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# INDIRECT DETERMINATION OF SPECIFIC RETENTION VOLUMES IN GAS CHROMATOGRAPHY
## USE OF THE RETENTION INDICES OF McREYNOLDS' SAMPLES

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## SUMMARY

The specific retention volumes of *n*-decane on 24 liquid stationary phases of the silicone type were calculated from the retention indices of the samples used by McReynolds in his characterization of gas chromatographic stationary phases. The average error of prediction was 2.24%. The effects of errors on the logarithm of the relative retentions of consecutive *n*-alkanes and the values of the retention indices were studied, and also its dependence on stationary phase polarity.

## INTRODUCTION

Stationary phases in gas chromatography are usually characterized by the values of their McReynolds' constants[1], a measure of the departure of their chromatographic behaviour from that of the stationary phase squalane[2]. The constants not only give a good idea of the selectivity of the stationary phase, but are also useful for the prediction of the retentions of other substances on a chromatographic column containing the same stationary phase[3]. The possibility of evaluating specific retention volumes ($V_g$) with the help of McReynolds' constants has not, however, been fully investigated. The prediction of $V_g$ values of *n*-alkanes using retention values of McReynolds' samples relative to *n*-decane[4] has been shown to be a very promising way of obtaining values of a magnitude difficult to measure directly because of the many experimental parameters to be kept under control. There is a relationship between the retention volume of a compound and its retention index as defined by Kováts, so there must be a possibility of predicting specific retention volumes of *n*-alkanes from the values of the retention indices of the ten samples used by McReynolds to characterize stationary phases. These values can easily be deduced from the MacReynolds' constants, given for each stationary phase in any commercial catalogue, or published whenever a new stationary phase is presented.

The practical advantage of using retention indices instead of retentions relative to *n*-decane would be that the chromatographic column need not be constructed to measure experimental data and therefore certain decisions involving a knowledge of specific retention volumes may be taken even before the column arrives in the laboratory.

THEORETICAL

The expression used in this paper is derived from that used earlier[4] based on retention data relative to *n*-decane (eqn. 1):

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

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 substance relative to that of *n*-decane on the same chromatographic column.

The modification of eqn. 1 to involve retention indices instead of relative retention data can easily be seen in Fig. 1, where only two solutes are shown for the sake of clarity: compound *i* and *n*-decane. If we call the slope of the straight line *s*, we can write

$$\ln (t'_{Ri}/t'_{R10}) = s(I_i - I_{10}) \tag{2}$$

That is, a linear relationship exists between the logarithm of the relative retention and the retention index difference.

According to eqn. 2, eqn. 1 becomes

$$\ln V_{g_{n\text{-decane}}} = a_0 + \sum_{i=1}^{11} a_i s(I_i - I_{10}) \tag{3}$$

where the coefficients $a_i$ ($i = 0, 1, ..., 11$) have the same values as in eqn. 1, $I_i$ is the retention index of compound *i*, $I_{10}$ is the retention index of *n*-decane and *s* is the
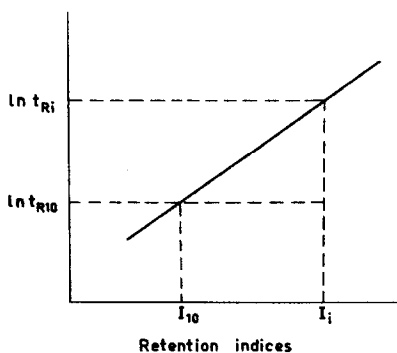


Fig. 1. Plot of the logarithm of the retention parameter $t_R$ *versus* retention index.

slope of the straight line obtained according to Fig. 1. Eqn. 3 is therefore equivalent to eqn. 1, so using the same values for the coefficients $a_i$ an accuracy of prediction similar to that found earlier should be achieved.

## EXPERIMENTAL

Eqn. 3 was tested using the set of 24 silicone-type stationary phases reported previously[4]. Chromatograms were run at 120°C on 2 m × 2.2 mm I.D. stainless-steel columns. Packings were prepared with about a 15% liquid loading on Chromosorb W AW (80–100 mesh). Homogeneous mixed stationary phases were prepared by mixing the corresponding solutions with the solid support and evaporating the solvent under vacuum. Mixed packings were prepared by mixing the appropriate amounts of single-phase packings before the column was filled. Retention times were measured to 0.01 min with the help of an integrator and retention indices were deduced from the straight line obtained when the logarithms of the retention times of the n-alkanes in one chromatogram were plotted against their carbon number, once the correction of a mathematical dead time method had been applied[5]. Further details have been given elsewhere[4,6].

## RESULTS AND DISCUSSION

### Initial data

A list of the retention indices used throughout this paper for the ten samples used by McReynolds on the 24 chromatographic columns is given in Table I, where values of the slope, s, are also shown for all columns. Both retention indices and slopes are average values of several determinations. Retention indices of the McReynolds' samples were obtained as follows. Each chromatogram showing peaks corresponding to six or seven n-alkanes and one to three other substances produced values for the retention indices of those substances. For each substance, the retention index given in Table I is the average value of between five and fifteen such determinations, the number of points depending on the substance or the column. Values of the slopes were obtained in a different manner: between 50 and 200 chromatograms produced retention volumes for six or seven n-alkanes, for each column. A mean value of the retention volume, called the "mean experimental value", was obtained for each n-alkane. The natural logarithms of those mean experimental values, when plotted against the retention index of the corresponding n-alkane, define a straight line whose slope, evaluated by a least mean squares fit, is shown in Table I. The equation of that straight line was used to deduce the "theoretical retention volume" of each substance from the value of its retention index. The theoretical retention volume thus obtained is therefore slightly different from the "mean experimental value". Differences of less than 1% were normally observed for n-alkanes and the other substances. The use of either retention volume is explained later.

### Prediction of values of $V_{n\text{-decane}}$

Eqn. 3 was used with the data listed in Table I and the values of the coefficients $a_i$ which had been found previously from experimental retention data relative to n-decane by means of the mathematical procedure explained earlier[4]. Results are given

TABLE I

SLOPES AND RETENTION INDICES USED THROUGHOUT THIS PAPER

M denotes a homogeneous mixed liquid phase; MP denotes a mixing packing.

| Stationary phase | Slope × 10³ | Solute* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| OV-225 | 5.29016 | 874 | 953 | 873 | 1135 | 1079 | 968 | 1037 | 988 | 989 | 1117 |
| SP-2300 | 5.04809 | 969 | 1066 | 1061 | 1265 | 1216 | 1059 | 1124 | 1051 | 1116 | 1167 |
| SP-2310 | 4.5732 | 1072 | 1217 | 1102 | 1440 | 1364 | 1182 | 1210 | 1093 | 1255 | 1218 |
| SP-2330 | 4.43271 | 1145 | 1312 | 1259 | 1545 | 1469 | 1260 | 1274 | 1126 | 1345 | 1249 |
| SP-2340 | 4.56150 | 1194 | 1358 | 1222 | 1574 | 1508 | 1277 | 1277 | 1135 | 1388 | 1237 |
| SP-2300-MP** | 4.95468 | 998 | 1126 | 1017 | 1325 | 1257 | 1097 | 1127 | 1037 | 1155 | 1160 |
| SP-2310-M** | 4.49356 | 1125 | 1295 | 1161 | 1518 | 1438 | 1240 | 1242 | 1108 | 1323 | 1232 |
| SP-2330-M** | 4.26340 | 1178 | 1356 | 1210 | 1593 | 1507 | 1291 | 1285 | 1135 | 1385 | 1259 |
| OV-101 | 5.7412 | 672 | 664 | 688 | 726 | 777 | 736 | 823 | 869 | 719 | 1006 |
| OV-3 | 5.90191 | 693 | 676 | 708 | 772 | 790 | 744 | 853 | 886 | 739 | 1022 |
| OV-3M*** | 5.74693 | 688 | 679 | 712 | 757 | 789 | 739 | 842 | 878 | 740 | 1017 |
| OV-7 | 5.951991 | 716 | 699 | 738 | 814 | 826 | 763 | 880 | 903 | 770 | 1038 |
| OV-7-MP*** | 5.715269 | 726 | 704 | 740 | 815 | 856 | 766 | 880 | 907 | 790 | 1041 |
| OV-11 | 5.938252 | 749 | 734 | 773 | 863 | 877 | 786 | 914 | 929 | 814 | 1061 |
| OV-11-MP(1)*** | 5.727358 | 747 | 725 | 759 | 845 | 882 | 778 | 900 | 921 | 813 | 1055 |
| OV-11-MP(2)*** | 5.69017 | 759 | 735 | 771 | 861 | 898 | 784 | 913 | 930 | 828 | 1064 |
| OV-17 | 5.8868 | 772 | 759 | 800 | 898 | 912 | 805 | 938 | 948 | 845 | 1077 |
| OV-17-M*** | 5.6678 | 772 | 745 | 788 | 881 | 912 | 792 | 925 | 939 | 838 | 1074 |
| OV-22 | 5.73073 | 804 | 782 | 822 | 931 | 959 | 821 | 966 | 970 | 882 | 1102 |
| OV-22-MP*** | 5.66161 | 811 | 776 | 823 | 932 | 962 | 817 | 967 | 973 | 889 | 1104 |
| OV-61 | 5.82444 | 754 | 732 | 771 | 862 | 876 | 784 | 916 | 930 | 814 | 1064 |
| OV-61-M*** | 5.69366 | 753 | 728 | 764 | 855 | 885 | 778 | 908 | 925 | 816 | 1060 |
| OV-25 | 5.61179 | 831 | 797 | 842 | 957 | 987 | 834 | 987 | 989 | 910 | 1120 |
| OV-275 | 5.2764 | 1317 | 1456 | 1381 | 1654 | 1615 | 1333 | 1346 | 1171 | 1501 | 1278 |

    * Solutes correspond to the McReynolds' samples. 1 = Benzene; 2 = *n*-butanol; 3 = 2-pentanone; 4 = 1-nitropropane; 5 = pyridine; 6 = 2-methyl-2-pentanol; 7 = iodobutane; 8 = 2-octyne; 9 = 1,4-dioxane; 10 = *cis*-hydrindane.
    ** Mixture of OV-225 and SP-2340.
    *** Mixture of OV-101 and OV-25.

in Table II. The errors are higher than those given in our previous paper[4], although they remain generally low, with the exception of column 8, with an error of 14.7%, which is certainly higher than expected. The reason for the difference in the mean error found (3.1% with the use of eqn. 3, 1.2% with eqn. 1) can be explained bearing in mind that the coefficients $a_i$ used had been obtained from "mean experimental values" of the retentions relative to *n*-decane, whereas the retention indices used in eqn. 3 were values deduced from a least mean squares fit. In order to compare eqns. 1 and 3, coefficients $a_i$ ($i = 0,1,...,11$) were again obtained with the same mathematical procedure[4], but using retentions relative to *n*-decane deduced from the semilogarithmic plot shown in Fig. 1. We call these "theoretical relative retentions", as shown in Table III. The solution of the overdetermined system (*i.e.* a system with more equations than unknowns) obtained with eqn. 1 produces the values of the coefficients listed in Table IV.

    With these new coefficients, values of the specific retention volume of *n*-decane

TABLE II

PREDICTION OF SPECIFIC RETENTION VOLUMES OF n-DECANE USING EQN. 3 WITH COEFFICIENTS FROM REF. 4

| Stationary phase | $V_g$ | | Error (%) | |
|---|---|---|---|---|
| | Exptl. | Calc. | This work | Ref. 4 |
| OV-225 | 40.66 | 41.0 | 0.83 | 0.32 |
| SP-2300 | 25.55 | 25.49 | 0.24 | 0.0 |
| SP-2310 | 12.92 | 11.96 | 7.42 | 2.4 |
| SP-2330 | 7.97 | 8.24 | 3.33 | 0.38 |
| SP-2340 | 5.59 | 5.26 | 5.88 | 1.25 |
| SP-2300-MP | 18.01 | 17.37 | 3.57 | 0.89 |
| SP-2310-M | 9.24 | 8.49 | 8.15 | 1.51 |
| SP-2330-M | 7.40 | 6.31 | 14.7 | 0.135 |
| OV-101 | 128.64 | 130.38 | 1.35 | 0.91 |
| OV-3 | 129.19 | 129.63 | 0.33 | 2.29 |
| OV-3-M | 116.58 | 117.38 | 0.68 | 0.66 |
| OV-7 | 119.83 | 119.37 | 0.38 | 1.07 |
| OV-7-MP | 94.89 | 96.42 | 1.61 | 1.33 |
| OV-11 | 97.51 | 97.71 | 0.20 | 1.83 |
| OV-11-MP(1) | 83.42 | 82.42 | 1.20 | 2.01 |
| OV-11-MP(2) | 76.97 | 74.68 | 2.97 | 0.01 |
| OV-17 | 83.60 | 85.70 | 2.51 | 1.14 |
| OV-17-M | 69.65 | 67.32 | 3.34 | 0.33 |
| OV-22 | 61.88 | 60.18 | 2.74 | 2.54 |
| OV-22-MP | 53.52 | 55.01 | 2.78 | 5.04 |
| OV-61 | 85.62 | 84.44 | 1.38 | 1.13 |
| OV-61-M | 76.88 | 76.65 | 0.29 | 0.21 |
| OV-25 | 49.36 | 47.03 | 4.72 | 1.05 |
| OV-275 | 1.39 | 1.34 | 3.38 | 0.72 |
| | | Mean: | 3.08 | 1.2 |

were calculated according to eqns. 1 and 3. Input data are given in Tables I, III and IV and results are given in Table V. The mean errors are now very similar, showing the equivalence of eqns. 1 and 3.

*Sensitivity test*

*Effect of errors in the slope value.* The effect of errors in the slope value was tested by introducing known errors in all slope values and recalculating the predicted specific retention volume of n-decane. Errors were evaluated with reference to the calculated value shown in Table V for each stationary phase, that is, the calculated value when no error is applied to the slope. Fig. 2 shows the effect of errors between + 5% and − 5% for three stationary phases of varying polarity. It can be observed that the effect of errors on the slope value is highest for the least polar column and is negligible for a highly polar stationary phase.

Fig. 3 shows the relationship between stationary phase polarity and the error in the calculated specific retention volume of n-decane for a given error in the slope value; in this instance all slopes have been incremented by 2%. Only two points are negative, and have been plotted in the form of an absolute value, and distinguished

TABLE III

THEORETICAL RETENTIONS RELATIVE TO n-DECANE

All retentions deduced from a least mean squares fit (see text).

| Stationary phase | Solute* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| OV-225 | 0.5135 | 0.7798 | 0.5107 | 2.0424 | 1.5188 | 0.8398 | 1.2162 | 0.9385 | 0.9434 | 1.8569 | 2.8806 |
| SP-2300 | 0.8508 | 1.3883 | 1.3606 | 3.8104 | 3.3672 | 1.3469 | 1.8700 | 1.2871 | 1.7960 | 1.1478 | 2.7445 |
| SP-2310 | 1.3837 | 2.6978 | 1.5871 | 7.4460 | 5.2840 | 2.2987 | 2.6008 | 1.5301 | 3.1952 | 2.7101 | 2.4959 |
| SP-2330 | 1.8933 | 3.9869 | 3.1522 | 11.2502 | 7.9962 | 3.1662 | 3.3540 | 1.7404 | 4.6150 | 3.0022 | 2.4268 |
| SP-2340 | 2.4227 | 5.1190 | 2.7528 | 13.7116 | 10.1470 | 3.5377 | 3.5377 | 1.8510 | 5.8698 | 2.9478 | 2.4900 |
| SP-2300-MP | 0.9852 | 1.8669 | 1.0508 | 4.9793 | 3.5727 | 1.6090 | 1.8761 | 1.1952 | 2.1553 | 2.1985 | 2.6937 |
| SP-2310-M | 1.7457 | 3.7643 | 2.0522 | 10.2076 | 7.1574 | 2.9400 | 2.9666 | 1.6246 | 4.2499 | 2.8362 | 2.4564 |
| SP-2330-M | 2.1360 | 4.5622 | 2.4483 | 12.4783 | 8.6481 | 3.4580 | 3.3707 | 1.7783 | 5.1407 | 3.0170 | 2.3461 |
| OV-101 | 0.1521 | 0.1453 | 0.1667 | 0.2074 | 0.2780 | 0.2196 | 0.3620 | 0.4714 | 0.1992 | 1.0350 | 3.1527 |
| OV-3 | 0.1633 | 0.1477 | 0.1785 | 0.2604 | 0.2896 | 0.2207 | 0.4200 | 0.5073 | 0.2143 | 1.1386 | 3.2556 |
| OV-3-M | 0.1664 | 0.1581 | 0.1908 | 0.2475 | 0.2974 | 0.2231 | 0.4033 | 0.4960 | 0.2244 | 1.1026 | 3.1562 |
| OV-7 | 0.1844 | 0.1667 | 0.2103 | 0.3305 | 0.3550 | 0.2440 | 0.4896 | 0.5614 | 0.2544 | 1.2538 | 3.2884 |
| OV-7-MP | 0.2089 | 0.1842 | 0.2263 | 0.3474 | 0.4391 | 0.2625 | 0.5037 | 0.5875 | 0.3011 | 1.2640 | 3.1363 |
| OV-11 | 0.2252 | 0.2061 | 0.2598 | 0.4433 | 0.4817 | 0.2806 | 0.6001 | 0.6560 | 0.3314 | 1.4365 | 3.2794 |
| OV-11-MP(1) | 0.2348 | 0.2070 | 0.2515 | 0.4092 | 0.5087 | 0.2804 | 0.5640 | 0.6361 | 0.3427 | 1.3703 | 3.1439 |
| OV-11-MP(2) | 0.2538 | 0.2214 | 0.2717 | 0.4534 | 0.5597 | 0.2926 | 0.6095 | 0.6753 | 0.3758 | 1.4393 | 3.1206 |
| OV-17 | 0.2613 | 0.2420 | 0.3081 | .5486 | 0.5957 | 0.3173 | 0.6942 | 0.7363 | 0.4020 | 1.5735 | 3.2458 |
| OV-17-M | 0.2746 | 0.2357 | 0.3007 | 0.5094 | .6073 | 0.3076 | 0.6537 | 0.7077 | 0.3992 | 1.5211 | 3.1067 |
| OV-22 | 0.3252 | 0.2867 | 0.3606 | 0.6734 | 0.7861 | 0.3585 | 0.8229 | 0.8420 | 0.5085 | 1.7839 | 3.1460 |
| OV-22-MP | 0.3430 | 0.2813 | 0.3671 | 0.6804 | 0.8064 | 0.3548 | 0.8296 | 0.8582 | 0.5334 | 1.8018 | 3.1028 |
| OV-61 | 0.2386 | 0.2099 | 0.2635 | 0.4476 | 0.4857 | 0.2842 | 0.6131 | 0.6652 | 0.3365 | 1.4946 | 3.2054 |
| OV-61-M | 0.2450 | 0.2125 | 0.2594 | 0.4380 | 0.5196 | 0.2825 | 0.5889 | 0.6524 | 0.3508 | 1.4072 | 3.1228 |
| OV-25 | 0.3874 | 0.3201 | 0.4097 | 0.7856 | 0.9296 | 0.3939 | 0.9296 | 0.9401 | 0.6035 | 1.9609 | 3.0721 |
| OV-275 | 5.1595 | 10.5953 | 7.1878 | 29.5457 | 24.1432 | 5.6059 | 5.9964 | 2.4231 | 13.3799 | 4.2169 | 2.8157 |

* Solutes 1–10 as in Table I; 11 = n-dodecane.

TABLE IV

SOLUTION OF EQN. 1 USING DATA FROM TABLE III

| | | | |
|---|---|---|---|
| $a_0$ = | 1.8379 | $a_6$ = | 0.74471 |
| $a_1$ = | −2.0956 | $a_7$ = | −3.9392 |
| $a_2$ = | −0.53845 | $a_8$ = | 3.4676 |
| $a_3$ = | 0.29384 | $a_9$ = | −0.10916 |
| $a_4$ = | 1.6887 | $a_{10}$ = | 0.52769 |
| $a_5$ = | −0.3611 | $a_{11}$ = | 0.28549 |

as black circles. Fig. 3 shows clearly that the absolute error of the predicted specific retention volume of *n*-decane increases with increasing value of the slope.

An examination of the slope values evaluated from individual chromatograms shows that the extreme values obtained, that is, the most erroneous values of the slope, differ by less than 2.5% from the average value when using highly polar stationary phases and by less than 1% when using non-polar stationary phasess. With

TABLE V

PREDICTION OF $V_{g_{n-decane}}$ USING THEORETICAL RELATIVE RETENTIONS AND RETENTION INDICES

| Stationary phase | $V_{g_{n-decane}}$ | | Eqn. 1 (theoretical relative retentions) | | | Eqn. 3 (retention indices) | | |
|---|---|---|---|---|---|---|---|---|
| | Exptl. | Theor. | $V_g$ (calc.) | Error (%) | | $V_g$ (calc.) | Error (%) | |
| | | | | Exptl. | Theor. | | Exptl. | Theor. |
| OV-225 | 40.66 | 40.50 | 42.15 | 3.7 | 4.1 | 42.27 | 3.9 | 4.4 |
| SP-2300 | 25.55 | 25.52 | 24.81 | 2.9 | 2.8 | 26.05 | 1.9 | 2.1 |
| SP-2310 | 12.92 | 12.93 | 12.63 | 2.2 | 2.3 | 12.42 | 3.9 | 3.9 |
| SP-2330 | 7.97 | 7.87 | 8.24 | 3.4 | 4.7 | 8.10 | 1.6 | 2.9 |
| SP-2340 | 5.59 | 5.59 | 5.61 | 0.4 | 0.4 | 5.60 | 0.2 | 0.2 |
| SP-2300-MP | 18.01 | 18.14 | 18.31 | 1.7 | 0.9 | 18.90 | 4.9 | 4.2 |
| SP-2310-M | 9.24 | 9.25 | 9.31 | 0.8 | 0.7 | 9.30 | 0.7 | 0.5 |
| SP-2330-M | 7.40 | 7.40 | 7.09 | 4.2 | 4.1 | 7.12 | 3.8 | 3.8 |
| OV-101 | 128.64 | 127.99 | 132.89 | 3.3 | 3.8 | 133.05 | 3.4 | 3.9 |
| OV-3 | 129.19 | 128.96 | 127.20 | 1.5 | 1.4 | 129.84 | 0.5 | 0.7 |
| OV-3-M | 116.58 | 116.49 | 115.90 | 0.6 | 0.5 | 115.97 | 0.5 | 0.4 |
| OV-7 | 119.83 | 119.36 | 116.79 | 2.5 | 2.2 | 116.83 | 2.5 | 2.1 |
| OV-7-MP | 94.89 | 94.52 | 94.52 | 0.4 | 0.0 | 94.55 | 0.4 | 0.03 |
| OV-11 | 97.51 | 97.30 | 95.58 | 2.0 | 1.8 | 95.57 | 2.0 | 1.8 |
| OV-11-MP(1) | 83.42 | 83.11 | 81.97 | 1.7 | 1.4 | 82.46 | 1.2 | 0.8 |
| OV-11-MP(2) | 76.97 | 76.60 | 74.40 | 3.3 | 2.9 | 73.12 | 5.0 | 4.5 |
| OV-17 | 83.60 | 83.46 | 84.65 | 1.3 | 1.4 | 84.60 | 1.2 | 1.4 |
| OV-17-M | 69.65 | 69.56 | 70.36 | 1.0 | 1.2 | 70.46 | 1.2 | 1.3 |
| OV-22 | 61.88 | 61.71 | 60.23 | 2.7 | 2.4 | 60.26 | 2.6 | 2.3 |
| OV-22-MP | 53.52 | 53.44 | 56.43 | 5.4 | 5.6 | 56.44 | 5.4 | 5.6 |
| OV-61 | 85.62 | 85.32 | 83.98 | 1.9 | 1.56 | 82.82 | 3.3 | 2.9 |
| OV-61-M | 76.88 | 76.76 | 77.43 | 0.7 | 0.9 | 75.75 | 1.5 | 1.3 |
| OV-25 | 49.36 | 49.40 | 49.60 | 0.5 | 0.5 | 49.78 | 0.9 | 0.8 |
| OV-275 | 1.39 | 1.41 | 1.41 | 1.4 | 0.09 | 1.37 | 1.4 | 2.9 |
| | | | Mean : | 2.06 | 1.98 | | 2.24 | 2.28 |

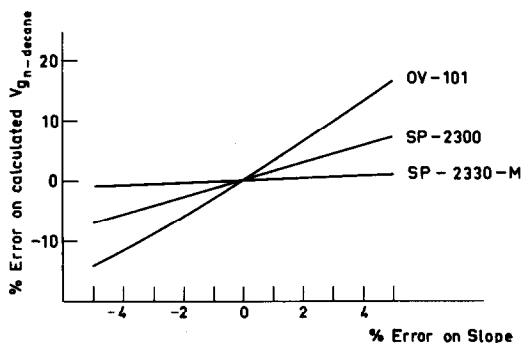Fig. 2. Effect of the slope error on the calculated specific retention volume of n-decane.

reference to Fig. 2, the highest errors found were 0.6% for OV-101, 1.37% for SP-2300 and 2.7% for SP-2330-M. These figures suggest errors below ca. 2% on the predicted specific retention volume of n-decane in all instances, and much lower errors if the slope value used is the average of a few determinations.

*Effect of errors in the values of the retention indices.* Specific retention volumes of n-decane were also calculated for all stationary phases using eqn. 3, assuming that all retention indices are erroneous. Four sets of determinations were performed, changing each retention index, as shown in Table I, by $+6$, $+3$, $-3$ or $-6$ units. Results corresponding to all stationary phases show that absolute error of the calculated specific retention volume of n-decane in all four instances is smaller than 0.13% when compared with the value shown in Table V. This kind of error (a general addition of a few retention index units) is normal when retention indices are calculated without the correction of a mathematically deduced dead time.
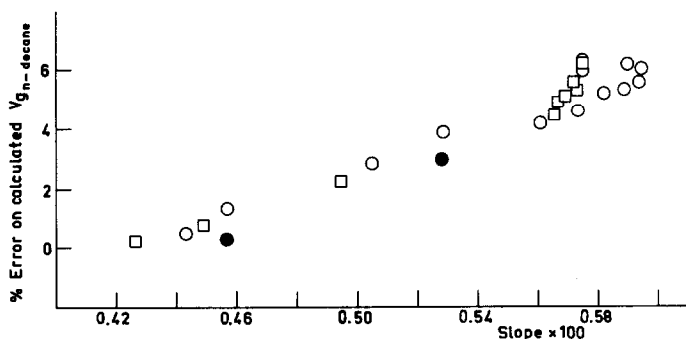


Fig. 3. Effect of a 2% error in the slope value on the specific retention volume of n-decane for different values of the slope. O, Denotes a single stationary phase; □, denotes a mixed stationary phase; ●, denotes a negative value, found for two single stationary phases. These have been plotted as positive values.

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