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Note

Rohrschneider constants: a correction in the method of calculation

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Rohrschneider constants[1] have become widely used in relating gas chromatographic retention behavior to the polarity of liquid phases[2–5]. The *Journal of Chromatographic Science*, in their "Guidelines for Publication of Retention Data"[6], includes Rohrschneider constants for the characterization of liquid phases.

Rohrschneider suggested that the retention behavior for a solute (i) on a liquid phase (j) could be approximated by

$$\Delta I_{i,j}(\text{calc.}) = a_i x_j + b_i y_j + c_i z_j + d_i u_j + e_i s_j \quad (1)$$

$\Delta I_{i,j}$ is the difference in Kováts indices between the phase of interest and squalane (*e.g.*, $\Delta I_{i,j} = I_{i,j} - I_{i,\,\text{squalane}}$). The terms x_j, y_j, z_j, u_j and s_j are calculated for each phase from the difference in Kováts indices of benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine, respectively (*e.g.*, $x_j = \Delta I_{\text{benzene},j}/100$). The terms a_i, b_i, c_i, d_i and e_i are empirical coefficients that can be calculated from retention data for each solute using various liquid phases. The five coefficients a, b, c, d and e required for the use of eqn. 1 could be calculated by using data from a minimum of five different liquid phases. However, in order to obtain a more widely applicable set of constants, Rohrschneider used 22 different liquid phases.

From the method of least squares, the best values of the coefficients for a given phase can be obtained by minimizing the sum of the squares of the differences (E_i) between the experimental and calculated values of ΔI:

$$E_i = \sum_j [\Delta I_{i,j}(\text{exp.}) - \Delta I_{i,j}(\text{calc.})]^2$$

$$E_i = \sum_j [\Delta I_{i,j}(\text{exp.}) - (a_i x_j + b_i y_j + c_i z_j + d_i u_j + e_i s_j)]^2 \quad (2)$$

A set of simultaneous equations for minimizing E is obtained by taking the partial derivatives of E with respect to each of the coefficients and setting each partial derivative equal to zero. The resulting five equations are:

$$\sum_j \Delta I_{i,j} x_j = a_i \sum_j x_j^2 + b_i \sum_j y_j x_j + c_i \sum_j z_j x_j + d_i \sum_j u_j x_j + e_i \sum_j s_j x_j \quad (3)$$

$$\sum_j \Delta I_{i,j} y_j = a_i \sum_j x_j y_j + b_i \sum_j y_j^2 + c_i \sum_j z_j y_j + d_i \sum_j u_j y_j + e_i \sum_j s_j y_j \quad (4)$$

TABLE I

CORRECTED ROHRSCHNEIDER CONSTANTS

Values in parentheses are taken from ref. 1.

No.	*Compound*	*a*	*b*	*c*	*d*	*e*	F_m*	$F_{max.}$**
1	Benzene	100.00						
2	Ethanol		100.00					
3	Methyl ethyl ketone			100.00				
4	Nitromethane				100.00			
5	Pyridine					100.00		
6	2,4-Dimethylpentane	−20.29 (−19.63)	0.39 (0.74)	12.33 (12.97)	− 1.15 (− 1.94)	0.75 (0.68)	3.2 (3.2)	9 (10)
7	2-Ethyl-1-hexene	20.19 (19.14)	− 0.34 (− 0.69)	5.48 (4.86)	− 2.22 (− 1.29)	0.01 (0.10)	1.9 (2.0)	4 (4)
8	Cyclohexane	32.11 (32.06)	−19.94 (−22.47)	−19.41 (−21.64)	2.40 (4.07)	27.53 (29.72)	5.8 (5.7)	13 (13)
9	Toluene	102.88 (108.33)	0.29 (3.77)	5.90 (8.75)	− 4.43 (− 7.01)	− 2.11 (− 7.61)	2.1 (2.6)	5 (5)
10	Styrene	120.33 (127.00)	− 2.90 (0.02)	−10.39 (− 8.08)	12.76 (10.67)	− 3.11 (− 8.94)	5.0 (5.3)	9 (11)
11	Phenylacetylene	116.89 (125.20)	1.51 (2.53)	−75.41 (−74.82)	58.84 (57.97)	5.90 (0.90)	5.8 (5.9)	11 (10)
12	Acetone	− 7.14 (− 5.30)	− 3.76 (− 4.61)	94.96 (94.94)	7.20 (7.90)	6.61 (5.64)	2.8 (3.1)	6 (7)
13	Propionaldehyde	10.34 (13.27)	− 3.08 (− 1.01)	72.28 (74.86)	6.97 (4.79)	4.09 (1.33)	2.8 (3.4)	5 (6)
14	2-Butenal	0.37 (− 7.86)	−12.11 (−17.59)	70.04 (65.75)	30.67 (37.49)	12.22 (17.21)	5.7 (6.2)	18 (18)
15	*n*-Butyl acetate	− 0.20 (− 3.77)	−11.10 (−13.31)	59.23 (57.29)	11.32 (13.88)	17.70 (19.98)	7.3 (7.5)	16 (15)
16	Acetonitrile	2.23 (2.86)	−14.37 (−16.38)	31.47 (30.09)	82.05 (84.10)	− 0.02 (0.03)	5.4 (5.3)	9 (9)
17	Nitroethane	− 1.73 (− 5.41)	− 7.57 (−11.07)	46.98 (43.66)	71.06 (75.66)	− 3.19 (− 1.28)	3.6 (4.6)	7 (9)
18	Dioxan	51.19 (45.86)	− 0.18 (− 2.89)	43.45 (40.20)	−11.51 (− 7.49)	36.92 (40.24)	5.1 (5.3)	11 (11)
19	*n*-Dibutyl ether	24.83 (17.34)	12.67 (9.77)	33.81 (29.73)	−18.28 (−12.48)	− 6.02 (− 2.79)	7.1 (7.3)	17 (15)
20	Thiophene	104.39 (105.69)	− 3.48 (− 4.19)	−30.05 (−31.53)	18.29 (20.10)	12.72 (11.22)	3.1 (3.4)	9 (10)
21	Chloroform	68.97 (69.71)	29.90 (28.91)	−70.35 (−72.62)	49.96 (53.05)	− 4.68 (− 6.29)	5.0 (5.1)	9 (9)
22	Carbon tetrachloride	70.15 (63.28)	−14.10 (−20.94)	−49.89 (−57.47)	20.30 (28.28)	27.07 (33.75)	6.3 (6.6)	16 (17)
23	Methyl iodide	76.66 (71.06)	− 9.76 (−14.95)	−37.64 (−42.57)	25.05 (31.77)	17.82 (21.58)	7.8 (8.0)	16 (16)
24	Ethyl bromide	46.59 (46.05)	− 6.40 (− 7.74)	0.32 (− 1.28)	16.31 (18.34)	9.04 (9.11)	4.5 (4.7)	9 (10)
25	$C_2F_2Cl_4$	14.18 (14.89)	−12.95 (−16.12)	−32.36 (−35.03)	27.10 (29.09)	30.96 (33.35)	9.5 (9.6)	20 (20)
26	*n*-Propanol	− 4.60 (− 9.42)	101.85 (105.26)	− 0.04 (0.25)	4.79 (6.63)	− 4.49 (− 7.49)	3.1 (3.9)	9 (9)
27	Isopropanol	−15.70 (−18.15)	92.10 (95.89)	14.10 (15.76)	− 6.41 (− 6.53)	5.47 (2.09)	5.2 (5.3)	9 (11)
28	Allyl alcohol	22.80 (18.11)	113.29 (116.45)	−21.71 (−21.27)	19.84 (22.06)	−19.68 (−23.35)	3.5 (4.3)	9 (8)
29	*tert.*-Butanol	−12.68 (−11.42)	72.20 (76.51)	30.40 (33.75)	−10.34 (−12.77)	4.83 (0.21)	11.0 (11.0)	23 (23)
30	Cyclopentanol	11.57 (2.08)	79.01 (77.84)	−15.79 (−20.48)	14.96 (21.69)	15.75 (17.75)	6.4 (7.1)	14 (17)

* Standard deviation.

** Maximum deviation.

$$\sum_j \Delta I_{i,j} z_j = a_i \sum_j x_j z_j + b_i \sum_j y_j z_j + c_i \sum_j z_j^2 + d_i \sum_j u_j z_j + e_i \sum_j s_j z_j \quad (5)$$

$$\sum_j \Delta I_{i,j} u_j = a_i \sum_j x_j u_j + b_i \sum_j y_j u_j + c_i \sum_j z_j u_j + d_i \sum_j u_j^2 + e_i \sum_j s_j u_j \quad (6)$$

$$\sum_j \Delta I_{i,j} s_j = a_i \sum_j x_j s_j + b_i \sum_j y_j s_j + c_i \sum_j z_j s_j + d_i \sum_j u_j s_j + e_i \sum_j s_j^2 \quad (7)$$

The best combination of the coefficients a_i, b_i, c_i, d_i and e_i according to the assumptions of least squares are obtained by solving eqns. 3–7 simultaneously.

However, rather than solving eqns. 3–7 directly, Rohrschneider introduced an additional special assumption[1]:

$$\sum_j [\Delta I_{i,j}(\text{exp.}) - (a_i x_j + b_i y_j + c_i z_j + d_i u_j + e_i s_j)] = 0 \quad (8)$$

Eqn. 8 can be combined with eqns. 3–7 to give a variety of values for the coefficients *a*, *b*, *c*, *d* and *e*. Hence the method of solution used by Rohrschneider is arbitrary and may lead to either good or poor results. In special cases this would have little or no effect. For example, if one of the coefficients *a*, *b*, *c*, *d* and *e* in eqn. 1 was not multiplied by a variable, eqn. 8 would be parallel to one of eqns. 3–7. Or, if a perfect data fit resulted, eqn. 8 would be a linear combination of eqns. 3–7. (It should be noted that Rohrschneider did not use this additional assumption in a later work[7].)

A direct simultaneous solution of eqns. 3–7 produces the results given in Table I. (Rohrschneider's values from ref. 1 are included for comparison.) In general, there are only minor errors in the constants reported by Rohrschneider; however, in some instances the errors are very significant. As would be expected, the errors are largest for compounds that are very similar to the compounds in the set of five standards.

The quantitative improvement in the method of calculation can be seen by comparing the standard deviation in the index differences of 25 solutes on Carbowax dioleate (Table V of ref. 1). Rohrschneider reported that the standard deviation for these data is 4.1 index units; using the corrected constants from Table I, the standard deviation is reduced to 2.9 index units. Similarly, using the data supplied by Rohrschneider (Table II of ref. 1), the standard deviation for the 550 index values is 5.9 while the standard deviation obtained by using the corrected values of *a*, *b*, *c*, *d* and *e* is 5.6.

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