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EVALUATION OF ERRORS IN THE DETERMINATION OF GAS CHROMATOGRAPHIC RETENTION PARAMETERS AND DERIVATIVE QUANTITIES*

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SUMMARY

The problem of the evaluation of errors in the determination of gas chromatographic retention parameters was discussed with reference to the types of errors that can be found practically, with reference to the type of quantities measured, to the retention parameters thereby obtained^{1,2} and finally to the type of derivative quantities (ΔH of evaporation)³.

The influence of random and systematic errors and the variation in the experimental conditions on the precision and accuracy of the net retention volume can be obtained by using the error transmission.

The determination of the specific retention volume also requires the correct determination of the quantities and types of phases that contribute to the retention, and the handling of correct expressions.

The precision and accuracy of the determination of ΔH obtained from the relation $\ln V_g = b/T_c + a$ (where T_c is the temperature of the column in °K) were discussed with reference to the presence of the following types of errors in the retention volume:

- (1) random errors;
- (2) systematic errors, constant in their relative values;
- (3) systematic errors, constant in their absolute values;
- (4) the retention volumes determined at different temperatures are affected by errors that depend stochastically on the time and on the temperature of operation of the gas chromatographic column;
- (5) the partition system is not homogeneous (many phases contribute to the retention).

In the first instance there is a no accurate value of ΔH , while ΔH is accurate in the second instance.

In the other instances the determination of ΔH is incorrect or not reliable from the physical point of view.

When there are only systematic errors, which are constant in their absolute values, it is then possible to apply the following expression:

$$\frac{d \ln (V_N + \Delta)}{dx} = b - \Delta b^2 \cdot \frac{dx}{d(V_N + \Delta)}$$

where $x = 1/T_c$ and $(V_N + \Delta)$ is the measured retention value, which is affected by a systematic constant error.

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We can obtain from such an expression, by successive approximation, the value of Δ and thence also of b and ΔH .

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