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CONTRIBUTION TO THE THEORY OF THE RETENTION INDEX SYSTEM

II. ERRORS ON THE DETERMINATION OF THE RETENTION INDICES:
THE ERDEY EQUATION

IN MEMORIAM PROF. L. ERDEY*

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SUMMARY

The increasing importance of the retention index system has stimulated the authors to investigate some of the problems in the field. On the basis of retention indices as defined by KOVÁTS and general methods of error calculation, the error of the determination of the retention indices under conditions of classical gas chromatography (T , F , p_i and j are all constants), and the effects of various factors on the error are discussed. An equation is presented for the calculation of the error. This equation was named after ERDEY. The results of the calculations support practical experience in many cases.

INTRODUCTION

The increasing importance of the retention index system has been pointed out in previous papers^{1,2}, as well as its role in qualitative analysis and other fields of chemistry. In the present paper one of the most important questions of the application of retention indices in qualitative analysis, namely the accuracy of the determination of retention indices, is discussed. Although this problem has already been successfully studied by several workers, no relationship has been deduced as yet to the calculation of the error of the index determination. Experience has shown that the error inherent in index determination first of all depends on the carbon number of the reference hydrocarbons. This, however, has not given any information on the size of errors. Realizing the importance of the calculation of error of index determinations and its dependence on various factors the authors have made extensive studies in this field.

* This is one of the last works of Prof. L. ERDEY of the Institute for General and Analytical Chemistry, as he died on February 21st, 1970. The equation giving the error of the determination of the retention indices (eqn. 9) has been named after ERDEY.

THEORY

In one of his recent papers KOVÁTS defined the retention index as follows³:

$$I_{\text{substance}}^{\text{stationary phase}}(T) = 100 \left[\frac{\log t_{R'}(x) - \log t_{R'}(z)}{\log t_{R'}(z+1) - \log t_{R'}(z)} + z \right] \quad (1)$$

where:

I = retention index under the conditions of classical gas chromatography
(T , F , p_i and j are all constants) (the index unit)

T = temperature of column (°K)

F = flow rate of carrier gas (ml/min)

p_i = inlet pressure of carrier gas (kp/cm²)

j = compressibility factor according to James-Martin

$t_{R'}$ = $t_R - t_M$ = reduced retention time (min)

t_R = retention time (min)

t_M = time of passage of the inert substance through the column (min)

x = symbol for the unknown substance

z and $z + 1$ = symbols for normal paraffins with carbon number z and $z + 1$, respectively

z = carbon number

As is familiar, the error of an equation describing a given process can be obtained by summing up the corresponding partial derivatives. The error of the determination of the index (E_I) can be given in a general form as follows:

$$\left[\left| \frac{\partial I}{\partial t_{R'}(x)} \right| \cdot \Delta t_{R'}(x) + \left| \frac{\partial I}{\partial t_{R'}(z)} \right| \cdot \Delta t_{R'}(z) + \left| \frac{\partial I}{\partial t_{R'}(z+1)} \right| \cdot \Delta t_{R'}(z+1) + \left| \frac{\partial I}{\partial t_M} \right| \cdot \Delta t_M \right] \cdot 100$$

where:

E_I = total error of the index determination (index unit) under the conditions of classical gas chromatography

$$\Delta t_{R'}(i) = \frac{|t_{R,1}(i) - \bar{t}_R(i)| + |t_{R,2}(i) - \bar{t}_R(i)| + \dots + |t_{R,s}(i) - \bar{t}_R(i)|}{n} \quad (3)$$

$$\bar{t}_R(i) = \frac{t_{R,1} + t_{R,2} + \dots + t_{R,s}}{n} \quad (4)$$

$\bar{t}_R(i)$ = average retention time (min)

i = symbol for x , z and $z + 1$

s = serial number

n = number of parallel measurements; in this case $n = 11$.

Forming the corresponding partial derivatives of eqn. (2) the following relationships were obtained:

$$\left| \frac{\partial I}{\partial t_{R'}(x)} \right| \cdot \Delta t_{R'}(x) = \left| \frac{1}{(t_{R'}(x) - t_M) \cdot \log \left(\frac{t_{R'}(z+1) - t_M}{t_{R'}(z) - t_M} \right) \cdot 2.30258} \right| \cdot \Delta t_{R'}(x) \quad (5)$$

$$\left| \frac{\partial I}{\partial t_{R'}(z)} \right| \cdot \Delta t_{R'}(z) = \left| \frac{\log \left(\frac{t_{R'}(z+1) - t_M}{t_{R'}(x) - t_M} \right)}{(t_M - t_{R'}(z)) \cdot \log^2 \left(\frac{t_{R'}(z+1) - t_M}{t_{R'}(z) - t_M} \right) \cdot 2.30258} \right| \cdot \Delta t_{R'}(z) \quad (6)$$

$$\left| \frac{\partial I}{\partial \bar{t}_R(z+1)} \right| \cdot \Delta t_R(z+1) = \left| \frac{\log \left(\frac{\bar{t}_R(x) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right)}{(\bar{t}_M - \bar{t}_R(z+1)) \log^2 \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) \cdot 2.30258} \right| \cdot \Delta t_R(z+1) \quad (7)$$

$$\left| \Delta t_M = \frac{\left(\frac{\bar{t}_R(x) - \bar{t}_R(z)}{(\bar{t}_R(x) - \bar{t}_M) \cdot (\bar{t}_R(z) - \bar{t}_M)} \right) \cdot \log \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) - \frac{\bar{t}_R(z+1) - \bar{t}_R(z)}{(\bar{t}_R(z) - \bar{t}_M) \cdot (\bar{t}_R(z+1) - \bar{t}_M)} \cdot \log \frac{\bar{t}_R(x) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M}}{\log^2 \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) \cdot 2.30258} \right| \cdot \Delta t_M \quad (8)$$

Eqns. 5-8 not only permit the exact calculation of the error of the index determination but also the study of the effect of various factors on the error.

Then, substituting the terms from eqns. 5-8 into eqn. 2:

$$\left\{ \left| \frac{1}{(\bar{t}_R(x) - \bar{t}_M) \cdot \log \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) \cdot 2.30258} \right| \cdot \Delta t_R(x) + \left| \frac{\log \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(x) - \bar{t}_M} \right)}{(\bar{t}_M - \bar{t}_R(z)) \cdot \log^2 \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) \cdot 2.30258} \right| \cdot \Delta t_R(z) + \left| \frac{\log \left(\frac{\bar{t}_R(x) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right)}{(\bar{t}_M - \bar{t}_R(z+1)) \log^2 \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) \cdot 2.30258} \right| \cdot \Delta t_R(z+1) + \left. \left| \frac{\left(\frac{\bar{t}_R(x) - \bar{t}_R(z)}{(\bar{t}_R(x) - \bar{t}_M) \cdot (\bar{t}_R(z) - \bar{t}_M)} \right) \cdot \log \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) - \frac{\bar{t}_R(z+1) - \bar{t}_R(z)}{(\bar{t}_R(z) - \bar{t}_M) \cdot (\bar{t}_R(z+1) - \bar{t}_M)} \cdot \log \left(\frac{\bar{t}_R(x) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right)}{\log^2 \left(\frac{\bar{t}_R(z+1) - \bar{t}_M}{\bar{t}_R(z) - \bar{t}_M} \right) \cdot 2.30258} \right| \cdot \Delta t_M \right\} \cdot 100 \quad (9)$$

This equation giving the error of the determination of the retention indices (eqn. 9) was named after ERDEY.

EXPERIMENTAL

Extensive experimental studies were made, by means of Carlo Erba Fractovap Model C, D, GD, GV and GI-452 gas chromatographs. As an example, calculations made with data obtained under the conditions given in Table I will be presented.

Experiments were repeated under the same conditions by a moderately skilled technician, to estimate the standard deviation. The number of replicate measurements was reduced to 5, since in practice this is more usual than the eleven used in the course of our investigations. The analysis of the errors of the determinations of the index and comparison of the results have shown that the skill of the gas chromatograph operator and the number of measurements only influences the value of $\Delta t(i)$, sometimes quite remarkably, but the reproducibility of the retention

TABLE I

GAS CHROMATOGRAPHIC PARAMETERS USED IN DETERMINING THE DATA FOR CALCULATION

Gas chromatograph: Carlo Erba Fractovap Model D
 Detector: FID
 Sensitivity: 16×100
 Sample introduction: 1.0 μ l gas by means of a Hamilton syringe, and 1.5 ml gas by semi-automatic introduction, respectively
 Column: aluminium spiral 3.0 m length and 2.0 mm I.D.
 Packing: 10.0 wt% squalane on Chromosorb W (60-80 mesh)
 Carrier gas: nitrogen
 Inlet pressure of carrier gas: 1.86 kp/cm²
 Auxiliary gases: hydrogen, inlet pressure: 1.27 kp/cm²; oxygen, inlet pressure: 1.74 kp/cm²
 Temperature of column: $70.0 \pm 0.1^\circ$
 Temperature of evaporator: $210.0 \pm 1.0^\circ$
 Recorder: Speedomax G; 2.5 mV; 1.0 sec
 Chart speed: 5.08 cm/min

times, *i.e.* stability of the operation of the gas chromatograph, is the most important factor in determining the error.

From practical considerations, three model compounds were chosen: ethene, which produced a peak between those of methane and ethane; cyclobutane, eluted between *n*-C₄ and *n*-C₅; and styrene, the gas chromatographic peak of which appeared between those of *n*-C₈ and *n*-C₉.

The time to pass through the chromatograph was calculated by mathematical

TABLE II

RETENTION DATA DETERMINED UNDER CONDITIONS GIVEN IN TABLE I AND USED FOR THE ERROR CALCULATIONS

Component	Average retention time (sec)	Value of $\Delta t_R(i)$ (sec)
Methane	28.3	0.26
Ethene	29.1	0.26
Ethane	29.9	0.28
<i>n</i> -Butane	43.0	0.45
Cyclobutane	53.0	0.55
<i>n</i> -Pentane	67.8	0.68
<i>n</i> -Octane	637.8	3.20
Styrene	1070.0	5.40
<i>n</i> -Nonane	1520.7	7.60
t_M	26.4	0.25

means on the basis of data published earlier⁴. Retention data used for the calculations are summarized in Table II.

As an example, the calculations concerning styrene will be presented here. The fraction of error of the determination of the retention index due to the error of the determination of t_M can be calculated by means of eqn. 8:

$$\left| \frac{\partial I}{\partial t_M} \right| \cdot \Delta t_M = \left| \frac{\frac{1070.0 - 637.8}{(1070.0 - 26.4) \cdot (637.8 - 26.4)} \log \left(\frac{1520.7 - 26.4}{637.8 - 26.4} \right) - \frac{1520.7 - 637.8}{(637.8 - 26.4) \cdot (1520.7 - 26.4)} \cdot \log \left(\frac{1070.0 - 26.4}{637.8 - 26.4} \right)}{\log^2 \left(\frac{1520.7 - 26.4}{637.8 - 26.4} \right) \cdot 2.30258} \right| \cdot 0.25 =$$

$$\left| \frac{\frac{432.2}{1043.6 \cdot 611.4} \cdot 0.38811 - \frac{882.9}{611.4 \cdot 1494.3} \cdot 0.23198}{0.15063 \cdot 2.30258} \right| \cdot 0.25 = \left| \frac{0.00387 \cdot 0.25}{0.3469} \right| = 0.00003 \text{ index units} \quad (10)$$

The fraction of error due to the error in the determination of the retention time of the hydrocarbon preceding the component in question can be calculated by means of eqn. 6:

$$\left| \frac{\partial I}{\partial t_R(z)} \right| \cdot \Delta t_R(z) = \left| \frac{\log \left(\frac{1520.7 - 26.4}{1070.0 - 26.4} \right)}{(26.4 - 637.8) \cdot \log^2 \left(\frac{1520.7 - 26.4}{637.8 - 26.4} \right) \cdot 2.30258} \right| \cdot 3.2 = \left| \frac{\log \left(\frac{1494.3}{1043.6} \right)}{(-611.4) \cdot \log^2(2.44406) \cdot 2.30258} \right| \cdot 3.2 =$$

$$= \left| \frac{0.15588 \cdot 3.2}{(-611.4) \cdot 0.3469} \right| = \left| \frac{0.4988}{212.09} \right| = 0.24 \cdot 10^{-2} \text{ index units} \quad (11)$$

The fraction of error due to the error of the determination of the retention data of the hydrocarbon, in this case *n*-nonane, following the component in question can be calculated according to eqn. 7:

$$\left| \frac{\partial I}{\partial t_R(z+1)} \right| \cdot \Delta t_R(z+1) = \left| \frac{\log \left(\frac{1070.0 - 26.4}{637.8 - 26.4} \right)}{(26.4 - 1520.7) \cdot \log^2 \left(\frac{1520.7 - 26.4}{637.8 - 26.4} \right) \cdot 2.30258} \right| \cdot 7.6 =$$

$$= \left| \frac{\log \frac{1043.6}{611.4}}{(-1494.3) \cdot \log^2(2.44406) \cdot 2.30258} \right| \cdot 7.6 = \left| \frac{0.23198 \cdot 7.6}{(-518.37)} \right| = 0.34 \cdot 10^{-2} \text{ index units} \quad (12)$$

Finally, the error contribution due to the inaccuracy of the determination of the retention time of the component in question is as follows, according to eqn. 5:

$$\left| \frac{\partial I}{\partial t_R(x)} \right| \cdot \Delta t_R(x) = \left| \frac{1}{(1070.0 - 26.4) \cdot \log \left(\frac{1520.7 - 26.4}{637.8 - 26.4} \right) \cdot 2.30258} \right| \cdot 5.4 =$$

$$= \left| \frac{5.4}{1043.6 \cdot 0.38811 \cdot 2.30258} \right| = \left| \frac{5.4}{932.79} \right| = 0.58 \cdot 10^{-2} \text{ index units} \quad (13)$$

The total error is the sum of the error contributions:

$$E_I \begin{matrix} \text{squalane} \\ \text{styrene} \end{matrix} (70.0^\circ\text{C}) = 0.24 + 0.34 + 0.58 + 0.00 = 1.2 \text{ index units}$$

TABLE III

CONTRIBUTIONS TO THE ERROR OBTAINED UNDER THE CONDITIONS GIVEN IN TABLE I

Component	Error (index unit) caused by				Total error (index units)
	$t_R(x)$	$t_R(z)$	$t_R(z+1)$	t_M	
Ethene	15.8	9.5	7.5	0.7	33.5
Cyclobutane	2.3	1.4	0.9	0.1	4.7
Styrene	0.6	0.2	0.3	0.0	1.1

The partial errors of the determination of the indices are summarized for the model compounds studied in Table III.

DISCUSSION

The deviation of the average retention index, calculated from a number of replicate measurements, from the correct index value does not give information about the reproducibility and accuracy of the index determination, since relatively high positive and negative deviations of single index values from the correct one may compensate each other. For this reason the error was studied on the basis of partial derivatives.

In this way our earlier experience could be supported by experimental results and conclusions drawn from them. The practical fact that the error of the determination of retention indices of substances with retention times similar to t_M is in most cases high is already known, as is also the fact that the error due to the inaccuracy of t_M determinations is practically equal to zero for components appearing in the chromatogram later; this could be proved by the calculations.

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