

Precision and accuracy of the gas–solid adsorption isotherms derived by the elution-by-characteristic-points method

Jeffry Roles and Georges Guiochon*

**Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1501 and Division of Analytical Chemistry, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120 (USA)*

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ABSTRACT

The influence of the fluctuations of the experimental parameters on the reproducibility of the overloaded band profiles used to determine the isotherms by the elution-by-characteristic-points (ECP) method was investigated using two new tools. A parameter measuring the difference between two similar curves, such as overloaded elution profiles or adsorption isotherms, was defined. The band profiles measured were compared with those calculated from the derived isotherm, using models from the theory of non-linear chromatography. The agreement between both profiles was defined as a distance lower than twice the average distance between two profiles measured on the same day on the same column. The degree of validity of the various assumptions made in the ECP method was assessed.

INTRODUCTION

In a companion paper [1], we described the procedure used for the acquisition of the experimental data needed for the accurate determination of equilibrium isotherms using the classical elution-by-characteristic-points (ECP) method [2–4]. In this paper, we discuss the sources of errors encountered in this determination and the procedures used to eliminate or reduce these errors and to validate the data obtained. In a further paper [5] we shall discuss the similar problems in the derivation of the adsorption energy distribution from the isotherm data. The aim of this work was the development of a procedure for the study of the solid surfaces encountered in a number of applications (*e.g.*, the manufacture of advanced ceramic materials, the production of fillers and pigments and the preparation of adsorbents for chromatography).

It is important for us to assess the precision and accuracy of the isotherm data because the experimental isotherm will be used to derive the adsorption energy distribution. This distribution is not accessible otherwise than by using a theoretical

model [6,7] and applying it to the experimental data. For reasons of experimental convenience [1], we have used the ECP method to derive the isotherm from the band profile acquired. It is important, therefore, to test carefully each step of the computation proving the validity of the model and to make sure that experimental errors are kept low enough and cannot generate significant artefacts. The situation is complicated by the fact that two models must be validated successively: the chromatographic model used to calculate the isotherm from the elution profile (ECP model [2–4]) and the Langmuir model of localized adsorption which is used to relate the adsorption energy distribution to the parameters of the experimental isotherm.

Although the determination of equilibrium isotherms using chromatographic methods has been discussed and reviewed abundantly and in detail [8,9], too little attention has been devoted to the precision and accuracy of the data obtained. In addition to the general lack of interest of most chromatographers in the study of accuracy, this apparent neglect stems from the difficulty of the problem. It is much more difficult to quantify

uncertainties in non-linear than in linear chromatography. For example, in the latter method the retention time is used to calculate the slope of the linear isotherm. The reproducibility of retention times is measured by a simple standard deviation. In contrast, in non-linear chromatography, one must measure the reproducibility of a whole chromatogram, consisting of a set of retention times as a function of peak heights. In order to quantify the uncertainty, various figures of merit can be chosen, *e.g.*, the distance, Δ , between two curves obtained by distribution function analysis [10,11]. The mere fact that several figures of merit are deemed necessary to describe and quantify the reproducibility is in itself an indication of the difficulty involved in this endeavor.

THEORY

As we are studying the properties of heterogeneous surfaces by determining the adsorption isotherms of probe components, we are only interested here in the band profiles of samples of single, pure compounds. This work is based on the use of the equilibrium-dispersive model of non-linear chromatography, which relates the elution profile of high-concentration bands, the equilibrium isotherm of the component between the two phases of the chromatographic system and the column efficiency [12]. We use the model in both directions. In the direct problem, we calculate the elution profile knowing the isotherm, the column efficiency and the sample size. In the inverse problem, we derive the isotherm from the recorded elution profile of a known amount.

From a purely mathematical point of view, the direct problem is well posed and its solution is straightforward, even if it is difficult or even impossible to derive a closed-form solution. The numerical calculation of solutions raises no difficulty of principle [13]. The inverse problem is still poorly understood by mathematicians and few fundamental results are available with which the physical chemist can work. As a consequence, it is investigated using only very simple boundary conditions, *e.g.*, frontal analysis. Although more complex in principle, ECP proves the point: it is based on the use of one of the few analytical solutions of the direct problem, in the case of the ideal model. ECP is widely used in gas

chromatography for its simplicity. A brief discussion of the direct and inverse problems of chromatography is useful.

Calculation of chromatographic band profiles from the adsorption isotherms

The elution profiles of single-component bands are obtained as solutions of the system of mass-balance equation for the component considered and for the mobile phase [12,14,17]:

$$\frac{\partial PuX}{\partial z} + P \cdot \frac{\partial X}{\partial t} + \frac{RTm_g}{V_g} \cdot \frac{\partial q}{\partial t} = D \cdot \frac{\partial^2 X}{\partial z^2} \quad (1a)$$

$$\frac{\partial Pu(1-X)}{\partial z} - P \cdot \frac{\partial X}{\partial t} = -D \cdot \frac{\partial^2 X}{\partial z^2} \quad (1b)$$

where $p = XP$ is the partial pressure of the probe, P the pressure of the mobile phase, X the mole fraction of the probe, q its concentration in the stationary phase, z and t the abscissa and time coordinates, respectively, u the local mobile phase velocity, R the universal gas constant, T the column absolute temperature, m_g the mass of stationary phase per unit column length, V_g the void volume per unit column length and D the apparent dispersion coefficient.

These two partial differential equations are completed by the equilibrium isotherm [$q = f(p)$], the apparent dispersion coefficient, D , related to the column efficiency, and the Darcy equation relating the mobile phase velocity and the pressure gradient [13–15]. In most instances, it is convenient to assume that the passage of the high-concentration band does not modify the pressure profile along the column [14]. The pressure profile remains the steady-state profile observed when pure carrier gas flows through the column:

$$P(z) = P_o \sqrt{\left(\frac{P_i}{P_o}\right)^2 - \frac{z}{L} \left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]} \quad (2)$$

where P_i and P_o are the inlet and outlet column pressures, and L is the column length.

It is not possible to derive analytical solutions of the system of equations of either the ideal or the equilibrium-dispersive model in gas chromatography [12–15]. On the other hand, numerical solutions can be easily derived, using a variety of calculation schemes [13,14,16]. As we discuss elsewhere, the band profiles supplied by such calculations are

in excellent agreement with experimental results [13,16,17]. Obviously, the agreement between the experimental band profile and the profile calculated as a numerical solution of the equilibrium-dispersive model of chromatography is a useful test of the validity of the model used to derive the isotherm from the experimental data and of the self-consistency of the approach used to interpret these experimental results.

Derivation of the adsorption isotherm from the profile of high-concentration bands

Several methods have been used to derive equilibrium isotherms from chromatographic data pertaining to pure compounds [9]. Among them, the ECP method is the most popular in gas chromatography because of the simplicity of its implementation [2-4]. It has been used in this work to derive adsorption isotherms from the profile of high-concentration bands of the probe components.

If we neglect the influence of the apparent dispersion on the band profile, assume the axial dispersion to be negligible and the rate of the mass-transfer kinetics to be infinite, we have a column with an infinite efficiency (*i.e.*, $D = 0$ in eqn. 1). In this case, it is easy to show that a velocity is associated with each concentration and that the band profile derives directly from the combination of these velocities [12,18]. In the case of a convex upwards isotherm, the velocity associated with a concentration increases with increasing concentrations. As high concentrations cannot pass low ones, the profile has a front shock and a diffuse rear [12,19]. The equation of the band rear [3,12,20] is

$$t = t_p + t_0 \left(1 + F \cdot \frac{dq}{dc} \right) \quad (3)$$

where t_p is the width of the rectangular injection plug, t_0 is the hold-up time, F a phase ratio and $q(c)$ is the equilibrium isotherm. The position of the shock is also easy to calculate [21], but is not useful in the present application. Eqn. 3 gives the band rear when the isotherm is convex upward, *i.e.*, when $d^2q/dc^2 < 0$, the band front in the other case. It is valid only in liquid chromatography, as it neglects the compressibility of the mobile phase and the difference in partial molar volumes of the component in the gas and the stationary phases. We discuss first the influence of the finite column efficiency,

then that of the mobile phase compressibility and density.

Influence of a finite column efficiency. The ECP method is directly derived from eqn. 3. In our case, it is applied to the rear of the profile. Unfortunately, the column has a finite efficiency and the rear profile is broadened by dispersion.

Golay has derived equations which yield the elution profile of a band in linear chromatography, with an open-tubular column, either with a liquid-coated wall [22] or with a porous layer along the wall [23]. These equations take effectively into account the influence of the axial dispersion and of the finite kinetics of mass transfers in the column. However, they are not applicable in non-linear chromatography. In this instance, the influence of the thermodynamics and the mass-transfer kinetics on the band profile cannot be separated. The problem has no exact analytical solution. Several approaches have been suggested.

Haarhoff and Van der Linde [24] and Conder and Purnell [15] studied the elution band profile in the case of a finite column efficiency and with a parabolic isotherm (*i.e.*, a two-term expansion of the isotherm). Neglecting the gas-phase compressibility, which was taken into account by Conder and Purnell, Haarhoff and Van der Linde derived an approximate equation which gives satisfactory results at moderate concentrations [9,20]. This solution, however, is not generally applicable for the determination of equilibrium isotherms, as it assumes that they are parabolic.

The calculation of numerical solutions of the differential mass-balance equation of the probe solute in a slice of the column (*i.e.*, eqns. 1) has been developed [13,16,25]. The algorithms for these numerical calculations are written on the assumptions that the column efficiency is high enough, the stationary phase is always almost in equilibrium with the mobile phase and the effect of a finite column efficiency can be accounted for by using an apparent dispersion term in place of the axial dispersion term in the mass-balance equation. These numerical solutions permit an accurate prediction of the band profile when the isotherm is known [26,27], provided that the rates of the mass-transfer kinetics and of the kinetics of adsorption-desorption are large enough and the column efficiency exceeds a few hundred theoretical plates.

In the adsorption of light vapors, such as diethyl ether (molecular weight, MW = 74 dalton, b.p. 34.5°C) or 1-chlorobutane (MW 92 dalton, b.p. 78.4°C), adsorbed on solid alumina particles, the mass-transfer kinetics have to be fast: the thickness of the porous layer coated on the column wall is of the order of 1 μm [1]. As long as the adsorption energy is not very high, the kinetics of adsorption-desorption are also fast, so we can expect the column efficiency to be high enough to warrant the use of the equilibrium-dispersive model for the calculation of band profiles in the case studied here. Chemisorption of ethers on alumina is a distinct possibility. However, chemisorbed molecules will not be eluted to a significant extent during the time of an experiment. The extent to which chemisorption is involved will be seen if a mass balance of the probe solute can be measured.

Gas-phase compressibility and density. If we take into account these effects, but still assume that the column efficiency is infinite (*i.e.*, $D = 0$ in eqn. 1), and consider the migration of a given partial pressure, we obtain an equation which can be integrated into [2-5,15]

$$V_g = J_3^2 RT(dq/dp) \quad (4)$$

where V_g is the specific retention volume of the partial pressure p and J_3^2 is the James and Martin correction factor [28]. (Assumptions made in the derivation of eqn. 4 are given in the Appendix.) Slightly different forms of this equation, which is the basis of the ECP method, have been published by Cremer and Huber [2-4], Chueh and Ziegler [29], Peterson and Helfferich [30] and Conder [31].

Eqn. 4 assumes that the mobile phase is an ideal gas. Conder and Purnell [15] derived an equation similar to eqn. 4, which relates the retention volume of a concentration, the gas compressibility factor, the non-ideal behavior of the carrier gas and the slope of the isotherm:

$$V_N = V_s(1 - ajy_o) \left(\frac{\partial q}{\partial C} \right)_{P=P_m} \quad (5)$$

where V_N is the net retention volume [$j(V_R - V_m)$], V_s is the amount of adsorbent in the column, y_o is the mole fraction of the characteristic point when it reaches the column outlet (note that a characteristic point in gas chromatography has a constant concentration, C , hence a rising mole fraction in the gas

phase as the pressure falls along the column), j is the actual pressure gradient correction factor (different from the James and Martin factor which assumes ideal gas behavior), the pressure P_m is an average pressure given by

$$P_m = P_o J_3^4 = \frac{3P_o}{4} \cdot \frac{\left(\frac{P_i}{P_o}\right)^4 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \quad (6)$$

and the other parameters are

$$a = \frac{b_2^1}{b_3^2} \left[1 + \frac{2y_o P_o B_{11}}{RT} (1 - y_o J_3^2) \right] \quad (7a)$$

$$b_n^m = 1 + k(1 - J_n^m y_o) \quad (7b)$$

$$j = J_3^2 \left[1 + \frac{y_o^2 P_o B_{11}}{RT} (J_3^2 - 1) \right] \quad (7c)$$

$$J_n^m = \frac{n}{m} \left[\frac{(P_i/P_o)^m - 1}{(P_i/P_o)^n - 1} \right] \quad (7d)$$

where k is the mass distribution coefficient, $qV_s/(CV_M^0)$ and B_{11} is the second virial coefficient of the pure solute vapor. It is often possible to simplify these equations and write $a = 1$ and $j = J_3^2$. Hence, under the experimental conditions used in our work (see below, *e.g.*, Fig. 5), the maximum outlet partial pressure of the probe is $3 \cdot 10^{-3}$ atm, thus y_o is 0.003; under our conditions, $J_3^2 = 0.849$; the second virial coefficient for diethyl ether at 60°C derived from the equation of Guggenheim and McGlashan [32] is $-826 \text{ cm}^3 \text{ mol}^{-1}$; hence, from eqn. 7c, $j = 1.000001 J_3^2$ and $a = 0.9998$. Thus,

$$V_N = V_s(1 - J_3^2 y_o) \left(\frac{\partial q}{\partial C} \right)_{P=P_o J_3^4} \quad (8)$$

The compressibility correction term J_3^2 is 0.849, so the correction term in eqn. 8 is $1.2 \cdot 10^{-3}$, which can be neglected. Then, eqn. 8 is equivalent to eqn. 4, as $V_g = V_N/V_s$ and $C = n/V = p/RT$. The point of the isotherm derived from a mole fraction y_o is referred to the partial pressure $y_o P_o J_3^4 = 1.186p$, which requires a significant correction on the isotherm, but one which is simple, corresponding to a mere expansion of the pressure scale.

EXPERIMENTAL

The equipment and the experimental procedures used have been described in sufficient detail in the companion paper [1]. A porous-layer open-tubular column was prepared with the powder under study, alumina in the present instance. A 0.53 mm I.D. quartz tube was filled with a slurry of the powder in a suitable solvent (dimethyl sulfoxide) in which it does not settle. One end of the tube was closed and the tube was slowly coiled by the other end inside an oven placed under a hood. As it entered the oven, the solvent vaporized and was vented out, leaving a regular layer of powder on the column wall. The column was then fitted within the oven of a Perkin-Elmer (Norwalk, CT, USA) Model 8500 gas chromatograph operated isothermally. Large samples of the probe compounds (diethyl ether and 1-chlorobutane) were injected and the elution band profiles recorded using an IBM PC interfaced with a Data Translation (Marlboro, MA, USA) I/O Board. The equilibrium isotherm was derived from the elution profile using the ECP method [2-4]. From this isotherm, it was possible to derive the distribution of the adsorption energy of the probe [7].

We discuss in this section the sources of errors encountered in the measurement of the experimental parameters needed for an accurate determination of the equilibrium isotherm.

Reproducibility of the primary parameters

We discuss in the next few sections the problems associated with the accurate determination of the primary parameters involved in the measurement of equilibrium isotherms by the ECP method and with their reproducibility. These parameters are the void volume of the column and the hold-up time, the volumetric flow-rate of the carrier gas, the splitting ratios, the peak areas, the sample size, the response factor of the detector, the column length and the mass of stationary phase that it contains. Our estimates of the reproducibility of the measurement of each of these parameters are summarized in Table I, which contains the confidence intervals at the 95% confidence levels.

Reproducibility of the hold-up time

This is an important parameter, which has to be subtracted from the retention times in order to calculate the corrected retention times and hence the

specific retention volume. Small errors in the hold-up time may have an important effect on the precision of the measurements because at high partial pressures the retention of the probe compounds decreases and may become very small. The corresponding retention time tends towards the hold-up time.

The experimental factors which influence the precision of the hold-up time are (i) the fluctuations of the oven temperature, resulting in variations of the carrier gas viscosity; (ii) the fluctuations of the column inlet and outlet pressures caused by a drift of the inlet pressure controller and by variations of the atmospheric pressure, respectively; (iii) possible fluctuations of the column permeability; (iv) errors made in the measurement of the actual injection time; and (v) errors in the time measurement.

The precision on the hold-up time was estimated by determining the reproducibility of ten replicate measurements. The determination of the uncertainty on the hold-up time was made over the time period necessary to complete a routine experiment. With the parallel columns in place, one void time measurement was made for each column every 30 min, allowing a total of 5 h for the complete experiment. The data sets were not skewed, demonstrating that the uncertainty is dominated by random errors. It should be noted that on some days ambient conditions (especially the atmospheric pressure) may change rapidly so that greater uncertainty may be observed on some days, especially during stormy weather. The estimated uncertainties on the void times of both columns are reported in Table I.

Reproducibility of the volumetric flow-rate

The same factors which affect the uncertainty of the void time also affect the uncertainty of the flow-rate. Several additional factors must be mentioned. First, a systematic error due to a leak in the chromatograph or in the connection between the column end and the flow meter is always a possibility. Second, the correction for the vapor pressure of water in the flow-rate measurements made with a soap-bubble flow meter introduces some error. Given the design of soap-bubble flow meters, the partial pressure of water in the gas may be slightly less than its vapor pressure; the temperature of the soap solution fluctuates; the leakage rate of helium through the bubble is unknown.

An experiment similar to that carried out for the

determination of the error of measurement of the void time was performed. Two flow-rates were measured, the split vent flow-rate and the combined outlet flow-rate of the two columns. The two parallel columns were connected to the two branches of the thermal conductivity detector and the flow-rate of the combined streams was measured. The precisions of both flow-rate measurements are reported in the Table I.

Reproducibility of the splitting ratios

The uncertainty of the flow-rate determination dominates the uncertainties of the values derived for the void volumes, the molar flow-rates and the splitting ratios. Therefore, the uncertainty of the splitting ratios was calculated from the error made on the flow-rate results. The variance of the splitting ratio was taken as twice the variance of the flow-rate.

Reproducibility of the peak areas

We do not measure the area of the peak used in the ECP method, except to determine the mass balance of the probe and the fraction that is not eluted at the end of the experiment (see below, *Assumption VIII*). The accuracy of this determination is not critical.

The peak area of importance in this work is the area of the elution band of the fraction of the sample which is injected into the calibration column. This area is used to compute the response factor of the detector. The data set used to determine the reproducibility of this peak area was obtained by making a 5.00- μ l injection of pure diethyl ether on six successive days. The peaks recorded were corrected for a possible baseline shift, but were not smoothed. At least 175 data points per peak were used in the trapezoidal rule integration.

It is interesting that the relative standard deviation

of the area of the peaks recorded at the exit of the test column was twice that for the calibration peaks. The poorer reproducibility was due to the difficulty encountered in the integration of the highly skewed elution profiles obtained. The time at which the integration was ended fluctuated widely. Note that on the days when the ambient temperature is high (*e.g.*, 28°C), the reproducibility of the peak area of diethyl ether is significantly reduced.

Reproducibility of the sample size

It is necessary that the syringes used be of the type in which the sample injected is contained entirely in the needle, so that one is certain that the entire desired injection volume is vaporized in the injection port. A 0–5- μ l Hamilton syringe, Model 7105NCH, obtained from Alltech (Deerfield, IL, USA), equipped with a Chaney adapter and a needle spacer was calibrated by weighing volumes of water on a Cahn (Cerritos, CA, USA) Model 28 automatic electro-balance. The standard deviation of the water injection volume, determined from the reproducibility of the weighings, was 10 nl. However, the weighing experiment fails to take into account either the variation in the splitting ratio over time or the sample losses resulting from the relatively high volatility of diethyl ether. As the peak-area reproducibility for diethyl ether was much worse than the reproducibility of the weighings, the uncertainty in the sample size was revised to the same relative standard deviation as that of the peak areas.

Reproducibility of the detector response factor

The reproducibility of the detector response factor was determined by collecting data over six consecutive days, on the same column, using diethyl ether as the probe. The precision observed is better than one would predict from an error analysis based

TABLE I
ESTIMATED UNCERTAINTY OF THE EXPERIMENTAL PARAMETERS

Parameter	Uncertainty (%)	Parameter	Uncertainty (%)
Void time ($t_{0,2}$)	1.0	Peak area	1.0
Void time ($t_{0,1}$)	0.9	Sample size	1.0
Flow-rate (column)	1.0	Response factor	3.0
Flow-rate (split vent)	0.8	Column length	0.1
Splitting ratio	2.0	Mass of stationary phase	6.5

on the contributions of the uncertainties of the peak area, the splitting ratio and the sample size, all parameters which are used in the calculation of the response factor. This may be explained by the fact that the estimated errors on some of these factors are related, so their contributions cancel out in part.

Reproducibility of the column length

The length of the column was measured by repeatedly marking off 1-m lengths, measured by a meter stick. This method is fairly accurate as the silica tubing tends to lie along a straight line. As sixteen successive measurements are necessary to obtain the length of a *ca.* 16-m column, and the estimated uncertainty for each measurement was 1 mm, the sum of the individual uncertainties was taken as the total uncertainty.

Reproducibility of the mass of stationary phase in the column

Because the ends of the column are cut off at the end of the preparation process, the gravimetric procedure for determining the mass of stationary phase is accurate only as long as the density of the silica tubing, or mass of the silica tubing per unit length, remains constant. This was confirmed experimentally. Nine columns were cut from the same continuous section of tubing. The relative standard deviation for the weight of these nine sections of empty dry tubing was 0.03%. Error analysis reveals, however, that this error propagates to produce a much greater relative uncertainty on the weight (*ca.* 40 mg) of the stationary phase in the column, because this amount is small compared with the column weight.

RESULTS AND DISCUSSION

Reproducibility of the retention data

In this section, we discuss the reproducibility of the set of retention data acquired in an experiment. The characterization of this reproducibility is not straightforward, as we are not collecting repetitive estimates of a single number, *e.g.*, a retention time, a retention factor or a peak area for which the determination of a standard deviation suffices. The result of a single experiment, *i.e.*, the record of a band profile, gives an entire section of the isotherm. This is the major advantage of the ECP method over

frontal analysis [4]. We summarize first the method used for assessing the reproducibility of these experimental results and the various calculations performed to supply estimates of the uncertainty of the retention data at the different stages in the process of calculating the isotherm.

We then report the results obtained. A three-step reproducibility experiment was performed. First, reproducibility was determined on the same column, on the same day. Six band profiles were measured and the same experimental parameters were used in the six calculations. Second, the same data were measured on the same column, but on different days, over a period of time. The experimental parameters (*e.g.*, the void time and the detector response factor) used for the processing of each of the six measurements were determined at the time of the measurements. Finally, a complete set of measurements was performed for three different columns. The protocol for determining the uncertainty for each step of the study is as follows. Each set of retention data is compared with all of the other sets obtained during the particular step considered. For example, for the same day and the same column step, six sets of data were collected and fifteen comparisons were made. The results are reported as the mean and the standard deviation of each of the comparison parameters for each step.

Distribution function analysis of the band profiles. The reproducibility of the thermodynamic parameters calculated from the retention data is closely related to the reproducibility of the band profiles used to calculate the isotherm. Recognizing the inadequacy of the classical parameters (*e.g.*, statistical moments) used to characterize chromatographic band profiles when they are applied to strongly skewed peaks, Rix [10] and later Excoffier *et al.* [11] used distribution function analysis (DFA) to detect small differences between the shapes of two similar peaks. In this method, the difference between the shape of two profiles is parameterized by the numerical calculation of a shape difference parameter, δ , defined below.

First, we emphasize that it is possible to compare only the rear portions of the elution profiles which cover the same range of signal, *i.e.*, for which the probe partial pressure is between zero and the lower of the two peak maxima. Of the two peaks to be compared, it is determined first which peak maxi-

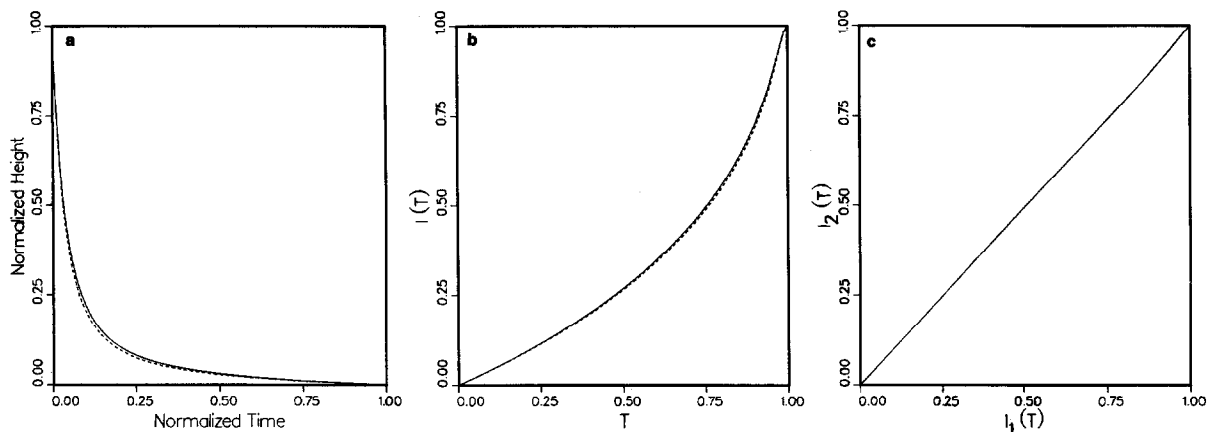


Fig. 1. Comparison between two normalized elution profile tails. Diethyl ether on RHCP alumina at 60°C, helium carrier gas. (a) Elution profiles, measured on the same day, with the same column. (b) Distribution function corresponding to the elution profiles in (a). The solid line corresponds to the normalized tail represented by a solid line in (a). (c) Plot of the distribution function I_2 represented by the dashed line in (b) versus the distribution function I_1 represented by the solid line. This particular curve is designated by $\Phi(I_2, I_1)$.

imum is the smaller and only the proper part of the other peak is considered. Similarly, the two profiles have to be stopped at some arbitrary set time, when the signal is too small to be significantly different from the baseline. As the band profiles are very similar, there is no difficulty in stopping them at the same time. We then need to digitize both profiles consistently. To that effect, both rear profiles, below the lower peak maximum, are fitted to a cubic spline. The range of peak height (between zero and the lower maximum) is divided into 500 evenly spaced points and, for each peak, the retention times corresponding to each of these 500 values of the peak height are evaluated from the spline. Each of these curves is then normalized in both dimensions. Each peak height is divided by the maximum peak height, producing a normalized peak height, I_N . A normalized time, τ , is then computed:

$$\tau = (t - t_1)/(t_2 - t_1) \quad (9)$$

In eqn. 9, the times t_1 and t_2 correspond to the maximum and the minimum peak heights of the profile considered, respectively; t_2 is the time when the chromatograms evaluated are ended. Two such normalized elution profiles, obtained the same day and on the same column are shown in Fig. 1a for illustration. These profiles are similar. To compare them quantitatively, the distribution function, $I(\tau)$, is calculated for each normalized profile:

$$I(\tau) = \int_0^\tau I_N(\tau) d\tau \quad (10)$$

The distribution functions corresponding to the normalized profiles shown in Fig. 1a, obtained the same day and on the same column, are shown in Fig. 1b. A numerical comparison between the two distribution functions is made by plotting one distribution as a function of the other one, *i.e.*, I_2 as a function of I_1 , τ now being the parameter of the point on the new curve. Such a plot is shown in Fig. 1c. The resulting curve is the diagonal line of the square defined by the origin of coordinates and the point (1,1), if the two distribution functions are identical. If they are not, the area of the surface between the curve and the coordinate bisector is taken as a measure of their difference. For symmetry reasons, the shape distance parameter, δ , is defined as

$$\delta = \frac{1}{2} \left\{ \sum_{i=1}^n [\Phi(I_2, I_1, i) - \Phi(I_1, I_2, i)]^2 + \sum_{i=1}^n [\Phi(I_1, I_2, i) - \Phi(I_2, I_1, i)]^2 \right\} \quad (11)$$

where $\Phi(I_2, I_1, i)$ is the curve obtained when I_2 is plotted as a function of I_1 and i is the rank, 0 to n , of the point considered. To reduce computation times, the distance, δ , is computed by considering only every fifth point (*i.e.*, n in eqn. 11 is 100). The two-dimensional sum of squares is performed to give the parameter the mathematical properties of a distance [11].

Parameters characterizing the reproducibility of the elution profiles. In addition to the distances, δ , between the profiles, their average and standard deviation for a series of determinations performed under the same set of experimental conditions, three parameters are used to assess the reproducibility of the retention data, a figure of the error on the retention times, a figure of the error on the amount adsorbed at equilibrium with a partial pressure P .

t_{RMS} is the root-mean-square relative error between the retention times corresponding to two elution profiles. It is calculated by summing the squares of the differences between the elution times of the same concentration on the two profiles for all the 500 concentrations measured, dividing by 500 and taking the square root. This parameter is calculated in the same time as the DFA data, from the retention times which were evaluated from the spline.

k'_{RMS} is the root-mean-square relative error between the values of the retention factor, $k' = (t_{\text{R}} - t_0)/t_0$, where t_{R} is the retention time of a concentration and t_0 is the hold-up time, for the two peaks. k' is calculated directly from the retention times (evaluated from the spline, as described in the previous sub-section) and is a function of the peak height.

q_{RMS} is the root-mean-square relative error be-

tween the isotherm points. As with the previously described parameters, it can be evaluated only for the portion of the data which overlap in the probe partial pressure range. Both isotherms were fitted to a spline and evaluated at equally spaced values of the partial pressure, within the common range of partial pressure. The deviation between the resulting isotherms were then compared.

For each difference parameter, an upper confidence limit was computed for each step of the reproducibility study (*i.e.*, same column, same day, same column, different days and different columns, different days). This upper confidence limit was taken as the mean of the difference parameter plus twice the standard deviation.

Results of the study of the retention data. These results are given in Tables II (reproducibility) and III (confidence limits). Several trends may be observed. As expected, the reproducibility of the retention factors was better than the reproducibility of the retention times. This was especially true for the data obtained on different days, with different columns, demonstrating the importance of comparing relative retention rather than absolute retentions.

As the value calculated for the amount adsorbed, q , at equilibrium with a vapor pressure P depends on both the flow-rate and the detector response factor, it is not surprising that the degradation of the reproducibility when going from k' to q is much worse in the second step (measures made on different days with the same column) than in the first one (measures made the same day), as the flow-rates and the response factor drift and have to be measured every day. The poor reproducibility of the absolute data (retention time and amount adsorbed at equilibrium) measured for different columns (compared with measures made with the same column. on

TABLE II
REPRODUCIBILITY OF RETENTION DATA

Mean value of the parameter (%) and relative standard deviation (%) in parentheses.

Comparison basis	Mean t_{TMS} (%)	Mean k'_{RMS} (%)	Mean q_{RMS} (%)	Mean Δ (%)
Same day, same column	1.1 (0.7)	0.9 (0.4)	4.0 (1.2)	8.1 (3.1)
Different day, same column	1.4 (0.6)	0.9 (0.3)	6.0 (1.1)	10. (3)
Different day, different column	4.3 (1.5)	1.1 (0.4)	10. (2)	12. (3)

TABLE III
CONFIDENCE LIMIT (CL) INTERVALS (%) FOR THE RETENTION DIFFERENCE PARAMETERS

Comparison basis	CL t_{TMS} (%)	CL k'_{RMS} (%)	CL q_{RMS} (%)	CL δ (%)
Same day, same column	1.8	1.3	5.2	11.
Different day, same column	2.0	1.2	7.1	13
Different day, different column	5.8	1.5	12	15

different days) can be explained by the error made on the determination of the mass of stationary phase in the column.

Reproducibility of the calculated parameters

Energy distribution functions were calculated for each set of retention data described in the previous section. Thus, we can compare the reproducibility of the calculated parameters determined in the three steps of the study, and corresponding to measures performed (i) on the same day, with the same column, (ii) on different days, with the same column and (iii) on different days, with different columns. The reproducibility results regarding the parameters of the adsorption energy distribution are given in Table IV. The reproducibilities given correspond to twice the relative standard deviation (R.S.D., %) of the mean.

As the energy distribution of the alumina studied has two peaks (both approximated by a Gaussian function), the data given here are those corresponding to the peak with the worse reproducibility for each given parameter. For example, for the first step

(data measured the same day, on the same column), the relative standard deviations of the monolayer capacities were 1% and 2% for the low and high-energy peaks. The worst of the two values, 2%, was reported in Table IV.

The reproducibility of the calculated values of the parameters of the adsorption energy distribution may be entirely explained by the retention data reproducibility itself. The increase in the relative standard deviation of the monolayer capacity when going from one step of the study to the next follows the same trend as q_{RMS} . In fact, it is nearly equal. It is remarkable that the average value of the adsorption energy is highly reproducible (R.S.D. = 1%). This is explained by the fact that it is a normalized quantity. It follows the same trend as the retention factor, k' . The variance of the peaks of the energy distribution should be a function of the shape of the normalized elution peak and therefore its reproducibility should be a function of the reproducibility of δ . This seems to be the case.

Assessment of the validity of the assumptions made in the model relating the isotherm to the primary chromatographic data

The classical theory of analytical chromatography [33,34] assumes that the solute is infinitely dilute in the carrier gas. Because of this assumption, a number of effects can be neglected. The retention time of the band is determined by the column capacity factor or retention factor, k' , proportional to the initial slope of the isotherm, that is, by the thermodynamics of the phase equilibrium. On the other hand, the band shape is determined by the kinetics of mass transfers in the chromatographic column. The peak is Gaussian, provided that the mass-transfer kinetics are fast. This profile is independent of the sample size. Further, there is no

TABLE IV
REPRODUCIBILITY OF THE CALCULATED PARAMETERS

Confidence intervals of the parameter (%).

Comparison basis	q_m (%)	E_{AVG} (%)	σ^2 (%)
Same day, same column	4.0	1.0	100
Different day, same column	6.4	1.0	126
Different day, different column	12	1.6	130

coupling between the thermodynamics and the kinetics of retention.

In contrast, non-linear chromatographic band profiles change shape with increasing sample concentration. The elution profile broadens and becomes unsymmetrical. Coupling between thermodynamics and kinetics of retention takes place [35]. In order to model the migration of high-concentration bands, the relative effect of the non-linear (*i.e.*, concentration dependent) factors must be assessed, so they can either be neglected or taken into account, depending on their significance. As the ECP method is based on a result derived from the ideal model (eqn. 4), we also need to assess the importance of the deviation from ideal behavior.

The assumptions which are made or implied in the derivation of eqn. 4 are listed in the Appendix. In this section, we address these assumptions and their degree of validity. To validate the method that we have developed for the determination of the adsorption energy distribution, it is necessary that quality control protocols be established and applied to insure that the data (*i.e.*, the experimental band profiles) are not significantly influenced by the effects of some non-ideal behavior. The validity of the model must be demonstrated for each set of data.

One of the simplest and most direct methods to ascertain the accuracy of the isotherm derived for a chromatographic system is to compare the recorded band profile for a large size sample with the profile calculated using a general model. Simulations are very important to this type of validity testing as they may allow the validity of each assumption to be tested independently. This practice is usually impossible experimentally. We have largely used this powerful tool which we have developed in the recent past. Details of the implementation of the program, together with an investigation of the influence of the column permeability on the actual band profile, are reported elsewhere [5].

Assumption I. The column is homogeneous. The column is filled with a homogeneous slurry, prepared by sonication. The rate at which the particles settle in the slurry is very low (only after 24–36 h is it possible to notice that they have settled to a significant extent) and the time needed to vaporize the solvent and to coil the column in the oven is *ca.* 4 h. After the column has been taken from the oven in which it has been coiled, the column is always kept

horizontal. Thus, all efforts are made to obtain and conserve a homogeneous column.

Assumption II. The column is isothermal. The range of temperature fluctuations experienced in a fixed point of the oven, under isothermal conditions, is of the order of $\pm 0.1^\circ\text{C}$. The temperature gradient in the oven is more important. The detector and injector are set at temperatures higher than the oven. Significant gradients may exist in the proximity of the heating elements. In the center of the oven, where the column is placed, the gradient is estimated to be of the order of $0.1^\circ\text{C cm}^{-1}$. The metallic cage holding the column may contribute to relax these gradients.

As discussed previously [36], the effect of these fluctuations of the temperature of the band on the retention data obtained with a coiled column will be small compared with that of the other sources of errors. At most they will contribute to a slight shift in the energy distribution, which has a negligible effect on the comparison made between different columns, as all the columns are carefully positioned at the same place in the oven.

Assumption III. The heat balance can be neglected. Gas–solid adsorption is an exothermic process. When the probe vapor is adsorbed at the band front, some heat is generated. Only part of this heat is conducted away, axially and radially. When the solute is desorbed on the band tail, heat is adsorbed in the process. Thus, the band front moves in a warm zone and tends to migrate faster than in an isothermal column. The rear of the profile is moving along a column zone whose temperature decreases and it tends to move more slowly than in an isothermal column. The band is broadened. The consequences of this effect are usually neglected. There is no evidence to suggest that this practice causes a significant error [14,16].

Assumption IV. The mobile phase viscosity is constant. Most organic vapors have a lower viscosity than helium. If the local probe partial pressure is high enough, this may alter the local viscosity of the mobile phase and hence its local velocity. The effect of a changing viscosity of the mobile phase as a band passes a point on the column has been discussed previously [14,37]. The viscosity change causes the pressure to deviate non-uniformly over the column and alters the pressure and the velocity profiles. Taking into account the viscosity effect in a chroma-

topographic model would be very difficult, however, and this has never been done before.

Fortunately, this effect may be neglected as long as the column is radially homogeneous [38,39]. In our study of the adsorption energy distribution on alumina particles, we determine the adsorption isotherm of diethyl ether and 1-chlorobutane in the range of partial pressure from 0 to less than $5 \cdot 10^{-3}$ atm, while the average column pressure is less than 1.2 atm. Although the partial pressure of the probe at the beginning of the column certainly exceeds 0.4% of the inlet pressure, the effect can be only minimal.

Assumption V. The mobile phase behaves as an ideal gas. In the Theory section, we have discussed the equation derived by Conder and Young [9] to take into account the deviation of the mobile phase behavior from that of an ideal gas. We have shown that, in the range of partial pressures of the probe at which the measurements are carried out, the corrections for non-ideal behavior that were introduced remain negligible.

Another, entirely different, approach leads to the same conclusion. We have seen above that the average column pressure is $J_4^3 P_o$ [15]. In order to estimate the magnitude of the effect due to the deviation of the behavior of the carrier gas from ideal, we can calculate the pressure, P' , under which the same amount of a real gas would be, if stored in the same column volume. The calculation uses the Beattie–Bridgeman equation [40,41], an empirical equation of state valid over the range of temperature and pressure of interest here. The value obtained is compared with the pressure calculated by the ideal gas equation.

Our experiments were conducted at an inlet pressure, P_i , of 1.340 atm and an outlet pressure, P_o , of 1.000 atm. The average pressure, $P_{4,3}$ is thus 1.186 atm. For the temperature of 333 K and a column volume of 3.29 ml, the number of moles of an ideal gas contained in the column is $1.428 \cdot 10^{-4}$ (molar volume $2.304 \cdot 10^4$ ml mol $^{-1}$). The Beattie–Bridgeman equation is written as [40]

$$P = RT \cdot \frac{1 - \frac{c_{BB}}{V_{BB} T^3}}{V_{BB}^2} (V_{BB} + B_{BB}) - \frac{A_{BB}}{V_{BB}^2} \quad (12)$$

where V_{BB} is the molar volume of the gas, and the coefficients are

$$A_{BB} = A_{0, BB} \left(1 - \frac{a_{BB}}{V_{BB}} \right) \quad (13a)$$

$$B_{BB} = B_{0, BB} \left(1 - \frac{b_{BB}}{V_{BB}} \right) \quad (13b)$$

The empirical constants for helium are [41]

$$A_{0, BB} = 2.16 \cdot 10^4 \text{ atm cm}^6 \text{ mol}^{-2}$$

$$a_{BB} = 59.84 \text{ cm}^3 \text{ mol}^{-2}$$

$$B_{0, BB} = 14.00 \text{ cm}^3 \text{ mol}^{-1}$$

$$b_{BB} = 0.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$c_{BB} = 4.0 \cdot 10^4 \text{ cm}^3 \text{ K}^3 \text{ mol}^{-1}$$

The value of the pressure calculated from the Beattie–Bridgeman equation is 1.187 atm. This agrees with the pressure of an ideal gas (relative error = 0.08%). The mobile phase (helium) may be assumed to behave as an ideal gas under the experimental conditions used in this work.

Assumption VI. The carrier gas is not retained. Helium is not significantly adsorbed on alumina at 60°C. The retention time of methane was compared with that of nitrogen on a 10-m column containing 60 mg of alumina. The retention factor of methane, assuming that nitrogen is not sorbed, was found to be 0.05. The columns we use for the determination of the adsorption energy distribution on alumina contain *ca.* 44 mg of alumina in a 15-m column. The phase ratio is thus twice as small and the retention factor becomes 0.025. A correction is made to the retention volume of methane when determining the void volume of a new column.

Assumption VII. Adsorption of the probe takes place only on the stationary phase. In order to check this assumption, elution profiles of the probe compounds were recorded on a blank column, made with a piece of clean, uncoated quartz tube, under the same experimental conditions as for the regular measurements of adsorption isotherms. The amount of solute injected was sufficient to cause the eluted peak to be as high as the peaks used for the ECP measurements. The elution profiles obtained with the two probes are shown in Fig. 2. Both peaks eluted at the void time and neither of them is skewed. The column plate number was computed numerically for each peak using the Foley–Dorsey equation [42]. In each instance it was 10–200 theoretical plates.

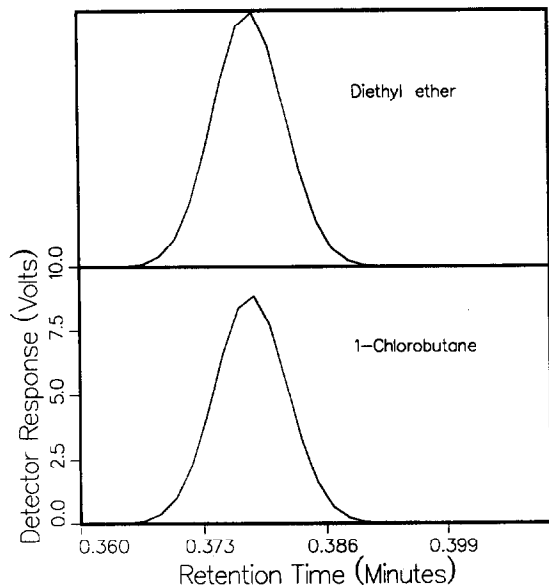


Fig. 2. Elution profiles of the probes obtained on a blank column. Chromatographic conditions: carrier gas: helium, pressure drop, 0.34 atm; outlet velocity, 56 cm^{-1} ; column, $15 \text{ m} \times 0.53 \text{ mm}$ I.D.; hold-up time, 22.7 s in both instances; temperature, top 60°C , bottom 40°C .

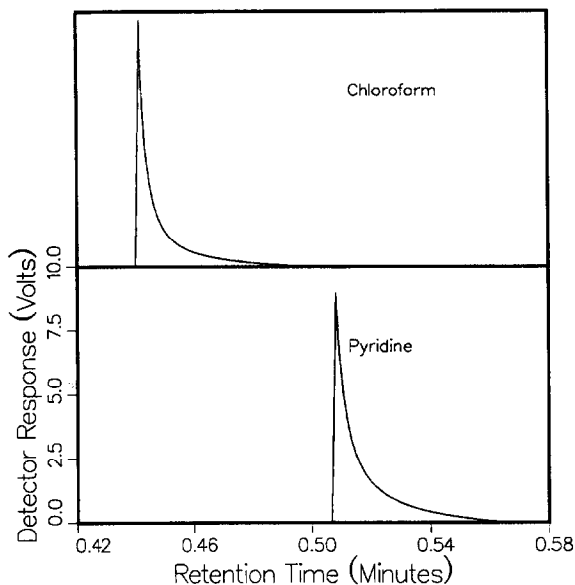


Fig. 3. Elution profiles of some vapors obtained on a blank column. Chromatographic conditions as in Fig. 2, except top chromatogram, chloroform, 100°C , hold-up time 28.4 s and bottom chromatogram, pyridine, 150°C , hold-up time 30.1 s.

It is interesting to compare this efficiency with that predicted by the Golay equation [22,23]. For a non-retained compound ($k' = 0$), this equation becomes

$$H = \frac{2D_g}{u} + \frac{d_c^2 u}{96D_g} \quad (14)$$

where H is the column HETP and d_c its inner diameter. The molecular diffusion coefficient of the probe, D_g , can be derived from the Fuller-Giddings equation [43]:

$$D_g = \frac{1.0 \cdot 10^{-3} T^{1.75}}{P \left[\left(\sum \varepsilon_i \right)_A^{1/3} + \left(\sum \varepsilon_i \right)_B^{1/3} \right]} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad (15)$$

where the subscripts A and B refer to the probe vapor and the carrier gas, respectively, P is the pressure in atm and ε_i is an atomic contribution to the diffusion volume of the molecule, found in a table [43]. For diethyl ether and helium, the volumes $\left(\sum \varepsilon_i \right)_A$ and $\left(\sum \varepsilon_i \right)_B$ are 91.3 and 5.4, respectively.

The diffusion coefficient of diethyl ether in helium at 60°C under atmospheric pressure is $2.1 \text{ cm}^2 \text{ s}^{-1}$. Hence, with a carrier gas outlet velocity of 66 cm s^{-1} , $H = 0.066 \text{ cm}$ ($N = 22\,700$ theoretical plates). The 50% loss of efficiency probably comes from extra-column contributions. As shown by the Golay equation, however, the band width increases very rapidly with increasing retention and the extra-column contribution becomes negligible for retained components.

For some other solutes, however, adsorption does occur on sites located on the column wall. Fig. 3 shows the elution profiles on the blank column for two compounds which were considered as potential probes, chloroform eluted at 100°C and pyridine at 150°C . These peaks are highly unsymmetrical, denoting the presence of some high-energy adsorption sites in the system. Because of the increase in the carrier gas viscosity with increasing temperature, the hold-up times at constant inlet pressure are 26.4 s at 60°C and 30.1 s at 150°C . Hence the band fronts are eluted nearly at the hold-up time. The retention of these two compounds on the blank column is probably only barely significant, however.

For example, for pyridine, the retention time

corresponding to the minimum detectable voltage (5 mV) is only 34 s, corresponding to $k' = 0.13$. When the elution profile of pyridine is recorded on an actual alumina column, the retention factor corresponding to the minimum detectable voltage is of the order of 7. Based on the upper confidence limit (Table III) for k'_{RMS} , one may assign a confidence interval of $\pm 1.3\%$ (i.e., 7 ± 0.1) to this measurement. As a correction could be made, the additional shift is virtually negligible, even for pyridine.

Assumption VIII. The entire amount of the probe compound injected is eluted. We have observed for diethyl ether, but not for 1-chlorobutane, that not all the amount injected into the column elutes before the detector response returns to the baseline [1]. Some of the sample, always less than 10% of the amount injected, elutes later. This elution can be observed, for example, during temperature programming of the column [1]. Such a thermal conditioning of the column is always performed between two successive experiments with a column. It is important to understand the reason for this phenomenon, which could be due to a slow desorption kinetics.

We can demonstrate that no measurable amount of diethyl ether remains chemisorbed on the column by making two successive large injections of the same amount of diethyl ether, separated by a thermal conditioning of the column, and comparing the peak areas. They are identical, and it is highly improbable that the same amount of sample would be absorbed irreversibly each time. The most probable explanation is that the tail of an isothermal elution profile is extremely long and is far from completely eluted when the detector signal appears to return to the baseline. In order to investigate this possibility, the following analysis was performed.

For diethyl ether on alumina, the area corresponding to the injected band profile was 0.91 V min. If we assume that 10% of the material injected remains on the column after the detector response decays to 5 mV, the peak area lost is 0.09 V min. If we approximate the portion of the tail of the elution profile below 5 mV by a right triangle, the time required to decay from 5 to 0 mV is given by

$$t_w = (2 \cdot 0.09)/(5 \cdot 10^{-3}) = 36 \text{ min}$$

If we assume instead an exponential decay, $y = y_0 e^{-kt}$, for the detector signal, beyond the time t_r

when we usually end the recording, with a time constant k , the area under the exponential is

$$A = \int_{t_r}^{\infty} y dt = \frac{y_0}{k} [-e^{-kt}]_{t_r}^{\infty} = \frac{y_0}{k}$$

With a value $y_0 = 5$ mV for the detector signal and an area of 0.09 mV min for the residual amount, we find a time constant of 18 min. After two time constants, the area has decreased by a factor of 7.4. An experiment was performed with an extended isothermal period of $7.5 + 36 = 43.5$ min, instead of the normal 7.5 min, prior to undergoing the regular thermal conditioning. This time, no peak was observed during temperature programming of the column. This experiment shows that the observation of residual amount of diethyl ether is due to the limited time window used for data acquisition of this profile.

Further evidence was provided by fitting the adsorption isotherm to a multi-Langmuir equation and extrapolating to infinite dilution. A bi-Langmuir equation was used in this case:

$$q(P) = \frac{a_1 P}{1 + b_1 P} + \frac{a_2 P}{1 + b_2 P} \quad (16)$$

Taking the first derivative and extrapolating to $P = 0$ gives a limit of dq/dP equal to $a_1 + a_2$. The retention time of the end of the profile predicted by the ideal model is

$$t_R = t_0 \left[1 + \frac{jRTm_s}{V_m} (a_1 + a_2) \right] \quad (17)$$

For diethyl ether on RHCP alumina at 60°C, the best-fit bi-Langmuir coefficients were $a_1 = 0.145$ and $a_2 = 0.0229$. The other parameters in eqn. 17 are $j = 0.846$, $V_m = 3.29$ ml, $m_s = 44$ mg and $t_0 = 0.372$ min. Using these values in eqn. 11 yields $t_R = 19.7$ min. While the three analyses yield values of the retention times at infinite dilution which appear to be in poor agreement, 19.7 min, 43.5 min and infinity, they all yield retention times which are significantly greater than the time at which the sensitivity of the detector mandates the end of the experiment. The only consequence of this loss, however, is a slight decrease in the accuracy of the isotherm measured at very low partial pressures.

Assumption IX. The shape and width of the injection profile have no influence on the elution profile. That the shape of the injection profile does not influence the profile of the elution bands may be concluded by studying the profiles of the peaks eluted from the blank column. These peaks are Gaussian and exhibit no or negligible tailing (Fig. 2). The width of these peaks is negligible compared with the width of the peaks used for the determination of adsorption isotherms using the ECP method.

Because the amount injected in the blank column, on which there is no retention and hence little dilution, is much lower than the amount injected for the determination of the elution profiles used for isotherm calculations, the effect of the sample width or volume on the elution profile must be assessed in the case of large injections. First, the band profile is calculated with the semi-equilibrium model of chromatography, as explained elsewhere [5,13,17,25], using the narrowest possible profile. Next, the cal-

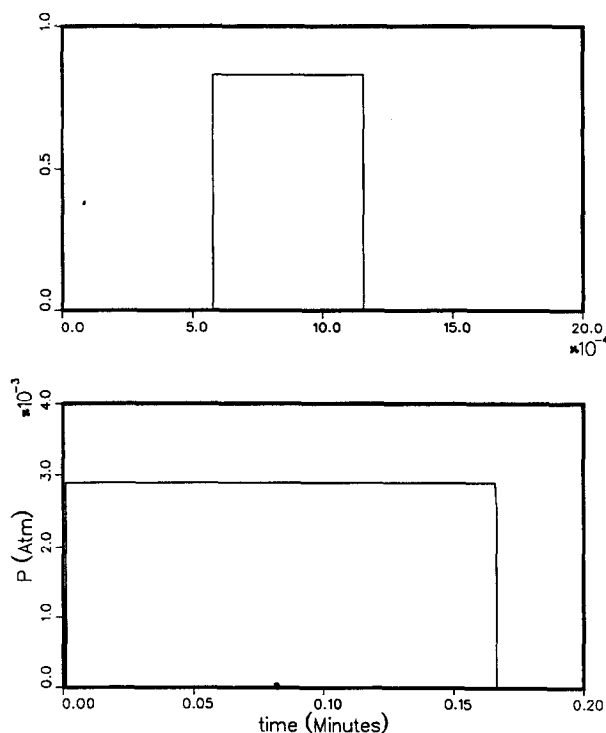


Fig. 4. Injection profiles used for the simulation of the elution profile of diethyl ether on RHCP alumina at 60°C. Experimental conditions as in Fig. 2. Peak area, $4.80 \cdot 10^{-4}$ atm min; number of theoretical plates, 8000.

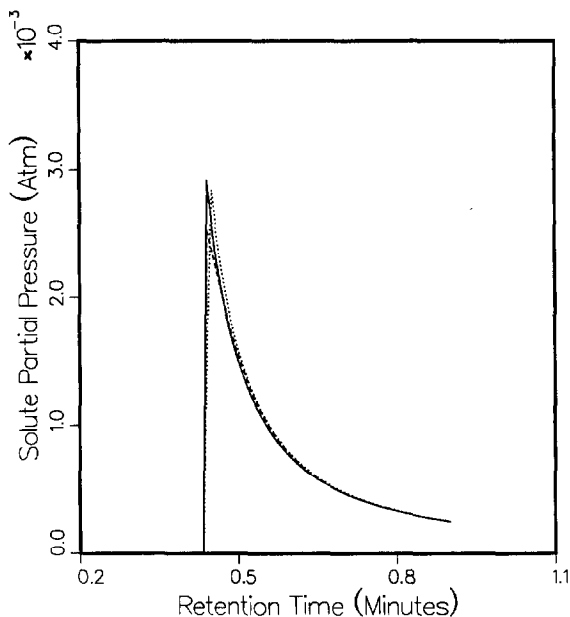


Fig. 5. Comparison between an experimental elution profile (solid line) and the profiles calculated with the semi-ideal model of chromatography, using the experimental isotherm and the injection profiles shown in Fig. 4. Dotted line, profile calculated with the narrow injection profile; dashed line, profile calculated with the wide injection profile. Experimental conditions as in Fig. 4. Number of theoretical plates, 8000.

ulation is repeated, assuming a rectangular profile with a height equal to P_{MAX} , the height of the elution profile at the detector. The width is nearly 10 s. Based on the results described in the last section, the plate number used for both simulations is 8000. The two injection profiles are shown in Fig. 4. The two calculated band profiles are compared with the experimental band profile in Fig. 5. Although the band height can only decrease during an isothermal elution, the dramatic increase in the injection width of the second calculated band has very little effect on its elution profile. We conclude that, as long as the injection profile does not tail badly, the effect of its profile on the determination of the isotherm is negligible. This result is in agreement with the findings of Knox and Pyper [44], who have shown that the sample volume does not affect the band profile up to a fairly large value.

Assumption X. The influence of the finite efficiency of the column is negligible. In order to insure that the effects of the non-ideal behavior of the column on

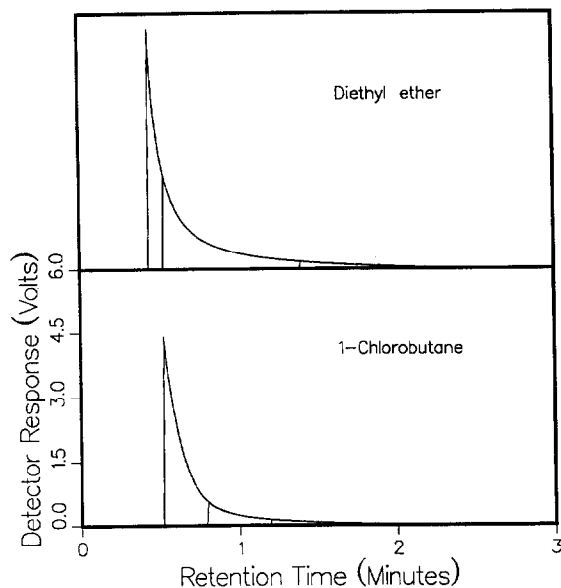


Fig. 6. Good coincidence of the tails of elution profiles corresponding to different amounts injected. Experimental conditions as in Fig. 2. Stationary phase, RHCP alumina; mass of stationary phase, m_s , 44 mg. Top chromatograms: diethyl ether; temperature, 60°C; hold-up, 22.7 s; sample sizes, large peak 0.460 μg (area 0.911 V min), medium peak 0.30 μg , small peak 0.035 μg . Bottom chromatogram: 1-chlorobutane; temperature, 40°C; hold-up time, 21.5 s; sample sizes, 0.18, 0.034 and 0.016 μg ; large peak area, 0.678 V min.

the probe band profile may be neglected, the method first suggested by Huber and Keulemans [45] is used. Several elution profiles corresponding to increasing amounts of the probe are recorded. These chromatograms are superimposed and it is determined whether or not their tails lie on the same curve. Huber and Keulemans [45] stated that, if the tails do coincide, then one may safely conclude that the effects of the apparent axial dispersion may be neglected. Although it is true that this condition is necessary to obtain isotherms which are independent of the concentration (a minimum requirement), a significant efficiency is also necessary to minimize the contribution of band spreading on the ECP balance at low concentrations. In Fig. 6, we show the coincidence of the tails for three sample sizes of the two probe compounds (diethyl ether and 1-chlorobutane) used to characterize the alumina. In Fig. 7, two similar sets of data are shown, for chloroform at 40°C and methanol at 80°C. In this instance, the band tails of increasing size samples do

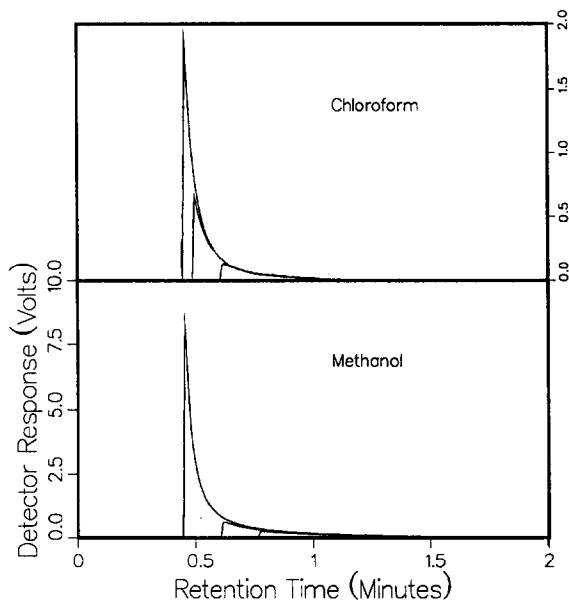


Fig. 7. Poor coincidence of the tails of elution profiles corresponding to different amounts injected. Experimental conditions as in Fig. 2. Top chromatogram: chloroform; temperature, 40°C; hold-up time, 21.6 s; sample sizes, 0.24, 0.10 and 0.06 μg ; large peak area, 0.331 V min. Bottom chromatogram: methanol; temperature, 80°C; hold-up time, 25.9 s; sample sizes, 0.36, 0.12 and 0.05 μg ; large peak area, 0.611 V min.

not coincide. This phenomenon is probably related to the concentration-dependent nature of the non-equilibrium effects [45]. Similar results (not shown) were also observed for benzene and pyridine.

The non-equilibrium behavior manifested by chloroform and methanol may be due to slow kinetics of adsorption-desorption. We expect that methanol chemisorbs to some extent as those alcohols which are structurally capable of losing a water molecule dehydrate rapidly in contact with alumina. However, the deviation of the tails from one another in Fig. 7 is small and this phenomenon deserves a more detailed study.

In order to simulate the effect of the finite column efficiency on the profiles of the bands of probe compounds recorded, a series of simulations were performed [13,17,25]. Using the adsorption isotherm for diethyl ether on RHCP alumina at 60°C, the band profiles predicted by the equilibrium-diffusive model on three hypothetical columns having efficiencies of 6000, 8000 and 20 000 theoretical plates,

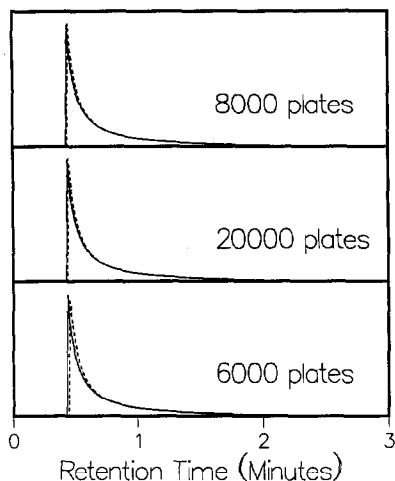


Fig. 8. Comparison between the experimental chromatogram of diethyl ether on RHCP alumina at 60°C (solid line) and the elution profiles calculated with the semi-ideal model, the adsorption isotherm derived by the ECP method and using different column efficiencies. Dashed line: simulated chromatogram with a column efficiency of 8000 theoretical plates (top), 20 000 plates (middle) and 6000 plates (bottom). Experimental conditions as in Fig. 2.

respectively, were calculated (note that the real column used has 10 000 plates under the usual experimental conditions). The details of the calculations involved will be published elsewhere [5]. The numerical solutions obtained were compared with the actual band profiles. The results are shown in Fig. 8.

We see in Fig. 8 that there are no significant differences between the experimental profiles and the profiles calculated for columns having 8000 and 20 000. The nearly perfect coincidence between the experimental profile and the two numerical solutions validates the whole calculation process and the experimental isotherm. A systematic deviation between calculated and experimental profiles appears for an efficiency of 6000 plates and would increase for lower efficiencies. In practice, the efficiency of a porous-layer open-tubular column appears necessary for accurate determinations of isotherm data by the ECP method.

Assumption XI. There are no sources of extra-column band broadening. Extra-column volumes, whether swept or dead, contribute to band broadening. The injector and the detector both behave as mixing chambers. In contrast with analytical chromatography, these contributions cannot be dealt

with simply using the rule of the additivity of the contributions to the band variance. It is easy to show that, in non-linear chromatography, the extra-column contributions have the effect of a shift-variant convolution [46]. The variances contributed by the band broadening sources which are upstream of the column are no longer additive. However, the variances contributed by the sources placed downstream remain additive.

It is as imperative as in analytical applications to keep to a minimum the extra-column contributions to band broadening. A well designed splitting device is needed to ensure a narrow, rectangular injection plug. As shown above, the equipment contributes significantly to the broadening of non-retained component bands under linear conditions, but this contribution is small enough to become negligible with retained components. Further, the extra-column band broadening contributions become less important in non-linear chromatography because the band profile is more controlled by thermodynamics than by kinetics.

Assumption XII. The sorption effect has negligible effect. The sorption effect, a dependence of the local mobile phase velocity on the local solute partial pressure, is due to the large difference between the partial molar volumes of the solute in the stationary and the mobile phases and to the fact that the carrier gas flow-rate is held constant at the column inlet. This has been pointed out and studied by Bosanquet and Morgan [47]. As the front of a finite concentration band passes a point in the column, sorption of the probe vapor occurs and the mobile phase is partially depleted. Because of this depletion, the mobile phase flow-rate downstream of the band is slower than at the band front. Similarly, at the rear of the band, the local mobile phase velocity is lower upstream of the band than in the band itself. The effect of this flow-rate profile on the probe concentration profile in the band is similar to the effect caused by a Langmuir isotherm [14,47]. The front boundary of the band is self-sharpening and the rear boundary is diffuse.

For a given amount of the probe compound, the magnitude of the sorption effect is related to the magnitude of the column pressure drop (or rather to the average column pressure). If the pressure drop is high, the carrier gas density is high and the mole fraction of the probe solute is relatively low

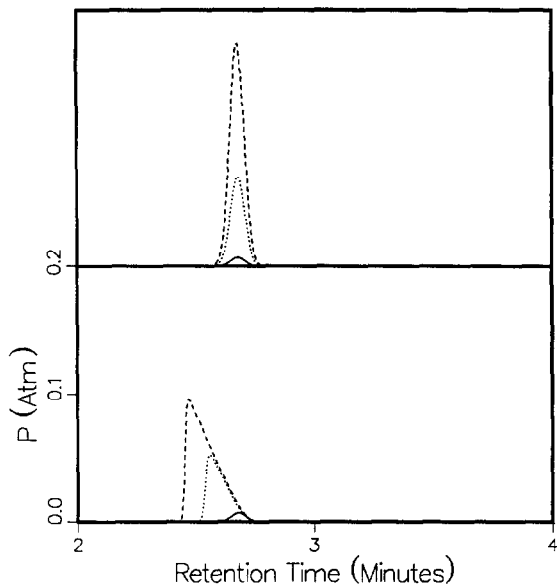


Fig. 9. Theoretical study of the sorption effect. Comparison between calculated elution profiles for different size samples. Experimental conditions as in Fig. 4 (top), except linear isotherm with a slope of $0.02 \text{ mol g}^{-1} \text{ atm}^{-1}$. Column efficiency, 8000 theoretical plates. Top chromatograms: profiles calculated without sorption effect. Bottom chromatograms: profiles calculated with a program including the carrier gas mass balance and the sorption effect. Sample sizes, 0.51, 5.1 and $12.6 \mu\text{g}$; peak area, solid line $0.53 \cdot 10^{-3}$, dotted line $5.3 \cdot 10^{-3}$, dashed line $13.2 \cdot 10^{-3} \text{ atm min}$.

over most of the column length. The mobile phase flow-rate is less perturbed by the passage of the band. It would be possible to decrease the intensity of the sorption effect by increasing the average column pressure. In fact, one can even decrease the magnitude of the sorption effect by increasing both the inlet and the outlet column pressures, and hence the average column pressure, without increasing the pressure drop [13,14,38,19]. On the other hand, the sorption effect is important at low column pressure drops, which is almost always the condition under which wide-bore open-tubular columns are operated.

In order to estimate the degree of column overloading at which the sorption effect begins to be noticeable, simulations were carried out. Elution band profiles were calculated using the equilibrium-dispersive model, a linear isotherm and two computer programs. One of these programs ignores the sorption effect and the other takes it into account.

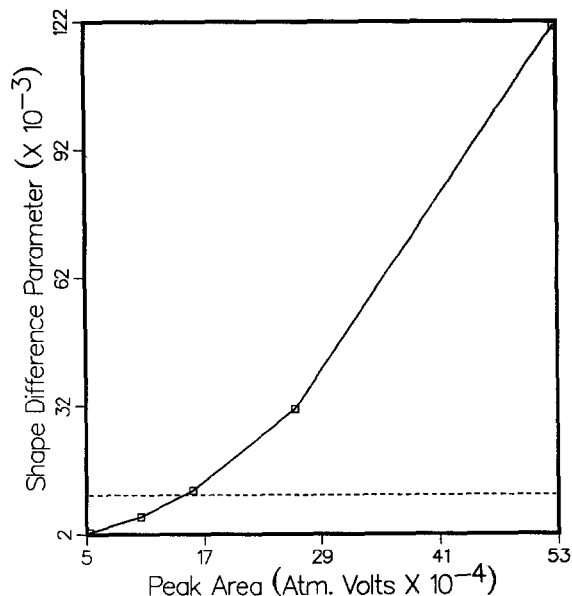


Fig. 10. Theoretical study of the sorption effect. Plot of shape difference parameter *versus* peak area for the comparison between the band profiles calculated with and without taking the sorption effect into account. Experimental conditions as in Fig. 9. Dashed line, upper confidence limit for the reproducibility of the shape parameter, for measurements made on the same day and with the same column.

The results are compared for three different sample sizes in Fig. 9. The smallest of the three peaks corresponds approximately to the amount injected in the determinations of the adsorption isotherms of the probes on the alumina samples. It is essentially the same in both parts of Fig. 9. No significant degree of column overloading is achieved with this small sample and non-linear behavior of the elution profiles is not observed. In contrast, such non-linear effects are important with the other two sample sizes. The shapes of the simulated band profiles were compared by calculating the shape difference parameter, δ , for each peak. A plot of the shape difference *versus* the peak area is shown in Fig. 10. This plot demonstrates that, under our experimental conditions, the shape difference caused by the sorption effect is insignificant unless the peak area exceeds $15 \cdot 10^{-4} \text{ atm V}$. Our measurements use sample sizes corresponding to peak areas between 0.5 and $1 \cdot 10^{-3} \text{ atm V}$.

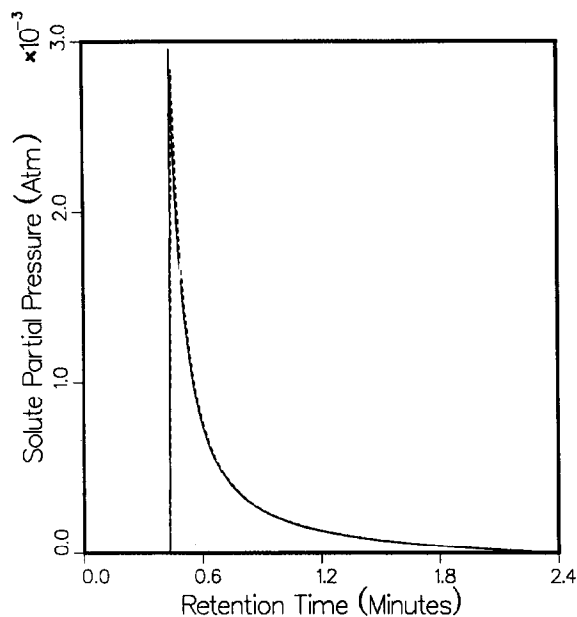


Fig. 11. Theoretical study of the sorption effect. Comparison between an experimental elution profile and the band profile calculated with the program taking the sorption effect into account. Experimental conditions as in Fig. 4 (top). The shape difference parameter, δ , is $1.1 \cdot 10^{-3}$.

Finally, we compare in Fig. 11 the elution band profile recorded for diethyl ether on RHCP alumina at 60°C and that calculated with the program taking the sorption effect into account. The narrow injection profile (Fig. 4) and a column efficiency of 8000 theoretical plates were used for this calculation. The value of the shape difference parameter between these two elution profiles is well below the confidence limit for profiles recorded on the same day and with the same column. This result completes the demonstration that the sorption effect and the pressure drop effect may be neglected under the experimental conditions used here.

These results also validate the use of our conventional liquid chromatography program [25] for the calculations reported in Fig. 8. Although the more complex program [5] taking the carrier gas mass balance (and hence the sorption effect) into account should have been used, it was not because it requires significantly more CPU time than the former program.

CONCLUSIONS

Many of the assumptions whose validity was assessed in this investigation remain valid from experiment to experiment as long as the experimental conditions and the instrument used are not significantly changed. These assumptions, however, must be tested each time a new powder sample is studied. They are (i) that adsorption occurs only on the stationary phase (*i.e.*, that the number of adsorption sites on the wall of the fused-silica tubing and on the extra-column surfaces is negligible); and (ii) that the effect of the finite column efficiency on the equilibrium isotherm derived by the ECP method may be neglected. The procedures for testing the validity of these assumptions have been described. These procedures are the quality control (QC) protocols which are necessary to test the models.

Before proceeding further with the use of the adsorption isotherms determined from elution profiles by the ECP method, it is necessary to test the reproducibility at the experimental data, *i.e.*, the band profiles, as the results of this test determine directly the reproducibility of the calculated isotherm data. The QC protocol for the reproducibility of elution profiles is as follows.

Detector response factor

If a probe is used for the first time, the response factor must be determined on two different days. The reproducibility of this factor may then be compared with the reproducibility data given in Table I. If the solute has been used before, and the response factor does not agree with earlier data, it is measured again on another day. Response factors are rejected even without different day reproducibility checks if the statistical data regarding the calibration graph are poor or if the peak-area reproducibility is not satisfactory.

Elution profile

Each elution profile used to calculate an energy distribution function is measured in duplicate. The shape difference parameter for these two measurements is calculated. If this parameter exceeds the value corresponding to the confidence limit for the reproducibility of the band shape on the same day and with the same column (see Table III), the data set should be rejected.

Accuracy of the data set

The accuracy of each data set is assessed by back-calculating the elution profile and comparing the values of the parameters t_{RMS} and δ for the simulated and the experimental band profiles with the upper confidence limits for values obtained on the same day and with the same column. If either of these parameters is greater than the corresponding upper confidence limit, the data set should be rejected.

Finally, our results demonstrate that high quality data in inverse chromatography may be obtained on an essentially unmodified, commercially available gas chromatograph. Specially designed and custom-built equipment does not seem as necessary now as it was 20 years ago [48,49]. The reproducibility of the parameters which can be calculated from the band profiles is determined almost entirely by the experimental reproducibility of these measurements. The general validity of most of the assumptions made in the derivation of the adsorption isotherm by the ECP method has been demonstrated. Only a few of the assumptions must be tested for each new set of experimental data.

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APPENDIX

Assumptions made in the derivation of eqn. 4

Assumption I. The stationary phase is distributed evenly along the length of the column.

Assumption II. The column is isothermal.

Assumption III. The thermal effect may be neglected.

Assumption IV. The viscosity effect may be neglected.

Assumption V. The mobile phase behaves as an ideal gas.

Assumption VI. The carrier gas is not sorbed by the stationary phase.

Assumption VII. Adsorption occurs only on the stationary phase, *i.e.*, the number of adsorption sites on the wall of the fused-silica tubing and on the extra-column surfaces is negligible.

Assumption VIII. The entire sample amount injected is eluted.

Assumption IX. The influence of the shape and finite width of the injection profile on the elution profile of the probe is negligible.

Assumption X. The effects of the axial dispersion and the mass-transfer kinetics on the band profile (*i.e.*, of the finite column efficiency) may be neglected.

Assumption XI. There are no extra-column sources of band broadening.

Assumption XII. The influence of the sorption effect and the pressure drop along the column on the elution profile are negligible.

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