INCREASED EFFICIENCY FOR LARGE-VOLUME GAS CHROMATOGRAPHIC SAMPLES

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INTRODUCTION

The effect of sample-size broadening has long been recognized in gas chromatography. Sample-size broadening should not be confused with peak diffusion due to large retention volumes resulting from long lengths of columns or large numbers of theoretical plates. Fig. 1 illustrates the progressive broadening and flattening of a peak as the sample size is increased. Ideally, the sample should be injected as a small slug, so as to occupy initially a space equivalent to only a small percentage of the plates in the column. The number of plates which may be nonrestrictively taken up by the sample increases as the number of plates in the column increases[1].

In regard to peak widths and shapes, DAL NOGARE[2] pointed out that determination of true column efficiency should involve the measurement of band spreading due only to the column and not to extra-column factors. JOHNSON AND STROSS[3] separated the effects on peak width into column and noncolumn factors. They also theoretically calculated and plotted noncolumn peaks (peaks due to the apparatus without the column). PURNELL[4] studied the effect of sample size of isopropanol on the efficiency of a firebrick column coated with 20% polyethylene glycol. WHATNOUGH[5] determined the effect on peak shape as larger quantities of methane were injected into an absorption column. PORTER, DEAL AND STROSS[6] theoretically calculated and plotted curves for varying sample sizes in the case of plug-type charging of a solute–gas mixture. Plug injection *versus* exponential injection for large samples was studied by DE WET AND PRETORIUS[7], who showed that higher column efficiencies may be obtained by introducing the sample in as concentrated a form as possible.

The purpose of this paper is limited to the effect of one factor on efficiency, *viz.*, the effect of an enlarged section in a packed column on peak shape, especially in those instances involving large samples of gases. The effect of increasing the diameter, in the case of uniform-diameter columns, has been studied by DE WET AND PRETORIUS[8]. Very little has been reported on the effects of cross-sectional geometry on column efficiency, and it appears that the use of enlarged sections may afford excellent opportunities for easily improving efficiencies.

EXPERIMENTAL

Columns

Two columns were compared in this study. One column was made of 1/4-in. uniform-diameter copper tubing, 12 ft. long, and packed with 30/60-mesh acid-washed Chromosorb coated with tri-*m*-cresyl phosphate (20% by weight). The second column was identical to the first, with this exception: a 4 1/2-in. length of 3/8-in. diameter copper tubing, filled with packing identical to that in the columns, was attached to the forefront of the column[9].

Conditions of operation

Helium was used as a carrier gas in these studies, at an exit flow rate of 30 ml/min. The temperature of the two columns was maintained at 40°, as was the temperature of the thermal conductivity (thermistor) cell. All samples were injected through a rubber septum with a hypodermic syringe as rapidly as possible to simulate a slug-type charge.

Retention times were measured from the point of injection to the midpoint of the peak. Peak base lengths were measured between the intercepts of the tangents to the peak at the base line. Column efficiency is expressed in terms of numbers of theoretical plates, as recommended by a special committee of the International Union of Pure and Applied Chemistry[10], in July 1959:

$$n = 16\,(t_R/\Delta t)^2$$

where: n = number of theoretical plates
t_R = retention time
Δt = peak base measured at points where the extended tangents intersect the base line.

EXPERIMENTAL DATA AND DISCUSSION

The effect of varying the sample size, for a plug-type charge, is shown in Fig. 1 for samples of ethane. A small decrease in retention time, not indicated, was noted for each increase in sample volume. The series of curves in the figure resemble those calculated theoretically by PORTER, DEAL AND STROSS for plug-type charging of a solute–gas mixture[6]. As pointed out by these authors, the flattened top on the upper curve corresponds to the case in which the sample size is so large that it fills a substantial part of the column before the charging step is complete.

Fig. 2 shows the effect of using an expanded-section column on the elution curve for 40-ml samples of ethane. All conditions of operation and column construction were identical with the exception of the addition of a 4 1/2-in. length of 3/8-in. diameter packed tube at the forefront of one column. A marked increase in efficiency was noted with the expanded section; a similar increase was also present when the column was inverted so that the expanded section was next to the thermal conductivity detector used in this work. The total peak area is decreased, as is the retention time (the latter

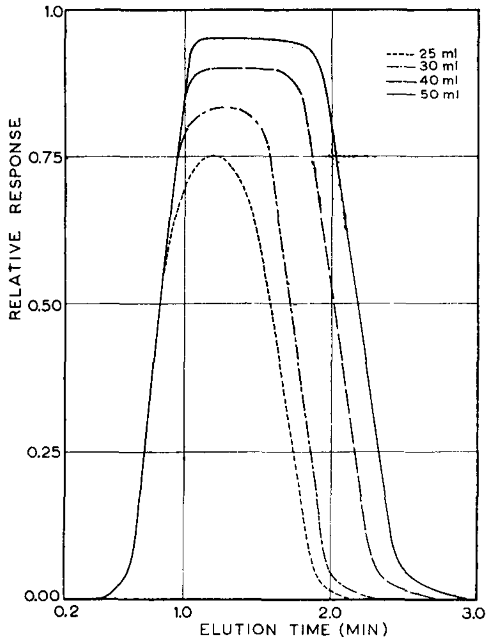

Fig. 1. Elution curves for variable samples of plug-injected ethane.

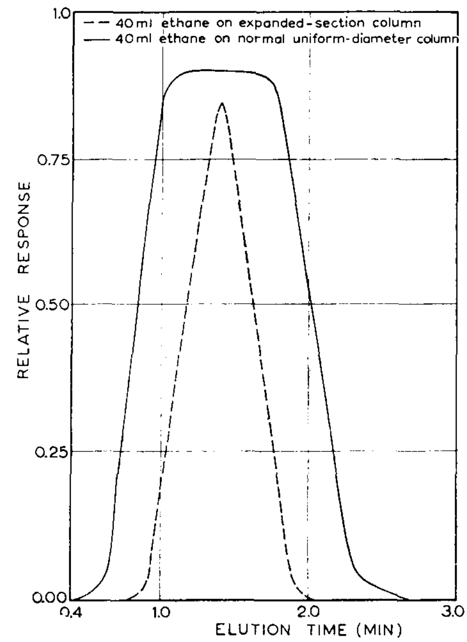

Fig. 2. Elution curves for equal-volume samples analyzed on expanded-section and normal columns. A short, packed, enlarged section was attached to the forefront of one of the columns; otherwise, both columns were identical. Conditions of operation were identical.

is not indicated in Fig. 2), for the peak resulting from the expanded-section column. The reason for the anomalous behavior in the decrease in peak area is not evident.

Fig. 3 shows the effect of sample volume on column efficiency for methane, ethane, and propane, with both a normal uniform-diameter column and a similar column containing an expanded section. The ranges of volumes studied increase in order of methane, ethane, and propane; *i.e.*, the uniform-diameter column gave maximum nonflattened peaks of 15 ml for methane, 25 ml for ethane, and 35 ml for propane.

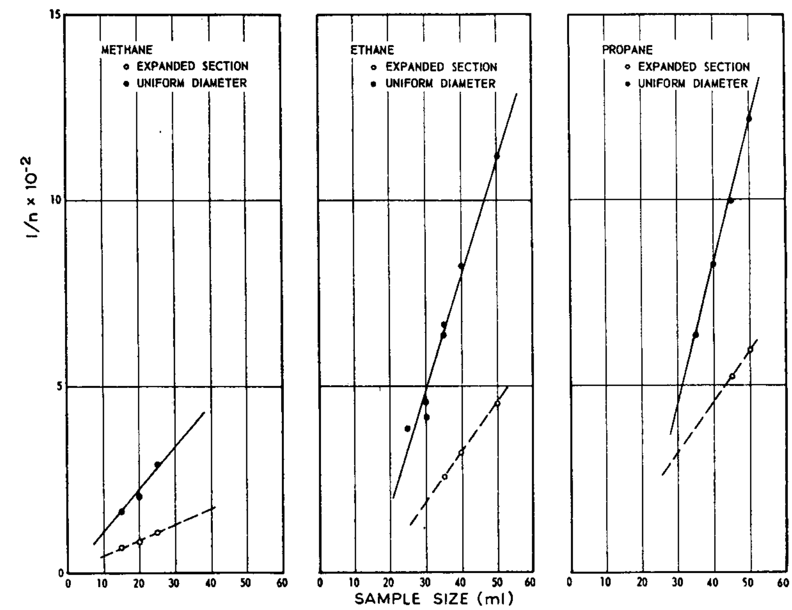

Fig. 3. Comparison of effects of sample volume on column efficiency for methane, ethane, and propane.

Also, these maximum values for usable sample sizes were increased, by the addition of the enlarged packed section, to 25, 40, and 50 ml respectively.

The effect of increasing volume on peak shape has been treated theoretically in detail[6,7,11], as has the effect of increasing diameter in uniform-diameter columns[8]. The beneficial effect of the enlarged (expanded) section in the work being reported is clearly evident. The maximum volume which could be handled was increased by a factor of about 1.5 by use of the expanded section. Since only a short section of increased-diameter tubing was used, the value of 1.5 seems reasonable compared to the value of about 2.3 calculated for a full length column on the basis that the volume of sample which can be handled by a column at a chosen efficiency is proportional to the square of the column diameter[8]. The enlarged section acts as a collector to compress the sample under a given peak into a shorter plug. This is probably due to increased lateral diffusion in the enlarged section.

The addition of expanded sections to normal uniform-diameter columns may prove beneficial in large scale preparative columns, or even perhaps capillary columns, by enhancing the efficiency and resolution. Enlarged sections have been used in this laboratory to improve the analysis of small quantities of multicomponent mixtures diluted by large volumes of carrier gas.

SUMMARY

The authors studied the effect of adding a packed, enlarged-diameter section to a gas chromatographic column. Two columns, identical in all respects except for one having an enlarged section, exhibit markedly different efficiencies. The use of the enlarged section increases the efficiency and also increases the maximum volume of sample which may be handled by the packed column.

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