Separation Efficiency Versus Column Length. An Experimental Study With Capillary Columns

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Abstract

The columns of different length used for studying the relation between HETP and column length are supposed to exhibit identical characteristics per meter. In the laboratory this condition cannot be rigorously fulfilled. The best approximation probably consists in starting the work with a relatively long capillary column followed by running shorter parts obtained by progressive cutting of the original column. Based on this procedure a marked increase of HETP with increasing column length is observed.

Introduction

There are two reasons to present experimental data on the relation between separation efficiency and column length:

1. *Practical efficiency versus column length:*

Although there is a common agreement that the relation is not linear, there seems to be some lack of knowledge about gaining a practical advantage by working with long columns. Trying to improve a difficult separation by running a longer column, many chromatographers still are very disappointed by their actual accomplishment. Most often they attribute the failing to poor column preparation whereas in fact they may have nearly reached the experimental optimum. There are few indications of such optima in the literature.

In agreement with the arguments of Kaiser (1) we found the *separation number* the best-suited concept to describe the effective separation power of a column. We therefore wish to list separation numbers for columns, the length of which has been changed by cutting or connecting.

2. *HETP versus column length:*

According to current theories of the chromatographic separation, HETP should be independent of column length. Halasz, Deininger and Gerlach (2), however, found a marked increase of HETP when two practically identical packed columns were coupled. They directed special attention to the uniformity of the connected parts since loss of plates had been attributed to coupling of dissimilar parts. Kwok, Snyder and Sternberg (3) have published a theoretical study concerning this problem.

Capillary columns are especially suited for the experimental evaluation of the function of column length. Progressive cutting of a long column and comparison of the performance of the original column with its own parts probably provides the best opportunity to eliminate trouble caused by nonuniformity of connected parts.

Experimental

All columns used were glass capillaries the inner surface of which, prior to coating with the stationary phase, had been treated in one of the ways described earlier (4,5). It is not the purpose of this paper to present excellent separation. We therefore used capillary columns of moderate quality since we did not like to lose our best columns by cutting them down.

The chromatographic work was done on Carlo Erba gas chromatographs Mod. GI with FID. On this equipment there is virtually no dead volume either in the sample introduction or in the detector portion.

Column A, 240 m long and .41 mm wide had been drawn, pretreated (inner surface carbonized), and coated in one piece with special attention to uniform coating over the entire length. The liquid phase was Ucon LB 550 with film thickness of .1 μ. We first ran the entire column at 62°C with an average gas velocity of 38 cm/sec. Due to the thin liquid film and the use of hydrogen as carrier gas this velocity was only twice as high as the optimum gas velocity. The sample was a mixture of undecane and dodecane allowing the determination of separation numbers. HETP values were calculated from the dodecane peak. The column was then cut into halves of 120 m length that were run at the same temperature and with the same average gas velocity. This procedure was continued up to 16 parts of 15 m length. Throughout the entire series retention times and column lengths showed excellent proportionality, which was not the case for separation numbers and HETP values as shown in Figure 1. The dispersion of average results

1. Kaiser, R., "Chromatographie in der Gasphase," 2nd. Ed. Vol. II, Bibliographisches Institut, Mannheim, West Germany, 1966.
2. Halasz, I., Deininger, G., and Gerlach, H.-O., J. Chromatog. 35, 1 (1968).
3. Kwok, J., Snyder, L. R., and Sternberg, J. C., Anal Chem. 40, 118 (1968).
4. Grob, K., Helv. Chim. Acta 48, 1362 (1965).
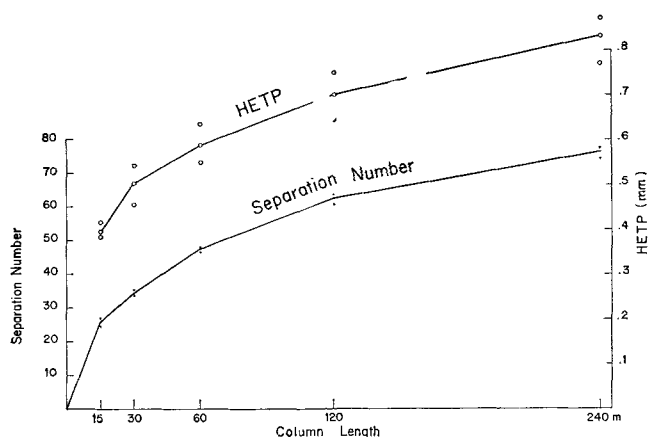5. Grob, K., Helv. Chim. Acta 51, 718 (1968).

Figure 1. Separation efficiency versus progressively shortened column length, Column A, 240 m/.41 mm, Ucon LB 550.

from different columns of the same length was much smaller than the dispersion of results from a single column. This proves the high degree of uniformity. The limits of dispersion ranges as shown in Figure 1 represent single determinations, not averages from single columns.

Column B, 66 m long and .35 mm wide, had been precoated with polytrifluorochlorethylene and coated with silicone oil F 50. The entire column, as well as its parts, were run at 66°C with 29 cm/sec average
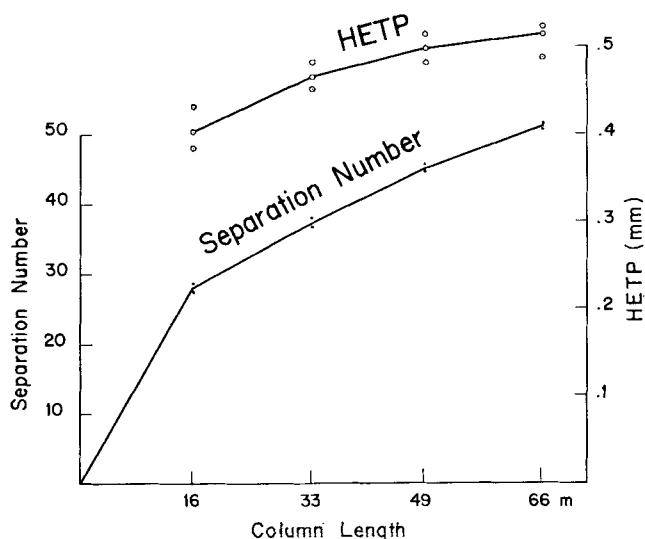

Figure 2. Separation efficiency versus progressively shortened column length, Column B, 66 m/.35 mm, silicone oil F 50.

gas velocity. Sample and handling of results were the same as for column A. Averages and dispersion ranges are shown in Figure 2.

Both columns were reconnected, column A up to 120 m, column B to its original length. In both cases

separation numbers for the connected columns did not differ significantly from the original values. This achievement, however, required very careful coupling. The exact plane cuts were fastened tightly together with Teflon shrink tubing as recommended by Zlatkis (6).

We connected a great number of capillaries of various length, width, and coating. The results varied. As a quality value we used the factor indicating the increase of the separation number caused by doubled length. This factor normally varied between 1.2 and 1.4. The maximum observed hitherto was 1.53 for two 15 m pieces. Even when the coupled parts had been drawn together and were coated in the same way, the effect of coupling was often disappointing, probably due to unnoticeable dissimilarities of the parts. As a rule, we found high factors for parts of high quality.

Conclusions

In agreement with Halasz et al (2) we found a significant increase of HETP with column length that cannot be attributed to nonuniform column characteristics. We therefore doubt whether concepts such as HETP or number of theoretical plates per meter are correct figures to describe the effective quality of a given column.

As can be seen from Figure 1 and 2 the separation number shows much less dispersion than HETP. This confirms one of the statements made by Kaiser in favour of the separation number as a direct quality figure.

As proven by repeated cutting and reconnecting of capillaries, careful coupling does no observable harm to the serapartion efficiency, at least not for capillaries with an inner diameter larger than .25 mm.

We conclude the following from the work with capillary columns. On one hand the increase of separation efficiency with length is relatively modest and is accompanied by prolonged analysis times. On the other hand the increase of efficiency with length is greater as the quality of the liquid coating is improved. These observations cause us to concentrate our attention first of all to the quality of the coating, i.e., to the spreading of the liquid phase on the column walls. Only in cases of assured quality coating does the preparation of long columns become worthwhile.

6. Zlatkis, A., private communication, 1967.