SECTION OF ANALYTICAL CHEMISTRY

PRELIMINARY RECOMMENDATIONS ON NOMENCLATURE AND PRESENTATION OF DATA IN GAS CHROMATOGRAPHY*

Following approaches made to the International Union of Pure and Applied Chemistry by Dr F. H. Stross and Dr D. Ambrose, a special group was formed under the auspices of the Section of Analytical Chemistry to make recommendations for a standard terminology in gas chromatography. The Group consisted of Dr D. Ambrose, Chairman (U.K.), Dr A. T. James (U.K.), Professor A. I. M. Keulemans (The Netherlands), Dr E. Kováts (Switzerland), Dr H. Röck (Germany), Dr C. Rouit (France) and Dr F. H. Stross (U.S.A.).

The Group adopted the following objectives:

(1) To recognize and encourage existing, well established conventions, to the extent that they are basically sound (consistent with accepted theory) and of general utility.

(2) To endeavour to suppress confusion by selecting a single term from the multiplicity that, in some cases, have been proposed to describe or measure a particular concept in gas chromatography. This is considered necessary regardless of how theoretically sound the various duplicating terms may be. Two or more terms for a single property should only be recognized when each of the terms has a specific area where its use is clearly of great advantage.

(3) To attempt to eliminate ambiguity by altering definitions or usages that are vague or inconsistent with the Recommendations.

(4) To make these Recommendations so clear and concise that they will find universal acceptance and utilization to the greatest possible extent.

The work of the Group has been conducted by correspondence and has resulted in the recommendations which follow; before being drawn up in their final forms they were shown to a large number of those interested in the subject and modifications were introduced in the light of comments received by the Chairman. In particular we must acknowledge the contribution made by the Groupement pour l'Avancement des Méthodes Spectrographiques who had independently been considering the same subject under the chairmanship of Professor P. Chovin. In submitting our recommendations

* Comments and suggestions should be sent to Dr D. Ambrose, National Chemical Laboratory, Teddington, Middlesex, England.

for wider consideration we express our hope that they will serve the purposes we have defined above and that, now a start has been made, it will be possible to revise them and keep them up to date as their inadequacies are revealed.

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1. INTRODUCTION

Gas Chromatography is so widely used that it has become necessary to standardize definitions and presentation of results. Recommendations having this objective should be in harmony with gas chromatographic theory and account has been taken of this in the following proposals.

Gas chromatography is almost always carried out by elution. The recommendations pertaining to the presentation of results and general background (item **5** and following) are restricted to elution, mainly gas–liquid, chromatography; further recommendations will be required for gas–solid chromatography. The definitions of terms (items **2** to **4**) are nearly all generally applicable without restriction.

2. NAME OF TECHNIQUE

Gas chromatography comprises all chromatographic methods in which the moving phase is a gas (the word chromatography itself implies that a stationary phase is present in addition to the moving phase).

Gas–liquid chromatography comprises all gas chromatographic methods in which the stationary phase is a liquid distributed on a solid support. Separation is achieved by partition of the components of a sample between the phases.

Gas–solid chromatography comprises all gas chromatographic methods in which the stationary phase is an active solid (e.g. charcoal, molecular sieves). Separation is achieved by adsorption of the components of a sample.

3. APPARATUS

Sample injector

A sample injector is a device by which a liquid or gaseous sample is introduced into the apparatus. The sample can be introduced directly into the carrier gas stream, or into a chamber temporarily isolated from the system by valves which can be changed so as to make an instantaneous switch of the gas stream through the chamber. The latter is a *by-pass injector.*

Column

Solid volume is the volume occupied by the solid support or the active solid in the column.

Liquid volume V_L is the volume occupied by the liquid phase in the column. $V_L = w_L/\rho_L$, where w_L is the weight of the liquid in the column, and ρ_L is its density at the column temperature.

Interstitial volume is the volume of the column not occupied by the liquid phase and its solid support, or by the active solid. It does not include any volume external to the column, such as the volume of the sample injector or of the detector.

Detector

A detector is a device that measures the change of composition of the effluent. A detector that measures instantaneous concentration is called a *differential detector.* An *integral detector* continuously measures the sample accumulated from the beginning of the analysis.

4. REAGENTS

Carrier gas or eluent gas is gas that is used to elute the sample as it passes through the column. The carrier gas forms the *mobile phase.*

Liquid phase is a liquid which is relatively non-volatile at the column temperature and is sorbed on the solid support, where it acts as a solvent for the sample. Separation depends on differences in solubility of the various components of the sample in the liquid phase.

Solid support is normally an inert porous solid, which sorbs the liquid phase. The particle-size range of the support affects column efficiency and the pressure differential necessary to achieve a given flow rate. Modifications of the method have been introduced for the achievement of special separations, in which the solid support is not inert but is an active solid. In capillary columns the inner wall of the column serves as the solid support and obviates the use of additional porous solids for this purpose.

Active solid is a porous solid with adsorptive properties by means of which chromatographic separations may be achieved. The separations resulting from this action follow laws different from those deriving from the partitioning action of the liquid phase.

In gas–liquid chromatography the *stationary phase* comprises the liquid phase without the solid support. In gas–solid chromatography the *stationary phase* is the active solid.

5. CHROMATOGRAM RECORDS

A *chromatogram* is a plot of the detector response *versus* time or volume of carrier gas. Idealized chromatograms obtained with differential and integral detectors for one component are shown in *Figure 1.*

The definitions in this paragraph apply to the chromatograms obtained directly by means of differential detectors or by differentiating the records obtained by means of integral detectors. The *base line* is that portion of a chromatogram recorded when only carrier gas emerges from the column. A *peak* is the portion of the chromatogram recording the detector response while a single component emerges from the column (if separation of a mixed sample is incomplete, two or more components may appear as one peak). The *peak base* CD is an interpolation of the base line between the extremities of the peak. The area enclosed between the peak and the peak base is the *peak area* and the distance BE from the peak maximum to the peak base measured parallel to the axis representing detector response is the *peak height.* The segment of peak base FG intercepted by tangents to

the inflection points on either side of the peak is the *peak width.* The line parallel to the peak base, bisecting the peak height, and terminating at the sides of the peak HJ is the *peak width at half height.*

The following definitions apply to chromatograms obtained with integral detectors. As a sample component passes through the detector, a sigmoid curve is obtained and the base line is displaced to a new position. The change in base line position caused by the sample component is known as a *step*, and the difference in the heights of the two base lines is the *step height.*

6. RETENTION PARAMETERS

Retention volume (uncorrected), V_R is the volume of gas required to elute the compound under study, and is given by

$$V_R = t_R F_c \tag{1}$$

where t_R is the *retention time*, the time for the emergence of the peak maximum after injection of the sample, and F_c is the volumetric flow rate of the carrier gas measured at the outlet pressure and the temperature of the column. V_R, t_R correspond to OB in *Figure 1* which, in the remaining definitions, is assumed to have the carrier gas volume as horizontal axis.

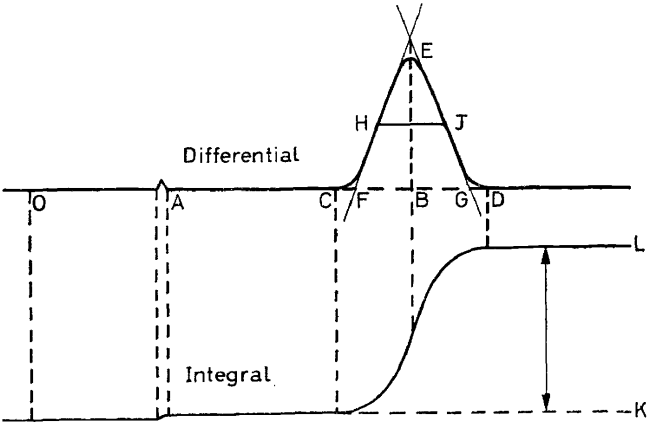

Figure 1

Gas hold-up, V_M is the uncorrected retention volume of a non-absorbed sample and is the volume of carrier gas required to transport such a sample from the point of injection to the point of detection at column outlet pressure. It includes contributions due to the interstitial volume of the column, and the effective volumes of the sample injector and the detector. It can readily be determined for any column by elution of some material for which the partition coefficient is very small compared with its value for other solutes. Gases such as nitrogen, air or the noble gases are normally employed for this purpose. The peak often produced by the presence of small amounts of air during the sample injection gives this information, and is referred to as the *air peak.*

For a capillary column the interstitial volume may be calculated from the dimensions. The interstitial volume divided by j (see below) is the contribution to V_M due to the column and the contribution due to the apparatus may therefore be determined.

Adjusted retention volume, V'_R is given by

$$V'_R = V_R - V_M = AB \tag{2}$$

Corrected retention volume, V°_R is given by

$$V^\circ_R = jV_R = j(OB) \tag{3}$$

This quantity is of limited use because it is influenced by the volumes of sample injector and detector as well as the interstitial volume of the column. The symbol j in equation (3) is the *pressure gradient correction factor* for a homogeneously filled column of constant diameter and is given by

$$j = \frac{3}{2}\left\{\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}\right\} \tag{4}$$

where p_i, p_0 are the pressures of the carrier gas at the inlet and the outlet of the column respectively. Use of the factor j allows for the fact that in gas chromatography the mobile phase is compressible. If in fact the flow rate is measured at the inlet of the column, the corrected retention volume may be obtained by using a suitably modified expression for j.

Net retention volume, V_N is given by

$$V_N = jV'_R = j(AB) \tag{5}$$

Specific retention volume, V_g is the net retention volume at 0°C per gram of liquid phase and is given by

$$\frac{V_N}{w_L} = \frac{V_g T}{273} \tag{6}$$

where T is the absolute temperature of the column. V_N/w_L is the net retention volume per gram at the column temperature.

Retention volumes may be expressed relative to the retention volume of a standard component on the same column at the same temperature. *Relative retention*, r is given by

$$r_{12} = \frac{V_{g1}}{V_{g2}} = \frac{V_{N1}}{V_{N2}} = \frac{V'_{R1}}{V'_{R2}} \neq \frac{V_{R1}}{V_{R2}} \tag{7}$$

where the subscripts refer to components 1 and 2. Component 2 is the standard. Relative retentions measured from the point of injection can only be considered independent of column dimensions if $V_M \ll V_{R1}, V_{R2}$. When, as is usual and desirable, relative retentions are determined from one chromatogram in which experimental conditions are constant and identical for both components, the determination is simplified to the measurement of the appropriate distances on the recorder chart (*i.e.* the distances corresponding to the adjusted retention volumes).

Partition coefficient, K is defined as

$$K = \frac{\text{(weight of solute)/(ml stationary phase)}}{\text{(weight of solute)/(ml mobile phase)}}$$

and is assumed to be independent of concentration at the concentrations prevailing in gas chromatography.

According to elementary theory, which has been adequately verified by experiment, the partition coefficient is related to the retention volume by

$$K = \frac{V_N}{V_L} = \frac{V_N \rho_L}{w_L} = \frac{V_g T \rho_L}{273} \tag{8}$$

The specific retention volume, the relative retention and the partition coefficient are independent of column parameters but they do depend upon the samples involved, the partitioning system and the temperature.

Meaning of qualifying signs—In definitions of retention parameters the superscript ° indicates that the pressure correction factor has been applied, and the prime ′ that measurements are made from the air peak. However, the symbol for net retention volume in accordance with this scheme is unduly cumbersome, and V_N has been substituted for it.

7. RECOMMENDATIONS: RETENTION DATA

Measurements of retention data should be reported in such a manner that they can be converted for use in experiments with other apparatus and under different conditions. This can be done on an absolute basis, by measurement of the partition coefficient or specific retention volume; or on a relative basis, by measurement of relative retentions, relative to a standard solute. For determining the relative retentions of a series of substances a standard should be chosen such that its retention volume falls near the middle of the series. Standards with very small retention volumes should not be used. The following substances are suggested as suitable standards for medium temperature work (*i.e.* up to 150°C):

n-butane
2,2,4-trimethylpentane (iso-octane)
benzene
p-xylene
naphthalene
methylethylketone
cyclohexanone
cyclohexanol

All these substances can be obtained easily in adequate purity and they cover a wide range of retention volumes, but if none of them is suitable for a particular problem some other easily available laboratory chemical should be used.

Temperature effects

Whenever possible the variation of retention volume with temperature should be found and results reported for at least two temperatures, as far apart as is practicable. If results are sufficiently extensive, a suitable graphical method is a plot of the logarithm of the relative retention against the reciprocal of the absolute temperature. Variation of specific retention volume may be expressed in a similar way or by means of an Antoine equation:

$$\log V_g = A + \frac{B}{t + C} \tag{9}$$

in which t is the column temperature in °C and A, B, C are constants. The relations so obtained can conveniently be used for interpolation.

Experimental details

The following experimental variables should be published with any set of results laying claim to being quantitative in nature:

nature and particle-size range of solid support;
nature, concentration and amount of liquid phase in the column;
sample size;
column dimensions (length and internal diameter);
column inlet and outlet pressures;
flow rate of carrier gas and method of measurement;
temperature of column and accuracy of temperature control;
description of detector, *e.g.* type of sensing element, cell geometry, cell volume, response time.

8. APPARATUS PERFORMANCE

Column performance—An expression of column performance in terms of theoretical plate number n can be calculated by the equation

$$n = 16 \times \left(\frac{\text{retention volume}}{\text{peak width}}\right)^2 = 16\left(\frac{OB}{FG}\right)^2 \tag{10}$$

(see *Figure 1*). The theoretical plate number may vary with the compound as well as the column. Therefore the compound used should be specified. The units for retention and peak width used in equation (10) must be consistent so that their ratio n is dimensionless. If the corrected retention volume is used, the observed peak width must also be corrected for pressure drop in the column.

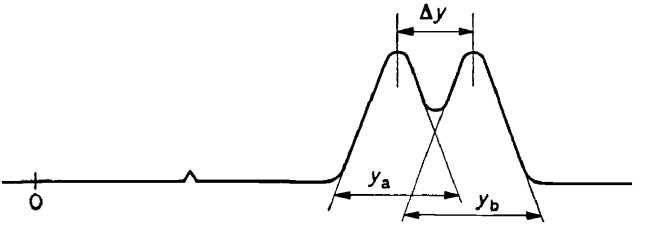

Figure 2

Peak resolution—If two compounds are well enough separated to permit a satisfactory estimation of the peak width, and the peaks are approximately Gaussian, as shown in *Figure 2*, the resolution may be expressed by

$$\text{Resolution} = 2 \times \frac{\text{difference between retention volumes}}{\text{sum of peak widths}} \qquad (11)$$

$$= 2\Delta y/(y_a + y_b)$$

By relating equations (7), (10) and (11), it is then possible to calculate the number of plates required for a specified resolution.

$$n = \left\{2 \times \text{Resolution} \frac{(r+1)}{(r-1)}\right\}^2 \qquad (12)$$

9. DISCUSSION

The partition coefficient for a given solute–solvent system is (for conditions prevailing in gas–liquid chromatography) a physical constant dependent only on the temperature, and gas–liquid chromatography provides a convenient method for its determination. The specific retention volume V_g has the same character of a general constant, and can easily be converted to K by relation (8). In the determination of K it is necessary to determine the density of the solvent at the column temperature (to about 1 per cent) while this is not necessary for the determination of V_g. The other column variables and operating conditions, however, have to be accurately known since they enter into the computation of K and V_g, as can be seen from the relations given above.

In the determination of relative retentions, it is not necessary to know any column variables (*e.g.* F_c, w, p_i, p_0), except the temperature; all that is necessary is that they remain constant. Furthermore, relative retentions do not vary with temperature as much as do absolute measurements and they are therefore to be preferred unless the variables listed can be determined with accuracy. Relative retentions, used with standard substances as suggested above, are immediately useful for the identification of compounds if tables of retentions including the compounds in question are available.

It is important to specify the ratio of liquid phase to solid support precisely. The activity of the latter can be such as to influence appreciably the chromatographic separations achieved; this effect will be more pronounced the lower the amount of liquid phase covering the solid.

Errors

The following factors can affect the retention parameters and will cause errors unless they are corrected for: sample size, method of injection and detector dead volume. These factors affect not only the retention parameters but also the peak shape, and therefore can give misleading results also in the calculation of efficiency and resolution. These calculations, then, should not be relied on unless the distorting factors are small, and the peaks obtained nearly Gaussian.

Experimental considerations

The flow rate F_c is required at the temperature and outlet pressure of the column, whereas measurements of flow are usually made at room temperature. Suitable corrections must therefore be made: if a capillary flowmeter is used, the pressure drop across the meter must be considered; with wet flowmeters allowance must be made for the vapour pressure of water. If F is the flow rate of the saturated gas determined from the flowmeter at pressure p, and p_w is the vapour pressure of water at the temperature of the flowmeter, the partial pressure of the carrier gas, p_M is given by

$$p_M = p - p_w$$

and

$$F_c = F(p - p_w)/p \qquad (13)$$

The carrier gas should enter the column at column temperature; the sample should be made to vaporize very rapidly on injection in order to avoid artifacts of efficiency or resolution.

In absolute measurements, account must be taken of the temperature of operation in assessing the life of the column before a significant change in w_L occurs. The rate of variation of the partition coefficient with temperature is similar in magnitude to that of vapour pressure, and the accuracy of temperature control, both with time and along the column, needs to be specified.

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TABLE OF TERMS

English	*French*	*German*	
Gas chromatography	Chromatographie des gaz	Gas-Chromatographie	
Gas–liquid chromatography	Chromatographie gaz-liquide	Gas-Flüssigkeit-Chromatographie	
Gas–solid chromatography	Chromatographie gaz-solide	Gas-Festkörper-Chromatographie	
Sample injector	Injecteur d'échantillon	Probeninjektor	
By-pass injector	Injecteur à dérivation	Umleitinjektor	
Differential detector	Détecteur différentiel	Differentialdetektor	
Integral detector	Détecteur intégral	Integraldetektor	
Solid volume	Volume solide	Festkörpervolumen	
Liquid volume	Volume liquide	Flüssigkeitsvolumen	
Interstitial volume	Volume interstitiel	Gasraumvolumen	
Carrier gas	Gaz porteur	Trägergas	
Mobile phase	Phase mobile	mobile Phase	
Stationary phase	Phase stationnaire	stationäre Phase	
Liquid phase	Phase liquide	flüssige Phase	
Solid support	Support solide	inaktiver *oder* aktiver fester Träger	
Active solid	Solide actif	Adsorbens	
Chromatogram	Chromatogramme	Chromatogramm	
Base line	Ligne de base	Basislinie	
Peak	Pic	Pik*	
Peak base	Base du pic	Pikbasis	
Peak area	Surface du pic	Pikoberfläche	
Peak height	Hauteur du pic	Pikhöhe	
Peak width	Largeur du pic	Pikbreite	
Peak width at half height	Largeur du pic à demi-hauteur	Pikbreite bei halber Höhe	
Step	Palier	Stufe (in einem Integral-Chromatogramm)	
Step height	Hauteur de palier	Stufenhöhe (in einem Integral-Chromatogramm)	
Retention volume	Volume de rétention	unkorrigiertes Retentionsvolumen	V_R
Adjusted retention volume	Volume de rétention réduit	reduziertes Retentionsvolumen	V'_R
Corrected retention volume	Volume de rétention limite	korrigiertes Retentionsvolumen	V°_R
Net retention volume	Volume de rétention absolu	Netto-Retentionsvolumen	V_N
Specific retention volume	Volume de rétention spécifique	spezifisches Retentionsvolumen	V_g
Pressure gradient correction factor	Facteur de correction du gradient de pression	Korrekturfaktor für den Druckgradienten	j
Gas hold-up	Retenue de gaz	Nullretentionsvolumen	V_M
Relative retention	Rétention relative	relative Retention	r_{12}
Partitition coefficient	Coefficient de partage	Verteilungskoeffizient	K
Column performance	Efficacité de la colonne	Trennschärfe der Kolonne	
Peak resolution	Résolution des pics	Pikauflösung	
Number of theoretical plates	Nombre de plateaux théoriques	Zahl der theoretischen Stufen der Kolonne	n

* In der deutschsprachigen Fachliteratur wird sehr oft das Wort "peak" als solches gebraucht. In der Umgangssprache wird das gleiche Wort so oft verwendet, dass die Autoren sich entschlossen, das Wort in obenstehender Schreibweise vorzuschlagen, umsomehr als es früher in der deutschen Sprache gebraucht wurde (vgl: *Der Grosse Duden*, Bibliographisches Institut AG, Leipzig, 1932: der Pik, des Piks, die Pike).