

CHROM. 5845

ESTIMATION OF ERRORS IN THE DETERMINATION OF HEATS OF EVAPORATION BY GAS CHROMATOGRAPHY*

F. DONDI, A. BETTI AND C. BIGHI

Istituto Chimico dell'Università di Ferrara, Ferrara (Italy)

(Received November 19th, 1971)

SUMMARY

The influence of random and non-random errors in the gas chromatographic determination of differential molar heats of evaporation (ΔH) on the basis of the relationship between the retention volume and temperature has been examined. A complete statistical analysis both of the precision in the determination of retention quantities and of the linear correlation between the logarithm of the retention volume and $1/T_c$ has been performed, in order to check the reproducibility and the consistency of the ΔH determinations when there are problems of reproducibility due to the past history of the column. The same problems have been examined in the determination of $\Delta(\Delta H)$.

INTRODUCTION

For analytical and thermodynamic purposes, it is useful to give an explicit form to the relationship between retention parameters and temperature¹.

In the first case, the relation adopted must express the behaviour of a partition system only for a definite range of temperature in a form that is accurate and easy to calculate²⁻⁴.

In the second case, the type of function is formulated on thermodynamic grounds (*e.g.*, see ref. 5); the determination of the parameters of these functions represents one of the most interesting possibilities of gas chromatography⁶⁻¹². Theoretically, it is possible to determine the enthalpy and the entropy of evaporation (ΔH and ΔS), relative excess functions and ΔC_p .

So far, however, complete agreement has not been reached on the precision and accuracy of these measurements. For example, YOUNG⁸ states that it is very difficult to determine excess functions with great precision, in agreement with MARTIRE AND POLLARA¹² and with PURNELL¹³. BLU *et al.*¹¹ have proposed a procedure that is said to permit precise determinations of ΔH with a definite thermodynamic

* This investigation was carried out with a contribution from the National Research Council (C.N.R.).

TABLE I

PREPARATION AND USE OF THE COLUMNS

Preparations: A = slow evaporation of the solvent (maximum temperature 90°C), 16.39% of Cw 400 on Chromosorb; B = slow evaporation of the solvent (maximum temperature 90°C), 16.70% of Cw 400 on Chromosorb; C = drying of the support, conditioning of the Cw 400 for 30 h with a flow of dry nitrogen (temperature 85 ± 1°C), evaporation of the solvent with a flow of nitrogen (maximum temperature 70°C); D = same as C, 17.5% of Cw 400 on Haloport.

Preparation of the packing	Columns prepared	Parameter measured	Groups of retention data	The function $x = m \cdot n + q$; 16.55% of Cw 400 on Haloport; $x = 1/Tc$ ($^{\circ}K^{-1}$), $n=no$ of days		Preceding history	
				$\leq n \leq$	$q \cdot 10^3$ ($^{\circ}K^{-1}$)		
A	1,2	V_g	A(1 + 2) (r)	0-5	-0.386	2.853	Preparation A Preparation A; conditioning at 70-85°C with a flow of He for 50 h
			A(2) (d)	0-2	4.288	2.800	
B	1	V_N^0	B(1) (i)	0-9	-1.235	2.899	Preparation B Preparation B; operation of B(1) (i)
			B(1) (d)	0-4	2.080	2.796	
2		V_N^0	B(1) (r)	0-14	-0.347	2.867	Preparation B Preparation B; keeping in a desiccator at room temperature for 15 days
			B(2) (i)	0-8	-1.219	2.882	
			B(2) (d)	0-4	3.061	2.773	As for B(2) (i); operation of B(2) (i)
C	1	V_N^0	B(2) (r)	0-13	-0.173	2.845	As for B(2) (i)
D	1	V_N^0	C(1) (d)	Time of operation: 12 h at 73°C and 12 h at 84°C			Preparation C Preparation D
			D(1) (d)	Same as for C			

significance. Most authors, in determining ΔH , approximate the relationship between $\ln V_g$ and $1/T_c$ (where T_c is the temperature of the column in °K) to a linear function, as in general the instrumental precision is inadequate to appreciate variations of a higher order¹⁴. Other authors^{15,16}, adopting the same relationship and considering that the greatest cause of error lies in the instrumentation, have made the control of certain operating variables more accurate and have given determinations of ΔH with precisions better than ± 10 cal mole⁻¹, and of $\Delta(\Delta H)$ with precisions better than $\pm 0.02\%$.

Thus, many previous authors have rarely faced the problem of reproducibility, repeatability and consistency of the results.

In the present work, it is intended, by means of statistical analysis, to examine the problem of the postulated consistency between thermodynamic functions and experimental results when there are problems of repeatability connected with the past history of the column.

The measurements performed were designed in such a way as to permit a sufficiently clear definition of the stochastic relationship between $1/T_c$ and the operating variables of the column (time and past history), at the same time taking into account the field of variation of $1/T_c$. A theoretical outline is then given of the way in which a transformation of the partition system (or a generic source of non-random errors) is reflected in the final determination of ΔH [and $\Delta(\Delta H)$]. From this may emerge criteria for methods for the solution of certain problems connected with the presence of these types of error, and also criteria for a more realistic estimation of the precision of quantities such as ΔH and $\Delta(\Delta H)$.

DESIGN OF THE MEASUREMENTS AND EXPERIMENTS

Systems examined

The stationary phase was polyethylene glycol of molecular weight 400 (Cw 400). The solutes used were benzene, carbon tetrachloride, *n*-decane, ethanol, propan-2-ol and 2-methylpropan-2-ol. The support was silanized Chromosorb P, 60–80 mesh (pure products from C. Erba, Milan); in one case the support was Haloport F, 30–60 mesh (Hewlett-Packard). The temperature range used was 70–85°C (lower than 90°C, the maximum limit recommended for thermoderivatographic measurements¹⁷).

The partition system could exhibit instability¹⁸ and irreproducibility because of its history^{19,20}. The solute–stationary phase systems, because of the diversity of the molecular interactions involved^{21–23}, were indicative of possible chemical and physical transformations of the column^{20,24} and representative of a wider class of systems.

Preparation of the columns for use (Table I)

Four preparations of the stationary phase were carried out, A, B, C and D. Two columns were prepared from A (1 and 2) and V_g was determined for them. For the preparation B, the results obtained ($V_g \cdot w_L = V_N^0$, where w_L is the amount of stationary phase) on the two columns B(1) and B(2) were kept separate. Single columns were obtained from preparations C and D.

The order of imposition of the temperature to the gas chromatograph was controlled, especially in the case of the columns obtained from preparations A and B:

on the same column, retention data were determined first with a constant order and increasing in time (i), and then with a decreasing order (d), similar but the reverse of the preceding one. A combination of the two is indicated by (r) (random). The groups of retention results obtained will be identified by a succession of symbols indicating the type of the preparation (A, B, C or D), the type of column (1, 2 or 1+2) and the application of temperatures (i, d or r) (see Table I).

In the course of 24 h, the temperature was constant to $\pm 0.2^\circ\text{C}$ and the mean flow-rate of the carrier gas was $0.3\text{--}0.4\text{ cm}^3\cdot\text{sec}^{-1}$.

In order to express the stochastic relationship existing between the column temperature and the operating time, a function of the type $x = m \cdot n + q$ (where $x = 1/T_c$ and n is the number of days for which the column had remained in the gas chromatograph) was used; from q it is possible to find the temperature of the first day of operation, and from m the mode in which the temperature was varied. Besides q and m , Table I gives the coefficient of linear correlation (ρ) and the range of variability of n (total time of operation). By referring to Table I it is possible to find the various combinations realized both in relation to the operation in the gas chromatograph and in relation to the history preceding the operation.

Retention measurements and stability of the experimental conditions

For each value of the temperature (and therefore also for each day), four determinations of the retention time were performed for each solute, each being accompanied by four determinations of the flow-rate before and after the injection, keeping under control the outlet pressure (p_0), the pressure drop (Δp) and T_c . Consequently, the variation in V_g or V_N^0 also reflects the transformation undergone by the column as a function of time as well as of the variation in the column temperature.

During the time necessary to carry out the tests with each solute, the temperature of the column was constant to within $\pm 0.02^\circ\text{C}$, the flow-rate (about $1.000\text{ cm}^3\cdot\text{sec}^{-1}$) was constant to within $0.002\text{ cm}^3\cdot\text{sec}^{-1}$, and p_0 (about 760 mm Hg) was constant to within $\pm 0.5\text{ mm Hg}$. If it is assumed that the permeability of the column was also constant during this period (no drift in the permeability was observed over the whole time of operation of the columns), the inlet pressure (p_i) (about 1300 mm Hg) was constant to within $\pm 1\text{ mm Hg}$.

A total of 900 determinations of the retention volume was made. All these results have not been reported in detail; only the statistical treatments are given and from these it is possible to reconstruct a large part of the information contained in the experimental results. Table II gives the number (n) of retention volume determinations for each solute grouped according to the criteria of Table I, the value of \bar{l} ($\bar{l} = T_c - 273.16$, where T_c is the harmonic mean of the values of T_c corresponding to the tests performed), and the value of dl :

$$dl = T_c^2 \sqrt{\frac{\sum (1/T_{c_i} - 1/T_c)^2}{(n - 1)}}$$

It may be observed that the mean values and the mean temperature intervals, \bar{l} and dl , almost coincide, especially for the groupings arising from preparations A and B. Any variations in ΔH observed can, therefore, not be ascribed to the small differences in the width of the temperature ranges used.

Apparatus

A Fractovap Model B gas chromatograph (C. Erba, Milan) was used, modified with a liquid thermostat bath. The bath temperature was constant (to within $\pm 0.05^\circ\text{C}$) along the diagonals. The temperature T_c ($\pm 0.02^\circ\text{C}$) was measured with a mercury thermometer calibrated in the range of use with reference to fixed points. The pressure drop, Δp , along the column was measured with a U-tube mercury manometer (± 0.5 mm Hg) and the atmospheric pressure, p_0 , with a Fortin barometer (± 0.1 mm Hg). The pressure drop in the detector was assumed to be negligible. The detector was a direct-flow thermal conductivity device; the recorder (5 mV full-scale deflection) had a response time at full scale of 2.5 sec. The stainless-steel columns, 5 mm in internal diameter and 2 m long, were wound helically, the diameter of the helix being 15 cm. The carrier gas was helium (99.995%). The retention time (with respect to the inert sample, air) was measured at the maximum of the peak (mean peak height at half full-scale of the recorder) with a $\frac{1}{5}$ -sec stop-watch. The flow-rate, F_0 , was measured with a flow meter similar to that described by ADLAR *et al.*²⁵. The temperature of the thermostat bath of the flow meter was constant to within $\pm 0.02^\circ\text{C}$. The temperature of the injector was 120°C . The amount of sample injected was $0.5 \mu\text{l}$ (with a Hamilton microsyringe having a full-scale reading of $10 \mu\text{l}$). The amount of stationary phase, w_L , was calculated from the data relating to the preparation of the packing and by weighing the column before and after packing. To calculate V_g or V_N^0 , reference was made to the A.S.T.M. standards².

TREATMENT OF THE EXPERIMENTAL RESULTS

Hypotheses and method of investigation

It is known that the specific retention volume at a certain temperature, V_g , is a function of T_c . In this investigation, it was assumed¹ as a hypothesis that the function is of the type $\ln V_g = b/T_c + a$. If this hypothesis is valid, an analogous relationship exists between $\ln V_N^0$ and $1/T_c$, and in this case $\Delta H = b \cdot R$ (where R is the universal gas constant). ΔH is the differential molar heat of evaporation.

Putting $\ln V_N^0 = y$ and $1/T_c = x$, if there is a particular source of constant error, corresponding to a certain selected value, x_i , all the retention values measured (expressed in logarithmic form), z_{ij} , will be affected by the same error dw_i :

$$z_{ij} = y_{ij} + dw_i \quad (j = 1, 2, \dots, n_i) \quad (1)$$

where n_i indicates the number of tests and y_{ij} the result of a hypothetical measurement affected only by (random) instrumental errors. The significance of the error dw_i is also defined with this precision: by this are understood those types of errors or perturbations of the partition system that act on the whole series of repeated retention volume determinations for constant x . Given the logarithmic form adopted, dw expresses a relative error in the retention volume.

Consequently, the mean value $\bar{z}_i = \sum z_{ij}/n_i$, relative to x_i , will also be affected by the same error dw_i :

$$\bar{z}_i = \bar{y}_i + dw_i \quad (2)$$

The slope calculated from the observed experimental values is:

$$b_z = \frac{\sum n_i (x_i - \bar{x})^2 \left(\frac{\bar{z}_i - \bar{z}}{x_i - \bar{x}} \right)}{\sum n_i (x_i - \bar{x})^2} \quad (3)$$

where

$$\bar{x} = \frac{\sum n_i x_i}{\sum n_i} \quad \text{and} \quad \bar{z} = \frac{\sum n_i \bar{z}_i}{\sum n_i} \quad (4)$$

From eqns. 1-4:

$$b_z = b_y + b_w \quad (5)$$

where b_y and b_w are expressions analogous to eqn. 3 obtained by substituting y and dw , respectively, for z . Analogously:

$$a_z = \bar{z} = a_y + a_w \quad (6)$$

The experimental regression line determined by z , $Z(x)$ is therefore:

$$Z(x) = a_z + b_z(x - \bar{x}) = Y(x) + W(x) \quad (7)$$

Eqn. 7 indicates that if the dependence between y and x is expressed linearly by $Y(x)$, the experimental straight line $Z(x)$ is different from the hypothetical one, $Y(x)$, according to the way in which the phenomenon of perturbation, dw , can be expressed as a linear function of x . The manner (magnitude and sign of the slope) in which dw can be expressed as a linear function of x depends to a large extent on the type of stochastic and/or causal relationship between the two quantities.

For example, in the case of a transformation of the stationary phase, the generic source of error, dw , depends on the time and on the temperatures of operation that have followed one another. If a significant correlation has been found between the time and $1/T_c$ (the function $x = m \cdot n + q$, Table I), a high degree of stochastic dependence between dw and x with a non-zero value of the function $W(x)$ has also been established. For the same type of transformation, dw , that has followed itself in time, the sign of the slope b_w depends on the way in which the measurements have been performed, *i.e.* with a decreasing or increasing order of the temperatures with time (sign of m , Table I).

In addition to this, it must be observed that, in general, dw can no longer be expressed as a rigorously linear function of x and the presence of dw will therefore be indicated not only by the non-reproducibility of b_z but also by the lack of satisfaction of the statistical tests for linearity (based on variance analysis). The experimental points, \bar{z}_i , will deviate from the straight line $Z(x)$ more than is predicted from the instrumental error of measurement, because the residual part of dw not expressed linearly by $W(x)$ combines additively with the scatter deriving from the lack of instrumental precision (theorem of addition of variances).

For the same reasons, in the case of a zero correlation between dw and x , the value of b_w will be zero but the presence of dw will be revealed by the same tests for linearity or even more simply by an excessively high value of the error in the slope b_z .

Consequently, analysis of the values of b_z repeated on the same system and of the confidence intervals of b_z , and the application of the statistical tests for linearity performed, bearing in mind the type of operation of the column (Table I), will be complementary methods for showing the presence of the source of error,

$d\omega$. If, then, this study is also performed comparatively with solutes of different types, it will be possible to see whether there is a simple loss of stationary phase (same sign and magnitude of $d\omega$ and therefore the same error, b_{ω}) or a more complex transformation²⁰.

Finally, in the measurement in which the source of error, $d\omega$, will be regarded as negligible, it will be possible to draw a conclusion on the coincidence between $Z(x)$ and $Y(x)$. If a similar conclusion is reached by means of a rigorous check of the linearity test, it will also be possible to accept the hypothesis of a linear relationship between $\ln V_N^0$ and $1/T_c$. Only in this way is it possible to determine values of ΔH with maximum precision (that permitted by the experimental procedure) and maximum accuracy (that permitted by the statistical tests used).

Statistical treatment

From the experimental results (F_0 , $(t_R - t_M)$, Δp and p_0) (ref. 2), the retention volumes were determined and the analysis of linear regression between $\ln V_g$ (or $\ln V_N^0$) and $1/T_c$ was applied by means of a Fortran IV programme on an IBM 7090 computer. A more complete statistical analysis of these results was carried out with an HP 9100 B computer using the programmes collected in STAT-PAC Volume 1 (Hewlett-Packard). A significance level of 95% was adopted for the statistical tests, and general reference was made to the texts of HALD²⁶ and DIXON AND MASSEY²⁷ and to published statistical tables²⁸. A positive result of a test is shown in the tables by (+), a negative result by (-), and a doubtful result by (?).

TABLE III

PARTIAL ESTIMATE OF $s(\ln V_N^0) \cdot 10^3$

	$B(1)$		$B(2)$		$A(1 + 2)$	
Benzene	2.402	(+)	2.178	(+)	1.355	(+)
<i>n</i> -Decane	4.143	(+)	3.118	(+)	2.219	(+)
Carbon tetrachloride	1.518	(+)	1.961	(-)	2.523	(+)
Ethanol	1.720	(+)	1.934	(+)	2.310	(?)
Propan-2-ol	1.642	(+)	1.818	(+)	0.932	(+)
2-Methylpropan-2-ol	1.513	(+)	1.615	(+)	1.898	(+)

ESTIMATION OF THE ERROR IN THE RETENTION VOLUME AND IN ΔH

A corrected and not excessive estimation of the error in the retention volume is the fundamental basis for all the statistical tests that follow. The total error must be evaluated by combining in a suitable manner all the errors in the individual magnitudes measured²⁰⁻³¹. Because of the way in which the measurements were carried out, some of these errors (random errors in the determination of the flow read on the flow meter, F_1 (ref. 29), and in $(t_R - t_M)$) were determined directly from the statistical analysis of the repeated tests of retention volumes and the residuals from the analysis of the relationship between p_0 , Δp and F_0 (Darcy's equation³²).

For all the groups of repeated tests, the error, $s(\ln V_N^0)$, made in $\ln V_N^0$ was determined. The values found for the various solutes on the individual columns were equal to one another in the majority of cases (checked by Bartlett's test) in accordance

with the results observed by УНДЕОВ³³. Table III gives the estimate of the common value of $s(\ln V_N^0)$ and the test check. The characteristic values for the various solutes (excluding, in general, *n*-decane) are exhaustively explained by the errors made in F_1 (the value found from a separate analysis was 1%) and in the retention time^{20,31}. It must be borne in mind that the stability of the system (flow-rate, Δp , p_0 and T_c) is even better than that reported in the section on retention measurements. The lower precision for *n*-decane (and to a certain extent also for benzene) is probably connected with the sampling errors and with the non-linearity of the partition isotherm.

In order to evaluate the other sources of error, a two-stage analysis of variance in the column permeability (B_0) measurements was applied by using Darcy's equation. The measurements of B_0 in the second-order groups were carried out under the same conditions as the determination of V_N^0 (with Δp and p_0 constant). The first-order groupings were determinations of B_0 repeated with variations in Δp (and p_0) and in the operating conditions of the flow meter but performed on the same day so as to avoid intrinsic fluctuations in the column permeability.

The second-order fluctuations (1-2%) can be explained by the error made in the measurement of F_1 . The sources of error that determine the first-order fluctuations in B_0 (4-6%) are, on the other hand, all the residual sources of error in V_N^0 that were not taken into account in the preceding analysis (data in Table III). Where these fluctuations are derived only from Δp (± 2 mm Hg), an error of 1% is passed on (through J , Martin's factor) to V_N^0 ; if, on the other hand, they are connected with other operations of measuring the flow velocity, F_0 , (for example, variations in the vapour pressure of the soap solution, poor operating conditions of the flow meter²⁰) the error passed on to V_N^0 is higher (4-6%). However, the possibility that they are derived solely from errors made in p_0 can be excluded because of the low sensitivity of B_0 to these errors.

Consequently, this analysis indicates that other errors, in no case less than 1%, have certainly been made in V_N^0 . Even the uncertainty in the reading of the column temperature involves an error in the association operating between $\ln V_N^0$ and $1/T_c$ ($1/T_c$ is the independent variable, not affected by errors, in the linear regression of the first type³⁴). This error is passed on to $\ln V_N^0$ to the extent of about 0.5×10^{-3} (ref. 29). It is therefore considered that the measurement procedure involves, in addition to the errors in Table III, additional errors of about 1×10^{-3} - 2×10^{-3} in $\ln V_N^0$.

In the case of the grouping A(1+2), it is also necessary to consider the errors connected with the determination of the amount of stationary phase, w_L , present in the columns A(1) and A(2), which is necessary for the determination of V_θ (Table I). It was assumed that the amount, w_L , present in the columns A(1) and A(2) was proportional to the weight of the packing (since the preparation procedures were the same). The error that is passed on to V_θ by the operations of weighing the packing is about 1%. Any further error in V_θ is not important for the purposes of determining ΔH .

Taking all the preceding considerations into account, it is possible to evaluate the minimum error with which ΔH can be determined (e.g., ref. 26). For the majority of the substances (excluding *n*-decane) confidence intervals of between 30 and 80 cal mole⁻¹ are found, depending on the number of tests performed. These values must be

TABLE IV

 ΔH CONFIDENCE INTERVALS ($\text{cal} \cdot \text{mole}^{-1}$): LINEARITY TESTS

	Benzene	n-Decane	Carbon tetrachloride	Ethanol	Propan-2-ol	2-Methylpropan-2-ol
A(1+2) (r)	7511 ± 73 (-)	8419 ± 131 (-)	7350 ± 87 (-)	9133 ± 112 (-)	9275 ± 113 (-)	9231 ± 108 (-)
B(1) (r)	7396 ± 111 (-)	8338 ± 126 (-)	7217 ± 105 (-)	9172 ± 103 (-)	9238 ± 74 (-)	9212 ± 92 (-)
B(2) (r)	7753 ± 165 (-)	8629 ± 159 (-)	7526 ± 175 (-)	9367 ± 150 (-)	9502 ± 187 (-)	9433 ± 182 (-)
B(1) (i)	7349 ± 155 (-)	8339 ± 171 (-)	7329 ± 134 (-)	9274 ± 64 (+)	9302 ± 84 (?)	9342 ± 66 (+)
B(2) (i)	8155 ± 253 (-)	8888 ± 238 (-)	7899 ± 359 (-)	9753 ± 196 (-)	9986 ± 271 (-)	9974 ± 241 (-)
A(2) (d)	7480 ± 36 (+)	8398 ± 102 (+)	7165 ± 85 (+)	8961 ± 69 (+)	9123 ± 116 (+)	9054 ± 86 (+)
B(1) (d)	7484 ± 54 (+)	8340 ± 120 (+)	7096 ± 79 (+)	9007 ± 51 (+)	9100 ± 70 (+)	9014 ± 67 (+)
B(2) (d)	7387 ± 82 (+)	8346 ± 69 (+)	7186 ± 77 (+)	9005 ± 53 (+)	9137 ± 43 (+)	9072 ± 78 (?)
C(1) (d) ^a	7338	8273	7183	9000	9112	8997
D(1) (d)	—	—	—	8948 ± 79	—	—

^a Estimated confidence interval = ± 80 -100 $\text{cal} \cdot \text{mole}^{-1}$.

increased if the estimation of the experimental error has been too optimistic.

It must be borne in mind that the value of ΔH varies with temperature, and its variation can be regarded as being similar to that of the latent heat of vaporization, ΔH_v . For the solutes considered here, variations in ΔH_v of between 15 and 30 cal·°C⁻¹ mole⁻¹ have been found³⁵⁻⁴⁰. The effect of curvature is therefore of the same order of magnitude as the experimental precision.

It has not been possible to perform a reliable evaluation of the systematic errors of an instrumental nature owing to extra-column factors. Considerations based on the literature on this subject^{20,41-44} indicate that the error is about +1 cm³ (in V_N^0). The experimental results have not been corrected, and the error that could be passed on to ΔH is negative and is about 30-50 cal·mole⁻¹ (the maximum difference is obtained for solutes with the shortest retention times, *viz.* carbon tetrachloride, benzene and *n*-decane).

EVALUATION OF THE RESULTS

Determinations of ΔH

Table IV gives the results for ΔH , the confidence interval and the linearity test⁴⁵ relating to the combinations of Table I. The linearity tests were carried out with allowance for an additive contribution of 3×10^{-6} to s^2 ($\ln V_N^0$). Together with the significance limit of the test (95%), this hypothesis enables one to adequately avoid not recognizing a linearity when one exists.

The determinations of types (r) and (i) do not satisfy the linearity test and, in general, give higher values of ΔH . Exceptions are the apolar solutes on columns B(1)(r) and B(1)(i). It can be assumed that during period (i) of the operation there is predominantly a loss of stationary phase in the case of column B(2) and a chemical modification of the phase in the case of column B(1)^{18-20,46}. In fact, the differences in ΔH with respect to the observations of type (d) are almost constant for all the solutes (about 600 cal·mole⁻¹) in the case of columns B(2)(i) and are characteristic of the type of solute for columns B(1)(i). The cause of this diversity must probably be ascribed to the history preceding their operation, as the operation was the same in the two cases (almost coincident values of m , q and ρ , see Table I). A combination of specific retention volumes performed on only two columns does not give valid results, as in the case of A(1+2)(r), because the various sources of error combine with difficulty in a completely random manner.

Similarly, the two-way analysis of variances performed on the deviations from the calculated values and the experimental values of $\ln V_N^0$, grouped according to the type of solute and the day of column operation, showed a drift of the column during period (i). These deviations indicate a loss or transformation of the stationary phase and are proportional to the part of this phenomenon not expressed as a linear function of $1/T_c$. This drift was not apparent for the groupings of type (d). Consequently, it must be assumed that after a suitable period of conditioning under a flow of inert gas at the highest operating temperature, these types of columns become stabilized and provide ΔH determinations that are independent of the preceding history and independent of the time of operation, at least for a time varying between three and six days (see Table I, operation of columns A(2)(d), B(1)(d) and B(2)(d)). In fact, the determinations of ΔH in these cases show no significant differences

TABLE V

PARALLELISM OF REGRESSION LINES

Solute	Satisfaction of the test	Common value of ΔH (cal·mole ⁻¹)	Comparison C(1) (d) (cal·mole ⁻¹)
Benzene	B(1) (d)-A(2) (d) (+)	7483 ± 27	7338
	B(1) (d)-B(2) (d) (-)		
<i>n</i> -Decane	A(2) (d)-B(1) (d)-B(2) (d) (+)	8357 ± 53	8273
Carbon tetrachloride	A(2) (d)-B(1) (d)-B(2) (d) (+)	7152 ± 44	7183
Ethanol	A(2) (d)-B(1) (d)-B(2) (d) (+)	8996 ± 30	9000
Propan-2-ol	A(2) (d)-B(1) (d)-B(2) (d) (+)	9122 ± 42	9112
2-Methylpropan-2-ol	A(2) (d)-B(1) (d)-B(2) (d) (+)	9052 ± 42	8997

according to the type of column (paired observation test) and are equal to one another (parallelism test relative to the solutes, Table V). Column C(1)(d), the operation of which was subsequently limited to 24 h, also showed no significant differences (data are given for comparison in Table V). Consequently, it must be considered that a good reproducibility in the determination of ΔH was achieved only with these last columns.

Nevertheless, it is appropriate to observe that the tests used (linearity and parallelism, in particular), which establish the consistency and validity of the experimental measurements, have a limited power: with respect to the hypothesis that the effect of non-linearity is 1.4 times the experimental error in $\ln V_N^0$ and the non-parallelism 1.4 times the error in ΔH , the power is of the order of 80%. In addition, the linearity test was carried out with the adoption of a hypothesis (additive value to s^2 ($\ln V_N^0$) of 3×10^{-6}) which, although reasonable, is not completely demonstrable. Attempts to reduce this margin lead to non-satisfaction of the test in some cases. This could be due to many factors, not in the least to the lack of constancy of ΔH in the temperature range used (see the section on the estimation of the error in the retention volume and in ΔH). These considerations therefore also give the limits of the validity of the results.

The analysis of the precision of the determination of V_N^0 performed in the section on the estimation of the error in the retention volume and in ΔH also places some doubt on the significance of the ΔH measurements relative to the solutes benzene and *n*-decane (non-linearity of the partition isotherm shown by excessively high values of $s(\ln V_N^0)$).

More certain conclusions would have no great physical significance for the number of uncontrolled parameters (for example, the influence of the size of the sample, the gas-liquid and the gas-solid interfaces^{47,48}) and for the presence of systematic errors of instrumental origin. As an example, the value of ΔH for ethanol using Teflon as a support (column D(1)(d)) was re-determined. The result, $\Delta H = 8948 \pm 79$ cal·mole⁻¹, is similar to the preceding values, but combined with them it would change the final average results.

The errors estimated by means of this analysis were of the order of 200 cal·mole⁻¹ (for example, column B(1)(i), alcohols). These errors are probably due to very small amounts of transformation of the stationary phase, dw_t . Putting $b_w \cdot R = 200$ cal·mole⁻¹ and combining the equation $W(x) = b_w x + a_w$ with the expression $x =$

$m \cdot n + q$ (Table I), it is possible to estimate that the variation in the retention volume was -1% for each day of column operation. This error would have been very difficult to evaluate by means of a statistical check on the conditions of column stability performed under isothermal conditions.

Precision and reliability of the $\Delta(\Delta H)$ measurements

The observations on these factors can be largely deduced from the preceding ones. However, it is also well known that $\Delta(\Delta H)$ can be found not only from the difference in ΔH but also directly from the relative retention parameters. This second method is sometimes preferred, because it is faster and also because it leads to narrower confidence intervals for $\Delta(\Delta H)$. However, attention must be paid to the fact that in some cases the reduction of the confidence interval is fictitious and leads to a misunderstanding of the true significance of the parameters determined.

For example, if the value of $\Delta(\Delta H)$ for the pair ethanol (1)-propan-2-ol (2) with the linear regression of $\ln(V_N^0(1)/V_N^0(2))$ was obtained from the results for the grouping B(2)(i), the value $\Delta(\Delta H) = -233 \pm 130 \text{ cal} \cdot \text{mole}^{-1}$ would have been acceptable, because the regression performed has a positive linearity test and the confidence interval is sufficiently narrow. As the linearity test on the individual regressions of $\ln V_N^0(1)$ and of $\ln V_N^0(2)$ is not satisfied, however, the suspicion remains that the result for $\Delta(\Delta H)$ is incorrect. In fact, the value of $\Delta(\Delta H)$ that can be obtained from the data of Table V, $\Delta(\Delta H) = -126 \pm 53 \text{ cal} \cdot \text{mole}^{-1}$, [groupings B(1)(d), B(2)(d) and A(2)(d)], shows that in the regression of $\ln(V_N^0(1)/V_N^0(2))$ not all the errors are completely eliminated, probably because the loss of stationary phase (monomers and low-molecular-weight polymers) does not affect the two solutes in precisely the same way⁴⁶.

This example emphasizes the way in which the determination of $\Delta(\Delta H)$, usually more popular in gas chromatography, must also be subjected to the same critical analysis as is associated with the determination of ΔH .

ACKNOWLEDGEMENT

We are indebted to Dr. F. SIVIERI for assistance provided in the experimental part of this work.

REFERENCES

- 1 A. B. LITTLEWOOD, C. S. G. PHILIPS AND D. T. PRICE, *J. Chem. Soc.*, (1955) 1480.
- 2 A.S.T.M. COMMITTEE E-19 ON GAS CHROMATOGRAPHY, *J. Gas Chromatogr.*, 6 (1968) 1.
- 3 J. JANÁK, *J. Chromatogr.*, 53 (1970) D33.
- 4 N. C. SAHA AND G. D. MITRA, *J. Chromatogr. Sci.*, 8 (1970) 84.
- 5 J. H. PURNELL, *Gas Chromatography*, John Wiley, New York, 1962, Ch. 7.
- 6 J. C. GIDDINGS AND K. L. MALIK, *Ind. Eng. Chem.*, 59, No. 4 (1967) 18.
- 7 R. KOBAYASHI, P. S. CHAPPELEAR AND H. A. DEANS, *Ind. Eng. Chem.*, 59, No. 10 (1967) 62.
- 8 C. L. YOUNG, *Chromatogr. Rev.*, 10 (1968) 129.
- 9 J. R. CONDER, in J. H. PURNELL (Editor), *Progress in Gas Chromatography*, Interscience, New York, 1968, p. 209.
- 10 T. I. BERTUSH, A. V. KISILEV, A. A. LOPATKIN AND R. S. PETROVA, *Chromatographia*, 3 (1970) 369.
- 11 G. BLU, L. JACOB AND G. GUIOCHON, *J. Chromatogr.*, 50 (1970) 1.
- 12 D. E. MARTIRE AND L. Z. POLLARA, *Adv. Chromatogr.*, 1 (1965) 335.
- 13 H. J. PURNELL, *Gas Chromatography*, John Wiley, New York, 1962, p. 423.

- 14 A. B. LITTLEWOOD, *Anal. Chem.*, 36 (1964) 1441.
 - 15 J. E. OBERHOLTZER AND L. B. ROGERS, *Anal. Chem.*, 41 (1969) 1234.
 - 16 R. A. CULP, C. H. LOCHMÜLLER, A. K. MORELAND, R. S. SWINGLE AND L. B. ROGERS, *J. Chromatogr. Sci.*, 9 (1971) 6.
 - 17 J. TAKÁCS, J. BALLA AND L. MÁZOR, *J. Chromatogr.*, 16 (1964) 218.
 - 18 R. W. MCKINNEY, J. F. LIGHT AND R. L. JORDAN, *J. Gas Chromatogr.*, 6 (1968) 97.
 - 19 R. A. KELLER, R. BATE, B. COSTA AND P. FORMAN, *J. Chromatogr.*, 8 (1962) 157.
 - 20 R. A. KELLER AND G. H. STEWART, *J. Chromatogr.*, 9 (1962) 1.
 - 21 C. BIGHI, A. BETTI, G. SAGLIETTO AND F. DONDI, *J. Chromatogr.*, 35 (1968) 309.
 - 22 C. BIGHI, A. BETTI, F. DONDI AND R. FRANCESCONI, *J. Chromatogr.*, 42 (1969) 176.
 - 23 C. BIGHI, A. BETTI, F. DONDI AND G. SAGLIETTO, *Ann. Univ. Ferrara, Sez. V, Vol. II, No. 17* (1968) 193.
 - 24 S. H. LANGER AND R. J. SHEEHAN, in J. H. PURNELL (Editor), *Progress in Gas Chromatography*, Interscience, New York, 1968, p. 289.
 - 25 E. R. ADLAR, M. A. KHAN AND B. T. WHITHAM, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 251.
 - 26 A. HALD, *Statistical Theory with Engineering Applications*, John Wiley, London, 1952.
 - 27 J. W. DIXON AND F. J. MASSEY, JR., *Introduction to Statistical Analysis*, McGraw Hill, New York, 1957.
 - 28 Documenta Geigy, *Tables Scientifiques*, J. R. Geigy S.A., Basle, 1963.
 - 29 F. DONDI, A. BETTI AND C. BIGHI, *J. Chromatogr.*, 60 (1971) 1.
 - 30 O. VIČAROVÁ, J. NOVÁK AND J. JANÁK, *J. Chromatogr.*, 51 (1970) 3.
 - 31 M. GOEDERT AND G. GUIOCHON, *Anal. Chem.*, 42 (1970) 962.
 - 32 G. GUIOCHON, *Chromatogr. Rev.*, 8 (1966) 1.
 - 33 J. UHDEOVÁ, *J. Chromatogr.*, 51 (1970) 23.
 - 34 A. HALD, *Statistical Theory with Engineering Applications*, John Wiley, London, 1952, p. 621.
 - 35 A. D. BUCKINGHAM, *The Laws and Applications of Thermodynamics*, Pergamon Press, Oxford, 1964, p. 75.
 - 36 R. W. GALLANT, *Hydrocarbon Process.*, 45, No. 3 (1966) 161.
 - 37 H. T. COUCH, W. KOZICKI AND B. H. SAGE, *J. Chem. Eng. Data*, 8 (1963) 346.
 - 38 J. F. COUNSELL, J. O. FENWICK AND E. B. LEES, *J. Chem. Thermodyn.*, 2 (1970) 367.
 - 39 J. L. HALES, J. D. COX AND E. B. LEES, *Trans. Faraday Soc.*, 59 (1963) 1544.
 - 40 E. T. BEYNON, JR., AND J. J. MCKETTA, *J. Phys. Chem.*, 67 (1963) 2761.
 - 41 J. C. STERNBERG, *Adv. Chromatogr.*, 2 (1966) 205.
 - 42 I. G. MCWILLIAM AND H. C. BOLTON, *Anal. Chem.*, 41 (1969) 1755.
 - 43 I. G. MCWILLIAM AND H. C. BOLTON, *Anal. Chem.*, 41 (1969) 1762.
 - 44 H. OSTER AND E. ECKER, *Chromatographia*, 3 (1970) 220.
 - 45 A. HALD, *Statistical Theory with Engineering Applications*, John Wiley, London, 1952, p. 553.
 - 46 M. B. EVANS AND J. F. SMITH, *J. Chromatogr.*, 36 (1968) 489.
 - 47 D. E. MARTIRE, in J. H. PURNELL (Editor), *Progress in Gas Chromatography*, Interscience, New York, 1968, p. 93.
 - 48 P. URONE AND J. F. PARCHER, *Adv. Chromatogr.*, 6 (1968) 299.
- J. Chromatogr.*, 66 (1972) 191-204