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Retention Time in Nonlinear Gas–Liquid Chromatography. Influence of the Sample Size

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Summary

It is shown that sample size has a significant effect on the retention time in gas–liquid chromatography. The retention time was measured accurately by detecting the entry impulse as well as the response impulse.

The deviation from the retention time at infinite dilution is shown to be a consequence of a nonlinearity in the basic transfer relations. A specific approach based on a method of moments is proposed. It is assumed that the activity coefficient of the solute in the liquid phase does not vary with the concentration.

This deviation is correlated in terms of a single dimensionless parameter, and the agreement with the experimental data is good.

INTRODUCTION

Among the applications of gas–liquid chromatography, the determination of thermodynamic parameters by measuring retention times is of great importance. Many papers deal with the attempt to measure activity and partition coefficients, heats of solutions, crossed second virial coefficients, and excess properties of mixing. A general review of the subject is given by Kobayashi, Chappelear, and Deans (*1*), and the formulas relating these different thermodynamic parameters to the retention time at infinite dilution can be found elsewhere (*2*).

The effect of a finite concentration of the solute is considered in the following, and the retention time at infinite dilution is related to the retention time measured for a given sample size.

EXPERIMENTAL RESULTS

The apparatus which has been used is very similar to a conventional gas–liquid chromatography unit, equipped with a thermal conductivity detector. The carrier gas, containing the sample, goes through the detector twice before entering and after leaving the column. The entry impulse is known as well as the response impulse which allows an accurate measurement to be made of the retention time. The flow rate of the carrier gas is regulated by needle valves and measured when it leaves the column by a soap-bubble flowmeter at atmospheric pressure. The volume of pure solute injected is determined by measuring the peak area. Different columns of various lengths (from 0.5 to 2 m) and various diameters (⅛ or ¼ in.) are used. They are packed with Fluoropak and immersed in a liquid bath at $25 \pm 0.1°C$.

The solutes are light gases such as propane, *n*-butane, isobutane, propylene, propyne, and 1,3-butadiene. Heptadecane is the solvent.

The solubility of all the gases considered is low, and the molar liquid fraction of the solute is small compared with the molar vapor fraction. This molar liquid fraction has no significant influence on the solute activity coefficient in the liquid phase. It will be assumed that this activity coefficient remains constant and independent of the solute concentration. This excludes some systems for which the activity coefficient varies rapidly with the concentration.

Figure 1 shows how the variation of the volume of the sample (in microliters) affects the retention time (in seconds) when the flow rate remains constant. The deviation from the retention time at infinite dilution (obtained by extrapolation) is equal to 10% for the largest sample injected. It appears that neglecting this deviation can lead to an important error in the value of the activity coefficient.

REVIEW OF PREVIOUS RESEARCH

Many authors (*3–8*) have noticed the variation of the retention time with the feed volume in gas chromatography. A great amount of research has been done in an attempt to predict the effect of a variable activity coefficient or of a nonlinear adsorption isotherm (*9–11*). But it has also been recognized that, even if the partition coefficient remains constant, the retention time varies with the sample size as a result of the solute partial pressure gradient along the column. Bosanquet and Morgan (*12*, *13*) first pointed out the importance of solute concentration; Schay (*14*) and Golay (*15*) analyzed the progression of a square wave. For finite concentrations a correction was proposed,

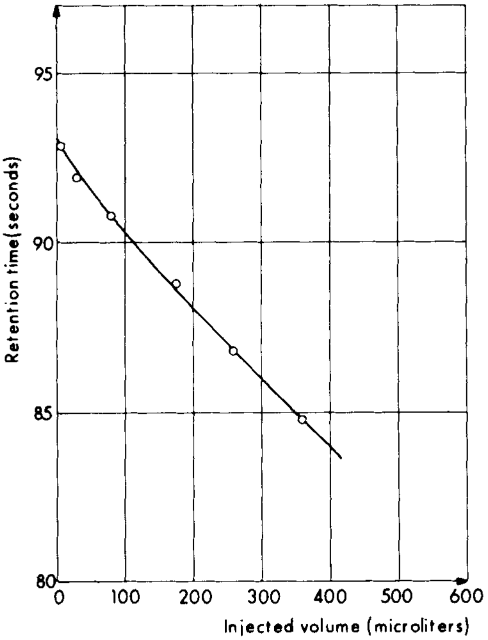

FIG. 1. Retention time vs injected volume. Solute: Propylene. Solvent: Heptadecane.

based on the consideration that the velocity of the mobile phase is greater in the pulse region. Peterson and Helfferich (*6*) have applied this theory to various cases, but their analysis is correct only if it is possible to assume that a constant solute concentration exists in the pulse region during its progression along the column. It appears possible to determine a correlation between the retention time and the sample size based on more general assumptions.

Experimental work is comparatively scarce. Porter, Deal, and Stross (*9*) have presented an experimental curve showing the variation of the apparent retention volume with the sample size, but the time origin is the time of introduction of the sample, and the correction includes the effect of band spreading in the injection chamber as well as the deviation due to finite concentrations in the column itself.

CORRELATION BETWEEN THE RETENTION TIME AND THE SAMPLE SIZE

The variation of the retention time versus the sample size must be the result of a nonlinearity in the basic transfer relations. In order to establish these relations the following assumptions will be made:

1. Constant activity coefficient of the solute in the liquid phase.
2. Constant total pressure along the column.
3. The carrier gas and the solute behave as ideal gases.
4. There is no influence of heat of sorption.

Let ϵ be the porosity of the solids in the column, S the section of the column, H the vacuum fraction occupied by the gaseous phase, a the liquid–gas interfacial area per unit volume, V the mobile phase molar volume, and K the transfer coefficient. A section in the column is located by its distance z from the entry. The flow rate F of the carrier gas is expressed in moles per unit time, and v denotes the ratio F/S.

If a large amount of component A is injected, it becomes necessary to distinguish between the concentration C_g, the mole fraction of A in the gaseous phase, and the concentration C'_g defined on an A free basis.

$$C_g = \frac{\text{moles of } A}{\text{moles of } A + \text{moles of carrier gas}}$$

$$C'_g = \frac{C_g}{1 - C_g} = \frac{\text{moles of } A}{\text{moles of carrier gas}}$$

In the liquid phase, only the mole fraction C_l is needed.

At equilibrium,

$$C_g = mC_l$$

The differential equations relating C_l and C_g or C'_g to z and to time t are obtained by a material balance on A around an element dz.

$$v \frac{\partial}{\partial z} C'_g + \frac{\epsilon H}{V} \frac{\partial}{\partial t} C_g + Ka(C_g - mC_l) = 0 \tag{1}$$

$$\frac{\epsilon(1 - H)}{V} \frac{\partial}{\partial t} C_l - Ka(C_g - mC_l) = 0 \tag{2}$$

As C_g is equal to the ratio $C'_g/(1 + C'_{g'})$, this system can be solved for C'_g and C_l. The differential equations relating C'_g and C_l to z and t are nonlinear on account of the nonlinearity of the relation between C_g and C'_g. If the solute concentration remains small, C'_g and C_g can be equated, and the differential equations become linear.

The boundary conditions are:

At $t = 0$

$$C'_g = C_l = 0 \tag{3}$$

At $z = 0$

$$C'_g(t) = C'_{ge}(t) \tag{4}$$

The boundary condition (4) introduces the time function $C'_g = C'_{ge}(t)$, representing the entry impulse. As the injection time is very short, the entry impulse is practically equivalent to a Dirac impulse $\delta(t)$, at $t = 0$.

If the set of Eqs. (1) and (2) is expressed in terms of Laplace transform variables $\overline{C_g}$, $\overline{C'_g}$, and $\overline{C_l}$, it is possible to eliminate $\overline{C_l}$.

The system of equations reduces to:

$$\frac{d}{dz}\overline{C'_g} + \pi\overline{C_g} = 0 \tag{5}$$

The factor π is a function of p:

$$\pi = \frac{p}{v}\left[\frac{\epsilon H}{V} + \frac{Ka\epsilon(1 - H)}{mKaV + \epsilon(1 - H)p}\right] \tag{6}$$

p being the Laplace operator.

Instead of trying to solve Eq. (5) in the general nonlinear case and to inverse $\overline{C_g}$, it is possible to make use of the method of moments which enables the retention time t_R to be determined directly.

If $C_g'^{(1)}$ represents the first moment, $C'_{g_1} = \int_0^\infty tC'_g(t)\, dt$ and C'_{g_0} the surface of the impulse curve $C'_g(t)$, $C'_{g_0} = \int_0^\infty C'_g(t)\, dt$, then:

$$t_R = \frac{C_g'^{(1)}}{C'_{g_0}} \tag{7}$$

Let N be the number of moles of A introduced at $t = 0$.

$$N = \int_0^\infty FC'_g(t)\, dt \tag{8}$$

Therefore:

$$C'_{g_0} = \frac{N}{F} = \frac{I}{VF} \tag{9}$$

with I being the volume of the sample of A, and VF the volumetric flow rate of carrier gas.

The moments $C_g'^{(n)}$ of the response impulse may be obtained by successive derivation with respect to the Laplace operator p and by use of the relation:

$$C_g'^{(n)} = (-1)^n \left[\frac{d^n\overline{C_g'}}{dp^n}\right]_{p=0} \tag{10}$$

Therefore, the mean retention time t_R may be directly calculated by differentiating both sides of Eq. (5) with respect to p:

$$\frac{d}{dz} C_g'^{(1)} = \pi_1 C_{g_0}' \tag{11}$$

In this equation, C_{g_0} represents the integral $\int_0^\infty C_g(t)\, dt$, and π_1 is equal to $[d\pi/dp]_{p=0}$

$$\pi_1 = \frac{1}{Vv}\left[\epsilon H + \frac{1}{m}\epsilon(1 - H)\right] \tag{12}$$

In the linear case, $C_{g_0} = C_{g_0}'$. Thus:

$$C_g'^{(1)} = \pi_1 C_{g_0}' z \tag{13}$$

$$t_{ml} = \frac{l}{Vv}\left[\epsilon H + \frac{1}{m}\epsilon(1 - H)\right] \tag{14}$$

In the general nonlinear case, C_{g_0} is different from C_{g_0}', and whereas C_{g_0}' remains constant, C_{g_0} is a function of z. For a Dirac entry impulse, C_{g_0} starts from zero and tends towards C_{g_0}' as the impulse curve flattens. In order to integrate the differential Eq. (11), it is necessary to estimate the function $C_{g_0(z)}$.

$$C_{g_0(z)} = \int_0^\infty \frac{C_g'(z,t)}{1 + C_g'(z,t)}\, dt \tag{15}$$

One way of doing this consists of introducing the linear approximation value of $C_g'(z,t)$ into integral (15). This integral is independent of any translation of the impulse curve.

The number of transfer units in gas-liquid chromatography is high (*16*). In this case, when the assumption of linearity is made, C_g' may be represented with good accuracy by the Gaussian curve:

$$C_g'(t) = \frac{C_{g_0}'}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(t - t_R)^2}{2\sigma^2}\right\} \tag{16}$$

The variance σ is given by:

$$\sigma = \alpha\sqrt{z} = \frac{\epsilon(1-H)}{m}\sqrt{\frac{2z}{vK_a}} \tag{17}$$

Therefore:

$$C_{g_0(z)} = C'_{g_0}\int_{-\infty}^{+\infty}\frac{e^{-u^2/2}\,du}{\sqrt{2\pi}+\dfrac{C'_{g_0}}{\sigma_s}e^{-u^2/2}} \tag{18}$$

Equation (11) becomes:

$$\frac{C'^{(1)}_g}{C'_{g_0}} = \pi_1\int_0^z dz\int_{-\infty}^{+\infty}\frac{e^{-u^2/2}}{\sqrt{2\pi}+\dfrac{C'_{g_0}}{\alpha\sqrt{z}}e^{-u^2/2}}\,du \tag{19}$$

Integration is done first on z and then on t. Finally, at $z = L$:

$$t_R = \frac{C'^{(1)}_g}{C'_{g_0}} = t_{Rl}\left[1-\varphi\left(\frac{C'_{g_0}}{\sigma_s}\right)\right] \tag{20}$$

with:

$$\varphi\left(\frac{C'_{g_0}}{\sigma_s}\right) = \frac{1}{\sqrt{\pi}}\frac{C'_{g_0}}{\sigma_s}+\frac{2}{\sqrt{3}}\left(\frac{C'_{g_0}}{\sqrt{2\pi}\sigma_s}\right)^2\ln\left(\frac{C'_{g_0}}{\sqrt{2\pi}\sigma_s}\right)-\frac{1}{3\sqrt{3}}$$
$$\times\left(\frac{C'_{g_0}}{\sqrt{2\pi}\sigma_s}\right)^2-2\left(\frac{C'_{g_0}}{\sqrt{2\pi}\sigma_s}\right)^2\sum_{n=1}^{\infty}(-1)^{n+1}\frac{1}{n\sqrt{n+3}}\left(\frac{C'_{g_0}}{\sqrt{2\pi}\sigma_s}\right)^n \tag{21}$$

t_{Rl} is the mean retention time calculated by assuming linearity and is given by Eq. (14). In Eq. (21), σ_s is the variance of the response impulse and $C'_{g_0} = I/VF$.

COMPARISON WITH EXPERIMENTS

As shown above, the volumetric flow rate VF and the injected volume I are measured for each experiment. The variance σ_s is determined on the experimental chromatogram.

It is now possible to plot the experimental value of φ versus the dimensionless parameter C'_{g_0}/σ_s.

The product $\varphi\cdot t_{Rl}$ is taken as the difference between the retention time at infinite dilution t_{Rl} obtained by extrapolation (see Fig. 1) and the measured retention time t_R for a given sample size:

$$\varphi_{\text{exp}} = \frac{t_{Rl}-t_R}{t_{Rl}}$$

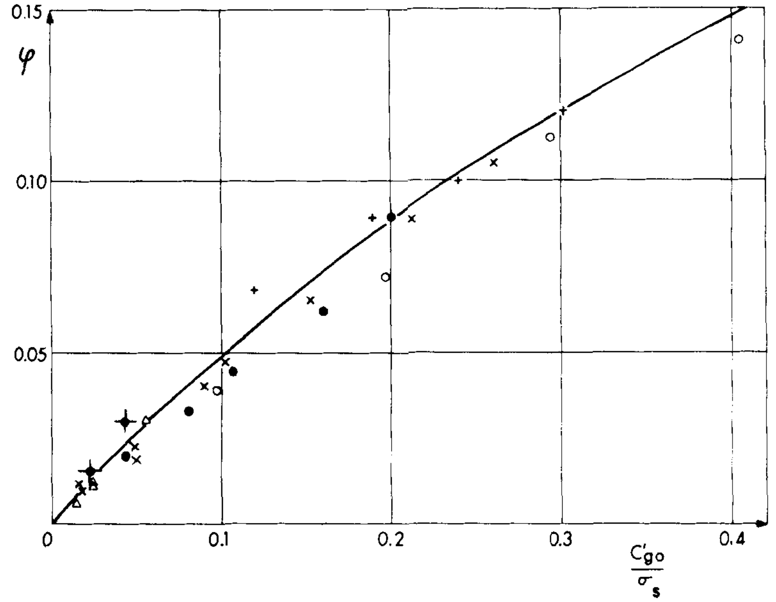

FIG. 2. Relative deviation of retention time from its infinite dilution value vs dimensionless parameter C'_{g0}/σ. Solutes: (●) propane, (×) propylene, (╋) butane, (△) isobutane, (+) 1,3-butadiene, and (○) propyne. Solvent: Heptadecane. (—) theoretical curve.

These experimental values of φ are compared with the values of φ calculated from Eq. (21) on a digital computer. They are plotted in Fig. 2. The agreement is good, and the deviations between experimental and predicted values do not exceed the experimental error in the values of the measured parameters.

CONCLUSION

The deviation of the retention time from its ideal value based on the linear assumption has been expressed in terms of the single parameter C'_{g_0}/σ_s. This deviation is shown to depend not only on the sample size but also, through σ_s, on the length of the column and its elution properties.

It should be noted that the correlation given applies only when the variance σ_s is much greater than σ_e, the variance of the entry impulse which has been assumed to be instantaneous. If not, the integration can be modified to take into account this new condition at $z = 0$.

It appears that the theoretical approach proposed in this paper could be extended to other cases, especially to the case of a variable activity coefficient.

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Nomenclature

a	liquid gas interfacial area per unit volume
C_g	mole fraction of solute in the gaseous phase
C_l	mole fraction of solute in the liquid phase
C'_g	mole fraction on a solute free basis
$C'_g(n)$	moment of order n of the impulse curve
$G_{ge}(t)$	entry impulse curve
$C_{g_0}(t)$	time integral of the impulse curve
F	flow rate of carrier gas
H	void fraction of the column occupied by the gaseous phase
I	injected volume of the solute
K	transfer coefficient
L	length of the column
m	equilibrium constant
N	number of moles of solute introduced at $t = 0$.
P	Laplace operator
S	section of the column
t_R	retention time
t_{Rl}	infinite dilution retention time
v	flow rate per unit section
V	mobile phase molar volume

Greek Letters

α	ratio of σ over $\sqrt{z}$
$\delta(t)$	Dirac impulse
ϵ	porosity of the solids
π	function of p
π_1	ratio of t_{Rl} over L
σ	variance of the impulse at z
σ_e	variance of the impulse at $z = 0$
σ_s	variance of the impulse at $z = L$
φ	relative deviation from the infinite dilution retention time

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