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EVALUATION OF ERRORS IN GAS CHROMATOGRAPHY*

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SUMMARY

An analysis of errors has been performed for the determination of gas chromatographic retention parameters, with emphasis on the specific retention volume.

The quantities directly measured (gas flow rate, inlet and outlet column pressure, retention time, weight of liquid phase in column) were examined, several sources of error are discussed and useful equations for the evaluation of error of the final derivative quantity (retention volume) were obtained.

Tables and graphs for an easy error evaluation are reported.

Possible correlations among different errors have been discussed from a qualitative point of view.

The problem of the column stability is also outlined.

Such consideration may become useful for the critical examination of experimental errors, for evaluation of the reliability of published data and for good design of gas chromatographic measurements.

INTRODUCTION

Retention parameters describe the behaviour of a certain partition system. They are quite often obtained from the observation of a large number of experimental quantities, and in this respect they are considered to be derivative quantities.

Evaluation of the errors of retention parameters from the errors of quantities measured directly can be useful in the solution of many problems, such as:

(1) Critical examination of experimental errors and estimation of errors in the final derivative quantity¹⁻³.

(2) Evaluation of the reliability of many data, which are published without any specific reference to their precision and accuracy, and with only the type of measurement being used.

(3) Design of experiments aimed at determining retention parameters with a defined degree of reliability^{3,4}.

There are essentially three ways of expressing the retention of a compound on

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TABLE I

GC RETENTION PARAMETERS

The symbols used in this table are defined in Ref. 5.

Parameter	Equation	Equation number	Condition
Relative retention	$r_{i,s} = \frac{t'_{Ri}}{t'_{Rs}} = \frac{t_{Ri} - t_M}{t_{Rs} - t_M}$	1	Column and flow rate stability
Relative retention	$r_{i,s} = \frac{V_{Ni}}{V_{Ns}}$	2	Column stability
Retention index	$I_x = 100 \left[z + \frac{\log r_{x,z}}{\log r_{(z+1),z}} \right]$	3	Column and flow rate stability
Retention index	$I_x = 100 \left[z + \frac{\log V_{Nx} - \log V_{Nz}}{\log V_{N(z+1)} - \log V_{Nz}} \right]$	4	Column stability
Specific retention volume	$V_g = \frac{V_N (273.16)}{w_L T}$	5	

gas chromatographic (GC) columns, which differ from each other in the number and type of primary quantities being measured, in the functional form and in the restrictions to which they are subjected. In Table I are the different expressions with particular reference to gas-liquid chromatography (GLC).

For use of eqns. 1-4, it is necessary that some experimental conditions are kept constant², while for eqn. 5 it is necessary for these specific conditions to be controlled quantitatively.

Our investigation will be limited to this last expression and the conclusions can be considered adequate for the other cases also.

Before starting the discussion of errors concerning the single quantities directly measured and their combination, it will be useful to consider eqn. 5 from both practical and theoretical aspects, as a ratio between two quantities:

$$V_g = Y/w_L \quad (6)$$

and, comparing eqn. 6 with eqn. 5 of Table I,

$$Y = V_N(273.16/T) \quad (7)$$

From an experimental point of view, Y is the result of the gas chromatographic measurement of retention, performed on a particular column, whilst from the thermodynamic point of view, it is an extensive quantity derived from the product of an equilibrium constant (partition constant) by the amount of the stationary phase in which the partition takes place (or better, in the most general case of n partition systems, it is the sum of n products of this type).

On the contrary, the complete definition of w_L implies parameters other than the chromatographic ones and requires physico-chemical assumptions (for instance, the GLC retention is only of the bulk type in the liquid phase).

The great interest about the possibility of describing a partition system through V_g is a direct consequence of the fact that it is an intensive quantity, directly connected to thermodynamic quantities⁶. The possibility of determining V_g requires therefore the definition of w_L and the precision and accuracy of Y . We shall deal first with Y , which is a complex function of a large number of experimental quantities.

When the flow rate is measured with a soap-bubble flowmeter and the retention time with a stopwatch, we obtain an equation such as:

$$Y = (t_R - t_M)F_1(1 - p_w/p_0) \frac{3}{2} \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \frac{273.16}{T} \quad (8)$$

Putting:

$$X_1 = 273.16/T \quad (9a)$$

$$X_2 = 1 - p_w/p_0 \quad (9b)$$

$$X_3 = F_1 \quad (9c)$$

$$X_4 = \frac{3}{2} \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \quad (9d)$$

$$X_5 = t_R - t_M \quad (9e)$$

eqn. 8 becomes

$$Y = X_1 X_2 X_3 X_4 X_5 \quad (10)$$

Eqn. 10 can be easily handled from the standpoint of the transmission of errors.

PROPAGATION OF ERRORS: Y AND X_i QUANTITIES

Random errors

By "random error" we mean the effect of a sequence of errors over which we have no control (*e.g.* interpolation in reading scales, fluctuation of experimental condition, *etc.*).

It is possible to prove that the relative error, or coefficient of variation, of the quantity Y is given by the following equation⁷:

$$C^2\{Y\} \simeq \sum_{i=1}^5 C^2\{X_i\} + 2 \sum_{i=1}^4 \sum_{j=i+1}^5 \rho_{ij} C\{X_i\} C\{X_j\} \quad (11)$$

When all the $\rho_{ij} = 0$, that is when all the errors on the quantities X_1, X_2, \dots, X_5 are stochastically independent or non-correlated, eqn. 11 becomes:

$$C^2\{Y\} \simeq \sum_{i=1}^5 C^2\{X_i\} \quad (12)$$

Random errors in X_i and X_j are said to be correlated when the deviations from the average of the single values of X_i that were measured are related to similar ones of X_j . This happens when there is a functional dependence. Another example of correlation occurs when X_i and X_j are derived from the measurement of two dimensionally equal quantities and we make use of the same standard⁸.

In the most general case, two intercorrelated quantities X_i and X_j have global errors σ_i and σ_j composed of two parts, one of which is stochastically independent (σ_{Ei} , σ_{Ej}) while the other is correlated (σ_{Xi} , σ_{Xj}). The relations between these types of errors are:

$$\sigma_i^2 = \sigma_{Ei}^2 + \sigma_{Xi}^2 \quad (13a)$$

$$\sigma_j^2 = \sigma_{Ej}^2 + \sigma_{Xj}^2 \quad (13b)$$

In this case, the correlation between the two errors (σ_i and σ_j) is small and the correlation coefficient ρ_{ij} is lower than the value ρ'_{ij} which would occur in the absence of the stochastically independent errors. The relation between ρ_{ij} and ρ'_{ij} is⁹:

$$\rho_{ij} = \frac{\rho'_{ij}}{\sqrt{\left[1 + \left(\frac{\sigma_{Ei}}{\sigma_{Xi}}\right)^2\right] \left[1 + \left(\frac{\sigma_{Ej}}{\sigma_{Xj}}\right)^2\right]}} \quad (14)$$

Therefore, for an exact evaluation of the random errors, we must consider: (1) the values $C\{X_i\}$; (2) the correlation between X_i and X_j ; and (3) the weight of the stochastically independent errors as regards the correlated errors, that is the size of the correlation coefficient.

Systematic errors

We call "systematic error" the discrepancy between the average value of the measure and the true value of the quantity.

When we know the size and the sign of this difference, it is convenient to use the following type of propagation:

$$\frac{\Delta Y}{Y} = \sum \frac{\Delta X_i}{X_i} \quad (15a)$$

If we know only the size, we can choose between the two following equations:

$$\frac{\Delta Y}{Y} = \sum \left| \frac{\Delta X_i}{X_i} \right| \quad (15b)$$

$$\left(\frac{\Delta Y}{Y}\right)^2 = \sum \left(\frac{\Delta X_i}{X_i}\right)^2 \quad (15c)$$

The choice of these equations cannot be arbitrary and when the final results are reported it is preferable to specify the type of transmission that has been used^{10,11}.

INDIVIDUAL X_i QUANTITIES

$$X_1 = 273.16/T$$

This represents the reduction of the flow rate to 0°C.

Random errors

$$C^2\{X_1\} \simeq (\sigma_{ET}/T)^2 + (\sigma_T/T)^2 \quad (16a)$$

σ_{ET} is the random error in the reading of temperature scale. An estimate of

this error can be achieved by letting, for example, the lowest scale division be equal to $\pm 3 \sigma_{ET}$ (range)¹². For instance, a thermometer graduated to 1°C gives $\sigma_{ET} = \pm 0.167^\circ\text{C}$; for $T = 298^\circ\text{K}$, $(\sigma_{ET}/T) = \pm 0.6\%$.

σ_T is the random error due to the temperature fluctuations of the bath of the flowmeter. The estimate of this error is obtained by determining a number of values of T and by separating (by variance analysis methods) the contribution to the error given by reading the scale, from the one given by the intrinsic fluctuation of the quantity.

Systematic errors

$$\Delta X_1/X_1 = - \Delta T/T \quad (16b)$$

$$\Delta X_1 = - (273.16/T^2) \Delta T \quad (16c)$$

Systematic errors in the determination of T can be attributed to many different sources. The use, for instance, of thermostatic flowmeters with poor heat transfer properties, may cause errors in determining the temperature of the flowing gas.

$$X_2 = (1 - p_w/p_0)$$

This gives the correction for the flow rate that has been read for the vapour pressure of the soap solution contained in the flowmeter.

Random errors

$$C^2\{X_2\} \simeq (1/X_2^2 p_0^4) (p_w^2 \sigma_{p_0}^2 + p_0^2 \sigma_{p_w}^2 - 2p_w p_0 \rho_{p_w, p_0} \sigma_{p_w} \sigma_{p_0}) \quad (17a)$$

$$C^2\{X_2\} \simeq [\sigma_{p_w}/(p_0 - p_w)]^2 + [\sigma_{p_0} p_w/p_0(p_0 - p_w)]^2 \quad (17b)$$

Eqn. 17b is a particular case of eqn. 17a, and holds only when there is no correlation between p_0 and p_w ($\rho_{p_w, p_0} = 0$).

$\sigma_{p_w}/(p_0 - p_w) = (dX_2/X_2)_{p_0}$ is the relative error in X_2 for an error in p_w . Since generally $(p_0 - p_w) = 730$ mm Hg, this error is small. A source of random error can be attributed to the fluctuation of the bath temperature. For example, $\sigma_T = \pm 1^\circ\text{C}$ gives $\sigma_{p_w} = \pm 1.4$ mm Hg and $(dX_2/X_2)_{p_0} = \pm 2\%$.

$\sigma_{p_0} p_w/(p_0 - p_w) p_0 = (dX_2/X_2)_{p_w}$ is the relative error in X_2 for an error in p_0 . Usually under normal conditions, this error is smaller than the previous one. For example, $\sigma_{p_0} = \pm 10$ mm Hg, $(dX_2/X_2)_{p_w} = \pm 0.4\%$.

Systematic errors

$$\Delta X_2/X_2 = p_w \Delta p_0/p_0(p_0 - p_w) - \Delta p_w/(p_0 - p_w) \quad (17c)$$

$$\Delta X_2 = (p_w/p_0^2) \Delta p_0 - (1/p_0) \Delta p_w \quad (17d)$$

$p_w \Delta p_0/p_0(p_0 - p_w)$ and $(p_w/p_0^2) \Delta p_0$ represent the contributions to the relative and absolute errors, respectively, for a systematic error in p_0 . Regarding the size of the relative error, the same applies as for a random contribution for the variation of p_0 and the sign is positive. The absolute error for $\Delta p_0 = + 10$ mm Hg is $+ 4.3 \cdot 10^{-3}$.

$-\Delta p_w/(p_0 - p_w)$ and $-(1/p_0)\Delta p_w$ are the relative and absolute errors for a systematic variation of p_w . The same applies as for about random errors and the sign is negative. A source of this type of error can be an incorrect estimate of the vapour pressure of the soap solution ($\Delta p_w \simeq 1-2$ mm Hg).

$$X_3 = F_1 = V/t = OL/t = Ov_{\text{bubble}}$$

This represents the measured carrier gas flow rate at the flowmeter.

Random errors

$$C^2\{X_3\} \simeq (\sigma_{EV}/V)^2 + 2(\sigma_{EL}/L)^2 + 2(\sigma_{Et}/t)^2 + (2\sigma_r/r)^2 + (\sigma_{X_3}/X_3)^2 \quad (18a)$$

The correlation has been neglected.

(σ_{EV}/V) represents the relative error in determining the flowmeter volume at calibration. If more determinations have been made, it will be possible to calculate σ_{EV} .

$\sqrt{2}(\sigma_{EL}/L)$ is the error in determining the two positions of the bubble. The error for a single operation (σ_{EL}) can be assumed to be equal to the apparent thickness of the bubble ($\simeq 0.5$ mm). For a flowmeter of 40 cm, $\sqrt{2}(\sigma_{EL}/L) = 1.8\%$. This error is independent of the flow rate.

$\sqrt{2}(\sigma_{Et}/t)$ is the error for the two timing operations. It can be shown that $\sqrt{2}(\sigma_{Et}/t) = \sqrt{2}(X_3/V)\sigma_{Et}$. For instance, for a flow rate of 1 cm³/sec, read on a flowmeter of volume $V = 40$ cm³, with an error for a single timing operation of about ± 0.2 sec, $\sqrt{2}(\sigma_{Et}/t) = 7\%$.

$(2\sigma_r/r)$ represents fluctuations in the flowmeter volume due to the variation of the internal radius (r) (*i.e.* variations in the thickness of the stationary liquid film on the walls of the flowmeter). It can be assumed that the size of these fluctuations is about the same or lower than the dispersion observed during the calibration.

(σ_{X_3}/X_3) represents intrinsic fluctuations of the carrier gas flow rate (F_0). Because of the different nature of the error sources now discussed, a correlation between them is considered to be unlikely. For this reason we have not taken the correlation terms into consideration in eqn. 18a.

Systematic errors

$$\Delta X_3/X_3 = \Delta V/V - \Delta t/t \quad (18b)$$

$$\Delta X_3 = \Delta V/t - (V/t^2)\Delta t \quad (18c)$$

Systematic errors can be attributed to incorrect calibration of either the stopwatch or the flowmeter. The calibration of the flowmeter must be particularly accurate in order to be able to measure the effective volume occupied by the gas flowing in the flowmeter.

Correlations among the quantities X_1 , X_2 , X_3

X_1 , X_2 . A good degree of correlation is possible between these two quantities: a change in the temperature of flowmeter is responsible for a variation in the vapour pressure of the soap solution and in this case the coefficient of correlation is positive. It is not possible to give a numerical value to the correlation coefficient.

X_2 , X_3 . The product of these two quantities represents the flow rate of the gas emerging from the gas chromatographic column (F_0). When this quantity remains constant, an intrinsic variation of X_2 (an increase, for instance) will cause an intrinsic variation of X_3 (a decrease) so that the new product will be the same as the previous one. This involves a negative coefficient of correlation.

X_1 , X_3 . Even here, the product of these two quantities can be considered to be constant (flow rate at given temperature). For the same reason as outlined earlier, the correlation coefficient is negative.

Note on the quantity X_2

Generally the quantity X_2 is not measured directly; it is calculated considering the temperature and the type of soap solution we work with. The most important aspect connected with X_2 is the one concerning the systematic error (accuracy). The intrinsic fluctuations of X_2 appear as intrinsic fluctuations of X_3 , because:

$$X_3 = F_0/X_2 \quad (19)$$

$$X_4 = \frac{3(p_i/p_0)^2 - 1}{2(p_i/p_0)^3 - 1} = \frac{3A^2 - 1}{2A^3 - 1}$$

This equation is Martin's factor when we deal with an ideal carrier gas.

Random errors

$$C^2\{X_4\} \simeq [2A^2/(A^2 - 1) - 3A^3/(A^3 - 1)]^2 [(\Delta p \sigma_{p_0}/A p_0)^2 + (\sigma_{\Delta p}/A)^2 - 2\sigma_{p_0, \Delta p} \sigma_{\Delta p} \sigma_{p_0} \Delta p / A^2 p_0] \quad (20a)$$

$(dX_4/X_4)_{\Delta p} = [2A^2/(A^2 - 1) - 3A^3/(A^3 - 1)](\Delta p \sigma_{p_0}/A p_0)$ represents the con-

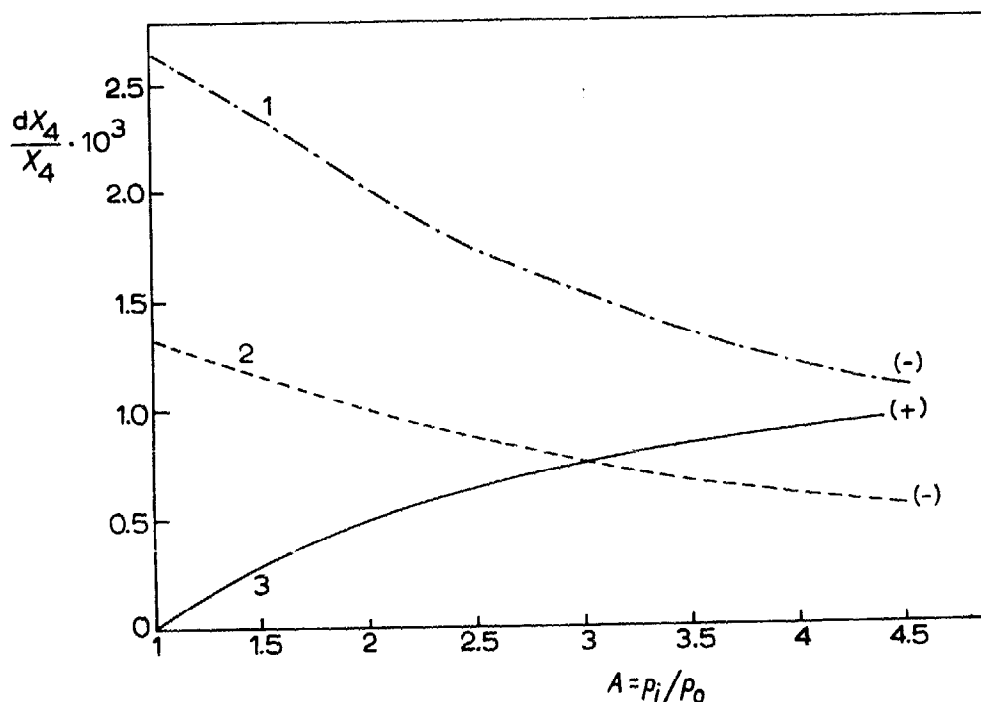


Fig. 1. Relative errors in X_4 vs. $A = p_i/p_0$, for outlet pressures around 760 mm Hg. 1 = $(dX_4/X_4)_{p_0}$, for $\sigma_{\Delta p} = \pm 4$ mm Hg; 2 = $(dX_4/X_4)_{p_0}$, for $\sigma_{\Delta p} = \pm 2$ mm Hg; 3 = $(dX_4/X_4)_{\Delta p}$, for $\sigma_{p_0} = \pm 1$ mm Hg.

tribution to the relative error due to an error in p_0 . Fig. 1 gives the values of $(dX_4/X_4)_{\Delta p}$ for outlet pressures around 760 mm Hg, when $\sigma_{p_0} = \pm 1$ mm Hg.

$(dX_4/X_4)_{p_0} = [2A^2/(A^2 - 1) - 3A^3/(A^3 - 1)](\sigma_{\Delta p}/A)$. The values of this error, for $\sigma_{\Delta p} = \pm 4$ mm Hg and $\sigma_{\Delta p} = \pm 2$ mm Hg, are also given in Fig. 1.

$2 \rho_{p_0, \Delta p} \sigma_{p_0} \sigma_{\Delta p} (\Delta p / A^2 p_0)$ indicates the correlation between p_0 and Δp . Sometimes it is effectively possible for fluctuations in the value of p_0 to be correlated with fluctuations in the value of Δp , due to the fact that very often the control system of the inlet pressure depends on the external pressure.

Systematic errors

The same equations we have outlined for the random errors apply to the systematic relative errors. The sign of $(\Delta X_4/X_4)_{\Delta p}$ is positive, while the one for $(\Delta X_4/X_4)_{p_0}$ is negative (see Fig. 1). Since the errors have opposite signs, there is a possibility that sometimes they will cancel each other out. It is possible to show that this happens when:

$$\Delta(p_0)/p_0 = \Delta(\Delta p)/\Delta p \quad (20b)$$

that is, when the systematic relative errors are the same.

$$X_5 = t_R - t_M$$

This represents the adjusted retention time.

Random errors

$$C^2\{X_5\} \simeq (\sigma_{t_R}/X_5)^2 + (\sigma_{t_M}/X_5)^2 + (\sigma_{X_5}/X_5)^2 + 2(\sigma_{Et}/X_5)^2 \quad (21a)$$

$\sqrt{2} \sigma_{Et}/X_5$ represents the timing error of the measurement. Fig. 2 gives the values of these errors *vs.* X_5 in both the cases when $\sigma_{Et} = \pm 0.2$ and ± 0.1 sec.

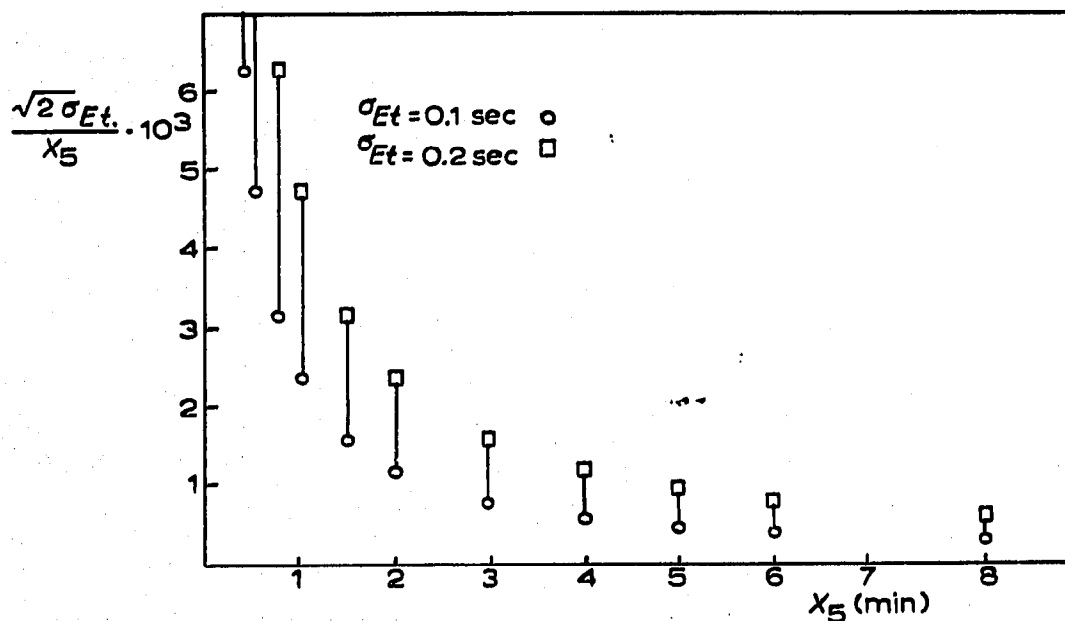


Fig. 2. Relative timing error in the measurement of retention time ($\sqrt{2} \sigma_{Et}/X_5$), *vs.* retention time (X_5).

σ_{t_R}/X_5 and $\sigma_{t_M}^n/X_5$ represent the errors connected with the localization of the two peaks (solute and unabsorbed gas). In fact, the maximum of the elution peak never appears as a sharp value.

We can examine the problem of the determination of these types of errors from two different points of view: (1) The observer makes an error in the estimate of the maximum displacement. The error is given by:

$$\sigma_{t_R}/X_5 = 2\sigma_h/Nh_{\max}. \quad (21b)$$

(2) The observer makes an error, v_m , in the estimate of the instant of rest (zero velocity):

$$\sigma_{t_R}/X_5 = v_m t_R / Nh_{\max}. \quad (21c)$$

Fig. 3 gives the values of σ_{t_R} vs. X_5 , letting $\sigma_h = \pm 0.5$ mm for the first method and $v_m = \pm 0.4$ mm/sec for the second method. We have examined the particular case of a column of 1000 theoretical plates and the registration of peaks at a height of 120 mm. For large values of X_5 , the first method gives better results. For very

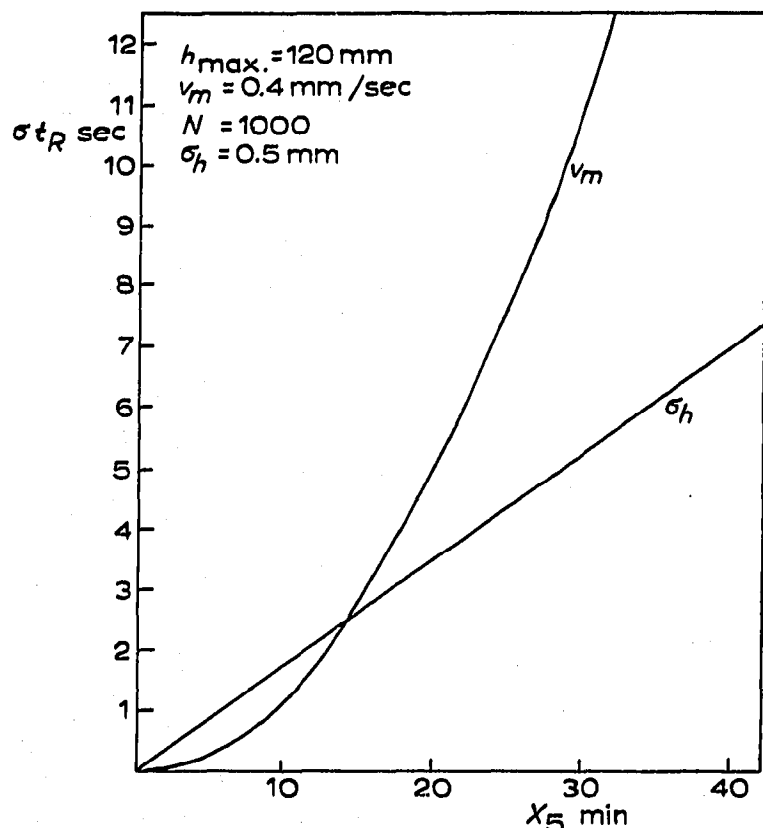


Fig. 3. Error in the localization of the maximum of the elution peak (σ_{t_R}) vs. retention time (X_5). σ_h plot: error in the evaluation of maximum displacement; v_m plot: error in the evaluation of the rest instant.

short times, the value of σ_{t_R} obtained using both methods has the tendency to be very small (less than the time of reaction of the observer). In these cases, the peak appears sharp and, for this reason, (σ_{t_M}/X_5) is negligible.

For the determination of eqns. 21b and 21c and for a more extensive discussion, references should be made to the literature^{1,13}.

σ_{X_5}/X_5 represents the intrinsic variation of the retention time.

Systematic errors

The propagation of systematic errors is quite simple:

$$\Delta X_5/X_5 = (\Delta t_R/X_5) - (\Delta t_M/X_5) \quad (21d)$$

However, the study of the sources of systematic errors always appears very difficult.

It has been observed that a common source of systematic errors in determining the retention time through the maximum of the elution peak is the presence of factors acting as exponential operators on the original elution peaks¹⁴. Among these factors we can mention, for instance, mixing chambers, diffusion chambers and time constants of an electrical nature of the detector-amplifier-recorder system.

TABLE II

τ/σ	$\Delta t_R/\sigma$
0.1870816	0.18128
0.1811248	0.17584
0.1749135	0.17011
0.1684182	0.16410
0.1616036	0.15776
0.1544258	0.15113
0.1468305	0.14390
0.1387477	0.13626
0.1300846	0.12801
0.1207144	0.11905
0.1104553	0.10917
0.0990286	0.09809
0.0859671	0.08534
0.0703622	0.07002
0.0498759	0.04975
0.0332964	0.03326
0.0249844	0.02497
0.0199920	0.01998
0.0099990	0.00999

Peak displacement values, normalized as regards the standard deviation, σ , of the elution peak ($\Delta t_R/\sigma$), are reported here *vs.* the normalized constants of the system τ/σ which acts as exponential operator. The values are reported in Table II and have been calculated by a method analogous to that of STERNBERG¹⁴. Such values are useful mainly when we deal with packed columns, where τ/σ values are very small.

For a discussion of other sources of error, many references may be consulted (*e.g.* refs. 14-16).

Correlations among the quantities X_3 , X_4 , X_5

X_3 , X_4 . Both these quantities are related to the quantity A (for X_4 and A , see eqn. 9d; for X_3 and A , see Darcy's equation¹⁷). An increase in A lowers X_4 and in-

creases X_3 . For this reason, a negative correlation between X_3 and X_4 may occur.

X_4, X_5 . An increase in A lowers X_5 and the correlation is positive.

X_3, X_5 . An increase in the flow is responsible for a decrease in the retention time. A negative correlation may thus occur between these two quantities.

QUANTITY Y AND THERMODYNAMIC PROPERTIES

The manner in which retention quantities change with temperature is well known. Such behaviour is explained, for example, in the case of quantity Y , on the basis of its thermodynamic meaning (eqn. 23a). On a theoretical basis, we also require the definition of the corresponding quantity p (ref. 18), in order to achieve a complete specification of Y . However, the effect of the variation of p is less remarkable.

Since a fluctuation of temperature increases the lack of precision of Y , it will be convenient to look for optimum conditions of temperature control. An example is reported here.

It is possible to show that in the case of a "bulk" type partition only, we have:

$$C\{Y\} = (\Delta H/RT_c)C\{T_c\} \quad (22)$$

If, for example, the method of measurement of Y implies an unavoidable $C\{Y\} \simeq 5\%$, eqn. 22 shows that there is also a further contribution of about 5% if the temperature is controlled to $\pm 0.1^\circ\text{C}$, when $\Delta H \simeq 10$ kcal/mole and $T_c \simeq 300^\circ\text{K}$. The coefficient of global variation is the square root of the sum of the squares, and the result is 7%, is not very different from the original value.

QUANTITY w_L : PROBLEMS CONNECTED WITH THE DETERMINATION OF V_g

In the most general case, Y (retention of a solute on a particular partition system) can be represented by:

$$Y = (273.16/T)V_N = (273.16/T)(\sum K_i V_{L_i} + \sum K_{A_i} A_i) \quad (23a)$$

where the various K_i stand for many bulk phases, each one giving a contribution to partition, and K_{A_i} for many interfaces, all contributing to the retention¹⁹.

The definition of V_g :

$$V_g = K(273.16/T)(1/\rho_L) = Y/w_L \quad (23b)$$

implies either that the existence of a unique bulk phase has been proved or that all the contributions in eqn. 23a (different from the one we are considering) have been evaluated^{20,21}. In other words, the possibility of having a quantity like V_g according to eqn. 23b, is realized if we can show that the regression between Y and w_L can be well represented by the following equation:

$$Y = \alpha w_L \quad (23c)$$

On an experimental basis, eqn. 23c cannot be proved by using only that column on which Y has been determined, but rather by comparing, through correlation analysis, the values of Y obtained on different columns (on which the various contributions have been modified, *i.e.* different supports, different surface developments).

The precision of V_g will then be deduced from the same linear regression analysis, eqn. 23c.

Eqns. 23a-23c allow the possibility of determining V_g , but we cannot omit the discussion of a further important problem, the establishment of the correct correlation between Y_i and w_{Li} . Indeed, the measurement of w_L is always preliminary or subsequent to the measurement of Y and the GC column is an entity that is variable with time. It follows that the different determinations of Y (necessarily performed at different subsequent times) can be neither comparable among themselves nor associated with the measured value of w_L .

It is therefore necessary, with GC technique, to consider the problem of the control of the column stability, as well as the errors discussed here. Generally this problem is never considered rigorously, but is usually solved quite intuitively and empirically.

However, we can use very sensitive statistical methods, known as "analysis of time series", which allow one to verify whether there is a relation between the variation of a quantity and the chronological order of the measurements^{22,23}. This also gives the possibility of formulating more accurately the concept of column stability and of handling equations different from those for V_g (Table I).

We have not considered developments of these last methods, which only require suitable experimental data.

The above discussions, the equations given for random and systematic errors, and the comments about the correlation among different quantities, have only a limited and indicative value. They may be helpful for a preliminary evaluation of the accuracy of the method and may be useful as a critical background for the analysis of experimental results (analysis of variance and covariance).

NOMENCLATURE

h_{max} .	maximum displacement of the pointer of the recorder
p_0	column outlet pressure
p_i	column inlet pressure
p_w	vapour pressure of water
r	internal radius of flowmeter
t	time for the bubble to travel from one level to the other in the flowmeter
v_{bubble}	speed of the bubble in the flowmeter
$A = (p_i/p_0) = (\Delta p + p_0)/p_0$	pressure ratio
A_i	surface area of interface i
$C\{X\}$	coefficient of variation of X
F_0	gas flow rate from column (at column exit temperature T and pressure p_0)
F_1	gas flow rate measured at flowmeter
K_i	partition coefficient (vapour-liquid)
K_{At}	partition coefficient at interface
L	distance between the two levels of flowmeter
N	theoretical plates
O	cross-section of flowmeter

R	gas constant
$T(^{\circ}\text{K})$	temperature at the point where gas flow rate is measured
$T_c(^{\circ}\text{K})$	absolute temperature of column
V	volume of flowmeter
V_{Li}	volume of stationary liquid phase
α	constant
ΔH	differential molar heat of evaporation
ΔX	systematic error of X (except ΔH , Δp)
Δp	pressure drop
ρ_L	density of liquid phase L
ρ_{ij}	coefficient of correlation for (X_i, X_j) if i and j are numbers, or for (i, j)
σ_i	standard deviation of X_i (if i is a number) or standard deviation of quantity i
σ_{Ei}	stochastically independent component of error of X_i (if i is a number) or of quantity i
σ_{Xi}	correlated component of error of X_i

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