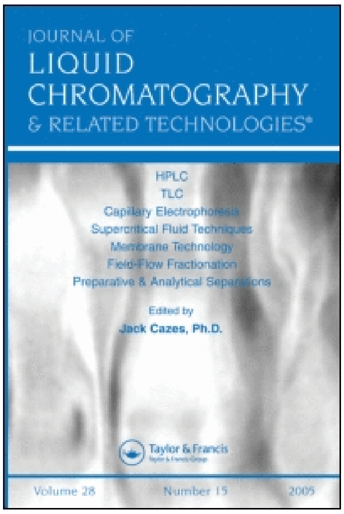

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Letter-On the Problem of Measuring t_0

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LETTER:

ON THE PROBLEM OF MEASURING t_o

Dear Sir,

We read with much interest the recent paper of Neidhart et.al. which appeared recently in this Journal (1). The problem of t_o, the so called "void time" or "inert time" is indeed a difficult one. Several reports have appeared recently discussing the measurement of t_o (e.g.2). The paper by Neidhart et.al.(1), however, raises some questions as to its validity. Take ,for example,the dead time determination using the Nucleosil 10-C_{18} column. From the given dimensions of the column - 25 cm length and 2.9 mm i.d- its empty volume is calculated to be 1.65 mL. Yet, the t_o calculated for that column was about 2.05 min.,which at a flow rate of 1 mL/min (as indicated by the authors), means a void volume of 2.05 mL. It is hard to imagine a column whose total porosity is greater than 1 ! Similar calculations for the other columns show that,while the void volume is less now than that of the unpacked columns, the porosities are much too high, e.g. 0.9. These findings require an explanation. Could it be that the dead volume of the system was very large ?

We tried to apply the approach of Neidhard et al. to the data of Vigh and Varga-Puchony (3). Table IV of reference 3 shows that ΔH values of n-hexanal-dinitrophenylhydrazone and 2-n-hexanone-dinitophenylhydrazone are almost the same - 4.17 kcal/mole vs-4.15 kcal/mole. For such a system, t_o should be obtainable via equation 6 of ref. 1. Since Vigh and Varga-Puchony did not report t_R values, we assumed t_o of 1 and have calculated "appearent t_R" values from the given capacity ratios. When these t_R values are used in conjunction with equation 6 of ref. 1,

t_o of 1 should result. However, the value obtained depends on the two temperatures chosen . For instance if T_1 is 20°C and T_2 60°C, then t_o is .786; if T_2 is 43.6°C, then t_o is 0.404, last, if T_1 is 43.6°C and T_2 60°C, then t_o is 1.101. The problem lies in the assumption used to arrive at equation 6 of ref. 1. If the ΔS values of the two solutes are very similar then, using the notation of ref. 1, we have:

$$t_{RA}\ (T_1) \approx t_{RB}\ (T_1)$$

and

$$t_{RA}\ (T_2) \approx t_{RB}\ (T_2)$$

In such a case equation 6 of ref. 1 demands very high precision of the measured t_R values, and its practicality diminishes. When the ΔH and ΔS values of the solutes are the same,the equation cannot be used. In that connection,it is not clear to us why the retention times in Fig.1 of ref. 1 are so different when the reported ΔH and k_o (a measure of ΔS) are so close in magnitude.

In summary, the method given in ref. 1 should be used, if at all, only after careful examination of the chromatographic parameters.

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REFERENCES

(1) B. NEIDHART, K.P. KRINGE and W. BROCKMAN, J. Liq. Chromatogr. 4, 1875-1886 (1981)

(2) M.J.M. WELLS and C.R. CLARK, Anal. Chem., 53, 1341-1345 (1981)

(3) GY VIGH and Z. VARGA-PUCHONY, J. Chromatogr. 196, 1-9 (1980)