	94.89	96.15	1.33
14 OV-11	97.51	95.72	1.83
15 OV-11-MP (1)	83.42	81.74	2.01
16 OV-11-MP (2)	76.97	76.96	0.013
17 OV-17	83.60	84.55	1.14
18 OV-17-M	69.65	69.42	0.330
19 OV-22	61.88	60.31	2.54
20 OV-22-MP	53.52	56.22	5.04
21 OV-61	85.62	84.65	1.13
22 OV-61-M	76.88	76.72	0.208
23 OV-25	49.36	48.84	1.05
24 OV-275	1.39	1.40	0.72
	Mean		1.2

## CONCLUSION

The results show that the use of the McReynolds probes is a very promising way of predicting specific retention volumes of *n*-alkanes from relative retention ratios, with errors which are much lower than previously expected<sup>3</sup>.

It is shown that mixing liquids to obtain improved selectivity does not affect the inherent precision of the prediction method employed.

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