Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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**To cite this Article** Hsu, H. W.(1971) 'Optimum Adsorbent Volume in Liquid Adsorption Chromatography', Separation Science and Technology, 6: 5, 645 — 652
**To link to this Article: DOI:** 10.1080/00372367108057960
**URL:** http://dx.doi.org/10.1080/00372367108057960

SEPARATION SCIENCE, 6(5), pp. 645–652, October, 1971

# Optimum Adsorbent Volume in Liquid Adsorption Chromatography

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## Summary

Chromatographic resolution in liquid–solid adsorption columns was analytically investigated to determine the adsorbent fraction in a column in terms of the solvent distribution coefficient. The quantitative results show that the resolution can be improved up to several times depending on the adsorbent fraction in the column and the solvent distribution coefficient.

## INTRODUCTION

Chromatographic techniques have been used for two purposes: (a) separation of a mixture into its pure components, and (b) removal of small impurities from large samples. In the former case, one is interested in the resolution of the separation, and in the latter case, the throughput is emphasized. In this investigation, the former case was studied.

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† The Molecular Anatomy Program is supported by the National Cancer Institute, the National Institute of General Medical Sciences, the National Institute of Allergy and Infectious Diseases, and the U.S. Atomic Energy Commission.

‡ Oak Ridge National Laboratory is operated by Union Carbide Corp. Nuclear Division for the U.S. Atomic Energy Commission.

The theory of resolution in liquid–solid adsorption column chromatography has been developed to only a limited extent. Consequently, most knowledge concerning the separation conditions rely largely on prior experience in choosing a set of separation conditions and techniques for a given sample. This approach proves adequate for most liquid–solid adsorption column chromatographic problems. When difficult separations arise, a simple theory of sample resolution improvement demonstrates to be of great practical benefit.

Snyder (*1*) has shown that the maximum bed efficiency in liquid–solid column chromatographic separation can be achieved if $K_2$ equals $2V^0/W$ (the ratio of free volume to adsorbent weight) under a constant plate height, $H$, condition: if $K_2 = 5$ under a specified separation time, $t$, and a given column length, $L$; and if $K_2 = 2.9$ under allowable maximum column pressure.

It is a well-known fact that bed structure in a column is an important factor affecting separation (*2*). Bed structure is determined by several factors: the material used to fill the column and particularly its average particle diameter; the technique used in filling the column; and the geometry of the column. All of these factors interact in a complex manner, thus complicating the explanation of column performance. Column filling techniques have received very limited attention in the literature (*3*). Customarily, the free volume of a chromatographic column is usually treated as a constant, depending on the material used in filling a column; and it is an uncontrollable parameter that is independent of the resolution in the column performance. However, with a new procedure of packing an adsorbent into a column, such as centrifugal packing currently under consideration by Anderson (*6*), the free volume in a packed column may become a controllable parameter.

In this paper, the ratio of adsorbent volume to total column volume was investigated analytically by maximizing the expression for resolution of the separation with respect to the adsorbent volume in a column. The expression for resolution is based on an empirical expression of Height Equivalent of a Theoretical Plate given by Waters et al. (*4*) and Simpson and Wheaton (*5*).

## DERIVATIONS OF OPTIMUM RATIO

The starting equation of the present investigation is the well-known resolution function given by Snyder (*2*),

$$R_s = \frac{1}{4}\left[\frac{K_1}{K_2} - 1\right](\sqrt{N})\left[\frac{K_2}{K_2 + (V^0/W)}\right] \tag{1}$$

where $K_1$ and $K_2$ are the distribution coefficients of the two band components, 1 and 2, which are equal to the total quantity of solute (1 or 2) in the stationary phase divided by the total quantity of solute in the moving phase at equilibrium. The quantity $N$ is the number of theoretical plates in the column and is an experimental quantity. $V^0$ and $W$ are the free volume and the weight of adsorbent in the column. The sample resolution in bed development of elution chromatography is thus due to the contributions from the adsorption selectivity $[(K_1/K_2) - 1]$, the bed efficiency $\sqrt{N}$, and the capacity factor $[K_2/(K_2 + V^0/W)]$. In the case of multicomponent separations, Eq. (1) may be used with an empirical expression, $N$, for multicomponent systems.

The number of theoretical plates, $N$, can be expressed by

$$N = L/H \tag{2}$$

in which $L$ is column length and $H$ the plate height, which is an experimental quantity. Small values of $H$ are obviously desirable for maximum resolution although larger values of $H$ can be compensated for by increases in column length. Waters *et al.* (*4*) and Simpson and Wheaton (*5*) have reported that $H$ can be approximately described for a number of liquid chromatographic systems by

$$H = 18d_p^{0.8}u^n \tag{3}$$

where $d_p$ is the particle diameter of adsorbent in the bed and $u$ is solvent velocity, in units of cm and cm/sec, respectively, and $n$ is an empirical exponent which varies from 0.3 to 0.6 for most of the liquid chromatographic systems (*4*, *5*).

If one considers a separation under the following set of operating conditions, the total separation time is limited to some value, $t$; $t$ is related approximately to the retention volume, $V_R$, of the last eluted peak and the solvent velocity $u$ by Eq. (4)

$$t = V_RL/V^0u \tag{4}$$

where

$$V_R = K_2W + V^0 \tag{5a}$$

$$= V^0[1 + K_2(W/V^0)] \tag{5}$$

so that

$$u = L[1 + K_2(W/V^0)]/t \tag{6}$$

Substituting Eqs. (2), (3), and (6) into Eq. (1), and rearranging Eq. (1), the reduced resolution function can be given as

$$\mathsf{R} = \frac{\phi(1 - \phi)^{n/2}}{[1 - \phi(1 - K_2)]^{1+n/2}} \qquad (7)$$

where

$$\mathsf{R} = R_s/A \qquad (8)$$

$$A = \frac{1}{12\sqrt{2}}\left(\frac{K_2}{K_1} - 1\right)\frac{L^{(1-n)/2}t^{n/2}}{d_p{}^{0.4}} K_2\rho_A{}^{n/2} \qquad (9)$$

$$V^0 = V_T - V_A \qquad (10)$$

$$W = V_A\rho_A \qquad (11)$$

and

$$\phi = V_A/V_T \qquad (12)$$

in which $V_T$ is the total column volume, $V_A$ the volume, and $\rho_A$ the density of adsorbent, respectively.

The conditions for maximum resolution with respect to adsorbent volume can be obtained by finding the stationary value of $\phi$, i.e., by finding a solution for

$$d\mathsf{R}/d\phi = 0 \qquad (13)$$

After the differentiation of Eq. (13), the stationary ratio between the volume of adsorbent and the total volume of the column, the optimum adsorbent fraction is found to be

$$\phi_{\text{opt}} = [1 + K_2(n/2)]^{-1} \qquad (14)$$

In order to assure that the stationary ratio is yielding the maximum resolution, the sign of the second-order derivative of Eq. (7) at the stationary ratio has to be negative. The second-order derivative at the stationary ratio, given in Eq. (14), is given by

$$\left.\frac{d^2\mathsf{R}}{d\phi^2}\right|_{\phi_{\text{opt}}} = -\left(1 + \frac{n}{2}\right)\left(\frac{n}{2}K_2\right)^2\left(1 + K_2\frac{n}{2}\right)^4 \qquad (15)$$

The quantities $K_2$ and $n$ are positive. Thus, the second-order derivative given by Eq. (15) is negative and the Eq. (14) is a maximum for the resolution function given by Eq. (7).

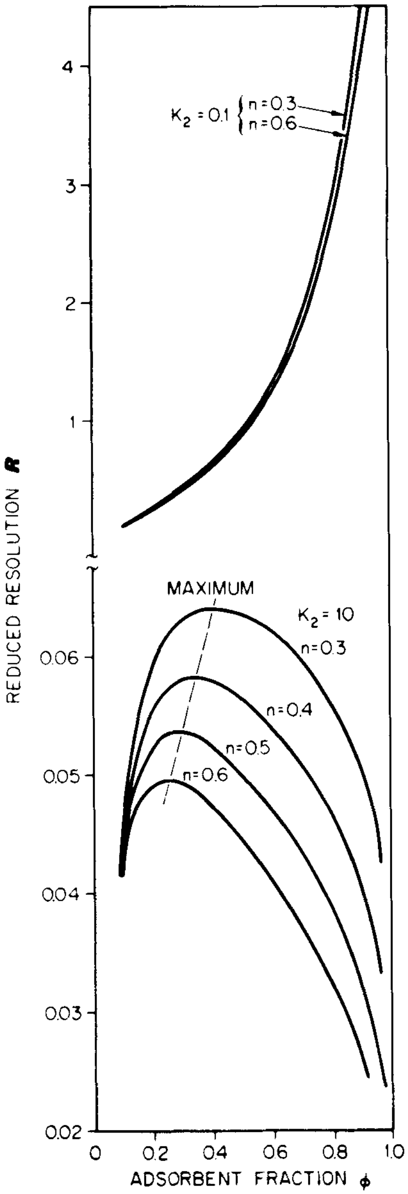

FIG. 1. Resolution as a function of adsorbent fraction in a column.

## DISCUSSION

In Fig. 1 the reduced resolution function, Eq. (7), was plotted as a function of adsorbent fraction, $\phi$, for $K_2 = 10$ and 0.1. For $K_2 = 10$, the maximum resolution is easily visualized from the curve. The resolution increases with decreasing $n$-values, the velocity parameter. The low value of $n$ means the low velocity of eluting solvent. With an increase in elution solvent velocity (increase in $n$), $\phi_{\text{opt}}$ decreases. This means that if the elution solvent velocity increases, there should be more free volume in the column. It is also easy to visualize that the maximum resolution at an optimum adsorbent fraction is an improvement of about 20–30% over an average resolution for $K_2 = 10$ and $n = 0.3\sim0.6$. For $K_2 = 0.1$, a very small distribution coefficient, it can be seen from Eq. (14) and Fig. 1 that the optimum adsorbent fraction is very close to unity. The same conclusion regarding the elusion solvent velocity holds for this case.

In Fig. 2, $\phi_{\text{opt}}$, is plotted against $K_2$ using Eq. (14). From the figure, one may conclude that $\phi_{\text{opt}}$ is insensitive to $K_2$-values greater than 40. That is to say, for $K_2 > 40$, an adsorbent fraction becomes independent of the resolution. The same conclusion, that the curve becomes insensitive to increases in $K_2$, can also be drawn from Fig. 1. The curves increase their peak heights with decreasing $K_2$-values for all $n$-values. The small

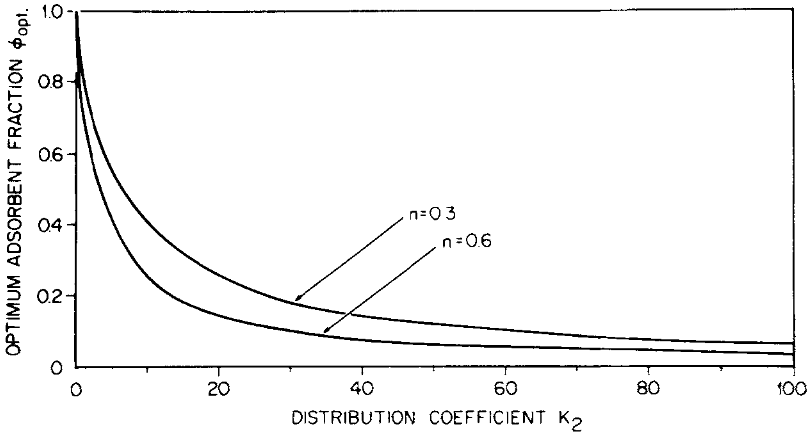

FIG. 2. Optimum adsorbent fraction as a function of solvent distribution coefficient.

$K_2$-value is more sensitive to changes in adsorbent fractions. By using a solvent with a small $K_2$-value, the resolution should increase significantly when one packs a column with adsorbent approaching the optimum ratio given by Eq. (14). The optimum ratio is close to unity.

It is very difficult but not impossible to achieve the optimum fraction for small $K_2$-values in practice. Therefore, it is suggested that one should select a solvent having a $K_2$-value ranging from 5 to 30 and fill the adsorbent into a column according to the optimum fraction given by Eq. (14). Then the resolution can be improved more than by using a higher $K_2$ solvent with an arbitrary adsorbent fraction.

## LIST OF SYMBOLS

| | |
|---|---|
| $A$ | coefficient defined in Eq. (9) |
| $d_p$ | particle diameter of adsorbent in bed (cm) |
| $H$ | height equivalent of a theoretical plate (cm) |
| $K_i$ | distribution coefficient for sample $i$ (ml/g) |
| $L$ | length of adsorbent bed (cm) |
| $N$ | number of theoretical plates in the adsorbent bed; defined in Eq. (2) |
| $\mathbf{R}$ | reduced resolution function defined in Eq. (8) |
| $R_s$ | resolution function defined in Eq. (1) |
| $t$ | separation time (sec) |
| $u$ | solvent velocity (cm/sec) |
| $V^0$ | column void volume (ml) |
| $V_A$ | adsorbent volume (ml) |
| $V_R$ | sample retention volume (ml) |
| $V_T$ | total volume of chromatographic column (ml) |
| $W$ | weight of adsorbent in bed (g) |
| $\rho_A$ | density of adsorbent (g/ml) |
| $\phi$ | fractional volume of adsorbent, as defined in Eq. (12) |

### Superscript

| | |
|---|---|
| $n$ | index for power |
| $0$ | void volume |

### Subscript

| | |
|---|---|
| $p$ | particle |
| $i$ | $i$th component |

| | |
|---|---|
| $A$ | adsorbent |
| $R$ | retention value |
| $S$ | resolution |
| $T$ | total value |
| opt | optimum value |

## Acknowledgments

The author wishes to express his sincere appreciation to Dr. Norman G. Anderson for his constant encouragement and valuable discussions, and also to Dr. John W. Eveleigh for valuable suggestions and discussions. The expert assistance from the staff of the Molecular Anatomy Program at Oak Ridge National Laboratory is always appreciated.

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*Received by editor January 14, 1971*