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Effect of Carbon Number, Phase Polarity, Temperature, and Flow Rate on Preparative Scale Gas-Chromatographic Separations of Saturated Methyl Esters*

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Summary

A study of the operating conditions giving the highest production rate for a preparative scale gas-chromatographic separation of saturated methyl ester mixtures in a 1-in. I.D. × 3-ft column is described. The results obtained on egs (polar) and SE30 (nonpolar) columns in general were quite similar, with the exception that the production rates obtained in the egs columns were about one-third to one-fourth of those obtained in the SE30 column under comparable operating conditions. It was found that the production-rate values for a mixture increased approximately linearly with increased carrier gas flow rates up to 4.00 liters/min. As the column temperature was increased for each sample mixture, the production rate increased and passed through a maximum value, after which the production rate decreased rapidly. The maxima in the production-rate curve occurred for relatively small samples which were rapidly eluted through the column. The production rate decreased with an increase in the carbon number of the constituents in the methyl ester mixtures.

Efficient preparative scale sample purification by gas chromatography can only be performed when the factors affecting the sample production rate are understood. Numerous studies have been made concerning analytical column resolution and efficiency over the past years. However, such studies are not necessarily applicable to preparative scale success because it is dependent on achieving

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efficient sample separation under quite different (i.e., much higher) conditions of solute concentration. These higher concentrations normally invoke noticeable changes in the separation factor and solute distribution coefficients. Also, the higher concentrations, along with the greater diameter of preparative columns, cause heats of absorption and desorption and heat-transfer rates to become important. When sizeable temperature changes and gradients occur, separation factors and distribution coefficients will be greatly influenced.

Published experimental studies of important operating factors which affect the performance of preparative columns are quite limited (*1,7,11*). Theoretical investigations pertaining to the effect of various parameters on the sample purification rate have been more extensively conducted (*2–6,10*). Experimental and theoretical work has undoubtably been hindered by the imposing list of interrelated factors which affect the operation of such columns and which greatly complicate an optimization of the system. Although the reported use of preparative scale work is increasing, there is a noticeable lack of adequate data to describe the preparative scale separations and performance of particular systems. Performance data is usually limited to theoretical plate measurements. It is important to determine the number of theoretical plates present in a column; however, theoretical plate calculations are based on an assumption of low sample concentration which is normally not used in preparative scale chromatography. It has consistently been the observation in this laboratory for the system under investigation that the practical results, in terms of sample production rate, are not related in an absolute manner to the number of theoretical plates achieved in a given column. In particular, the sample production rate has been found to be strongly affected by experimental operating conditions, whereas the number of theoretical plates were found to not vary at all or to vary in a manner which was not directly related to practical preparative performance. Therefore, it is far better to describe actual preparative scale performance in terms of the production rate that can be attained in a given system at specified operating conditions.

Previous publications from these laboratories (*8,9*) have given data on some of the important operating parameters for 1-in. I.D. preparative columns. The present paper extends this study to the influence that carrier gas flow rate and column temperature can have on the performance obtained in the same 1-in. I.D. columns.

NOMENCLATURE

The two basic terms, maximum separable sample size (ml) and maximum production rate (ml/hr), which will be used here as a measure of the preparative scale performance, were discussed in an earlier publication (*8*). It is especially important to note that these two terms refer to sample separations in which the individual component peaks, if trapped in their entirety at 100% efficiency, would yield individual component purities greater than 99%. The production rate is based on the total sample injected, not on the yield of a particular component; i.e., production rate = quantity of feed processed per unit time. All production rates would be increased considerably if lesser separation and rejection of an appropriate intermediate fraction were accepted.

Earlier publications (*8,9*) have discussed the effect that various column-inlet operating conditions, sample injection systems, and sample injection techniques have upon the sample separation and production rate. The column design and functional accessories have already been discussed and are not variable in this work. Variables to be considered here are sample injection time I, sample size S, column temperature T, carrier gas flow rate F, and carbon number C. Accordingly, it is desirable to devise a short-hand method of indicating which of these variables have been locally optimized.

Two maximum production rates are presented in this work. These are defined as:

Maximum production rate (I, S) = maximum production rate at a fixed column temperature, carrier gas flow rate, and for a specific feed mixture. Injection time I and sample size S have been locally optimized.

Maximum production rate (I, S, T) = maximum production rate at a fixed carrier gas flow rate and for a specific feed mixture. Injection time I, sample size S, and column temperature T have been locally optimized.

EXPERIMENTAL

The equipment and column packing procedures used in this work were the same as have been described previously (*8*).

All columns were 1-in. I.D. × 3 ft in length and packed with either 20% egs on 80/100 mesh Gas Chrom P or with 20% SE30 on the same support (Applied Science Laboratories, Inc., State Col-

lege, Pa.). A constant-temperature circulating-air oven was used to thermostat the column and associated apparatus. The column inlet cone in all cases was purposely maintained about 60°C higher than the operating column temperature. The inlet cone was heated by a Nichrome resistance winding placed around the cone. Helium was used as the carrier gas. The carrier gas flow rate, as reported throughout this work, is in liters per minute measured at atmospheric pressure and room temperature.

Sample injections used in this work were equal-weight binary mixtures of saturated fatty acid methyl esters covering the carbon number range 8 to 20. The component parts of the binary mixtures differed by two carbon atoms in each case. All data runs have been made with a modified injection technique, injection system, and column heating, as described in a previous publication (*8*).

Sample injections were made through a 22 gage syringe needle as a rotary spray issuing against the wall of an empty vaporizer block. Two layers of $\frac{1}{4}$-in.-diameter steel shot were placed over the exit port of the vaporizer to prevent unvaporized material from entering directly into the column.

The entire flow of sample and carrier gas issuing from the column passed through the $\frac{3}{8}$-in. I.D. gas channel of a thermal conductivity detector. The detector consisted of a 4-in. cube of carbon steel drilled to accept Gow-Mac W-9225 thermal conductivity filaments.

The maximum production rates (I, S) were determined for the various binary methyl ester mixtures over a range of column temperatures and carrier gas flow rates. The normal range of gas flow rates investigated was 1.25 to 2.86 liters/min. Results were obtained for one binary mixture at a gas flow rate of 4.00 liters/min. However, it was found that at the higher temperatures a column was ruined in a relatively short period of time at a 4.00 liters/min flow rate. Therefore, most of this work was limited to a maximum gas flow rate of 2.86 liters/min. The three binary samples used in this work were equal-weight mixtures of the following: methyl caprylate/methyl caprate; methyl myristate/methyl palmitate; methyl stearate/methyl arachidate.

RESULTS

Methyl Ester Injections on SE30 Column

The experimental procedures by which the maximum production rate was determined for a given set of column operating conditions

are presented in (8). The maximum production rate (*I*, *S*) for a specified column temperature and carrier gas flow rate was always obtained with the maximum separable sample size, which in turn was obtained over a range of optimum injection times.

Maximum-production-rate (*I*, *S*) values for an equal-weight mixture of methyl caprylate and methyl caprate were determined for the various column temperatures and carrier gas flow rates in an SE30 column as shown in Figs. 1 and 2. The maximum production rate (*I*, *S*) increased approximately linearly with increased carrier gas flow rates, as shown in Fig. 1. The manner in which the production-rate data are plotted in this paper was used to simplify the figures and not to indicate high accuracy of the data. There is obviously scattering of the data, and smoothed lines should in actuality be fitted to the data points. Although most of the gas-flow-rate data were not extended above 2.86 liters/min, Fig. 2 shows that the maximum production rate (*I*, *S*) continued to increase up to 4.00 liters/min. However, at column temperatures above about 215°C, the column could not survive this high flow rate. As the column temperature was increased, the maximum production rate (*I*, *S*)

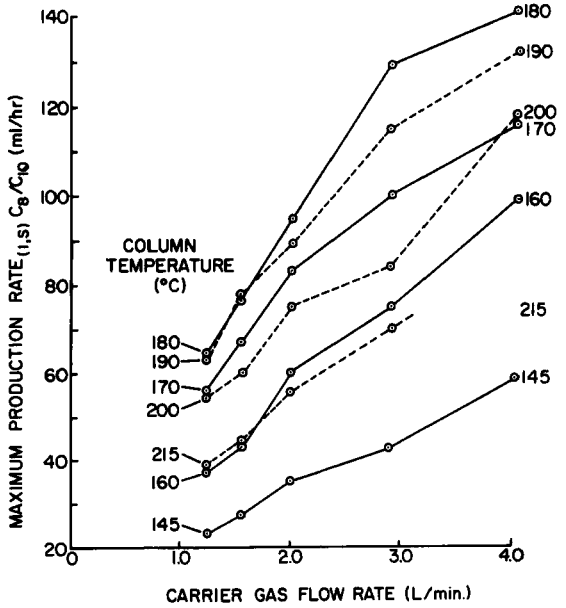

FIG. 1. Maximum production rate studies, C_8/C_{10} injection, SE30 column, 1-in. I.D. × 3-ft column.

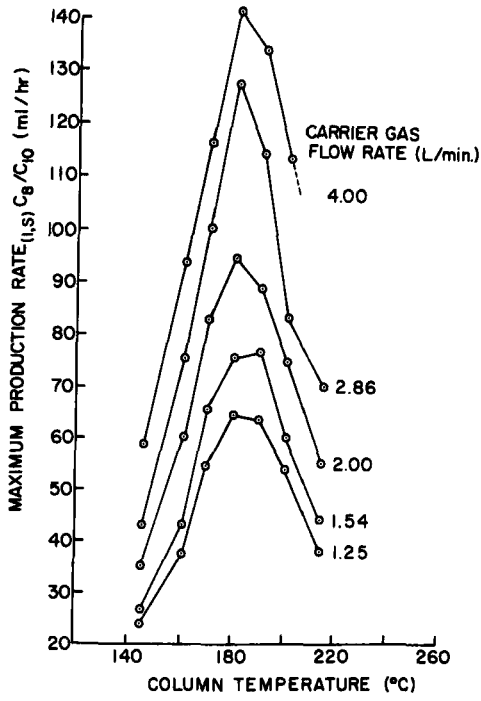

FIG. 2. Maximum production rate studies, C_8/C_{10} injection, SE30 column, 1-in. I.D. × 3-ft column.

reached a maximum value [maximum production rate (I, S, T)] and then declined, as shown in Fig. 2.

Maximum-production-rate (I, S) values at varying column temperatures and carrier gas flow rates were also determined for an equal-weight mixture of methyl myristate and methyl palmitate and for an equal-weight mixture of methyl stearate and methyl arachidate as shown in Figs. 3 and 4. The maximum production rate (I, S) versus carrier gas flow rate plots obtained for the above two sample mixtures were quite similar in nature to the results shown in Fig. 1 for the methyl caprylate/methyl caprate mixture. However, as the average carbon number of the sample increased, the maximum production rates (I, S) decreased.

The maximum production rate (I, S, T) for each binary mixture at the various carrier gas flow rates, as determined from Figs. 2, 3, and 4, occurs at a relatively high column temperature for each

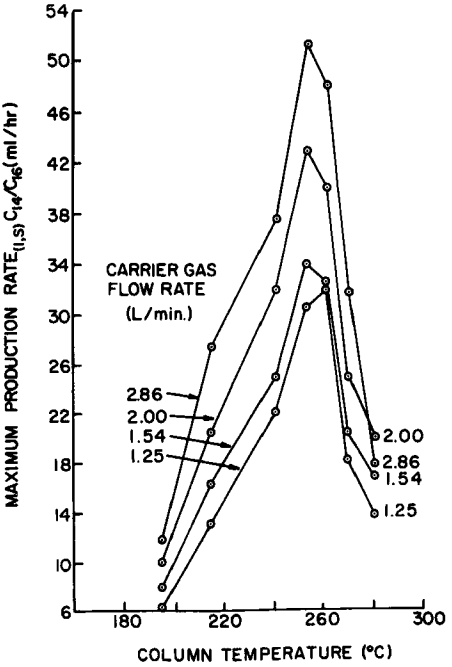

FIG. 3. Maximum production rate studies, C_{14}/C_{16} injection, SE30 column, 1-in. I.D. × 3-ft column.

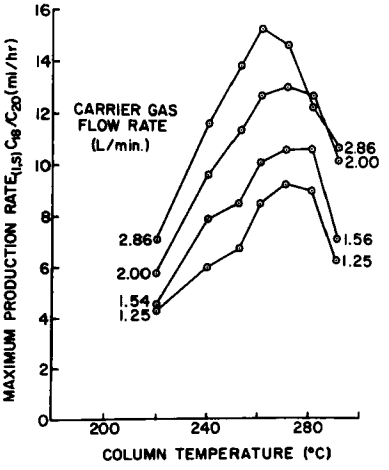

FIG. 4. Maximum production rate studies, C_{18}/C_{20} injection, SE30 column, 1-in. I.D. × 3-ft column.

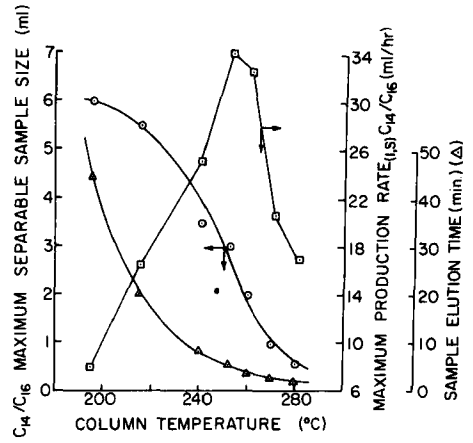

FIG. 5. Comparison of maximum production rate, sample elution time, and maximum separable sample size as a function of column temperature. 1-in. I.D. × 3-ft 20% SE30 column, carrier gas flow rate 1.54 liters/min, C_{14}/C_{16} (50/50 wt.) injections.

binary mixture. The maximum-production-rate (I, S) data at a carrier gas flow rate of 1.54 liters/min, as shown in Fig. 3, is reproduced in Fig. 5 along with the variation of the maximum separable sample size and the sample elution time with column temperature. Both maximum separable sample size and elution time decrease

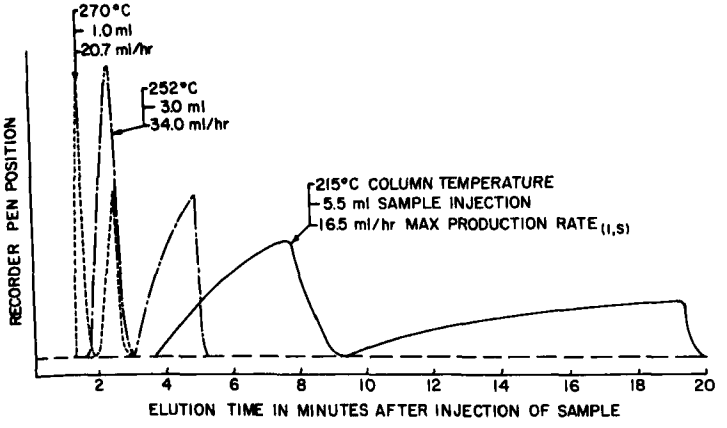

FIG. 6. Maximum separable sample size peak characteristics at varying column temperatures, C_{14}/C_{16} injection, SE30 column, 1-in. I.D. × 3-ft column, carrier gas flow rate 1.54 liters/min, attenuation = × 128.

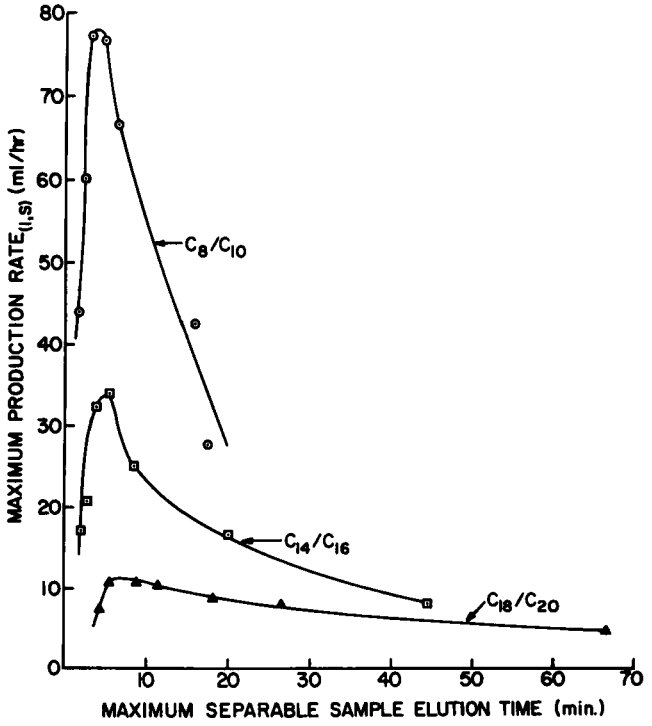

FIG. 7. Maximum production rate for varying sample cycle times for SE30 column, 1-in. I.D. × 3-ft column, carrier gas flow rate 1.54 liters/min.

with increasing column temperature. Initially the rate of decrease of elution time is greater than the rate of decrease of maximum separable sample size. However, a temperature is reached at which this trend reverses. This results in the maximum production rate (I, S) passing through a maximum value to give the maximum production rate (I, S, T). Figure 6 shows selected chromatographic curves which were used to prepare Figs. 3 and 5 and also illustrates that relatively high column temperatures and small injections result in rapid elution times and high sample production rates. Figures 7 and 8 illustrate the advantage of choosing the proper column temperature and therefore cycle or elution time to attain the highest production rates for the particular methyl ester injection in the SE30 column.

A very convenient means of summarizing all the information obtained for the methyl ester injections in the SE30 column is to

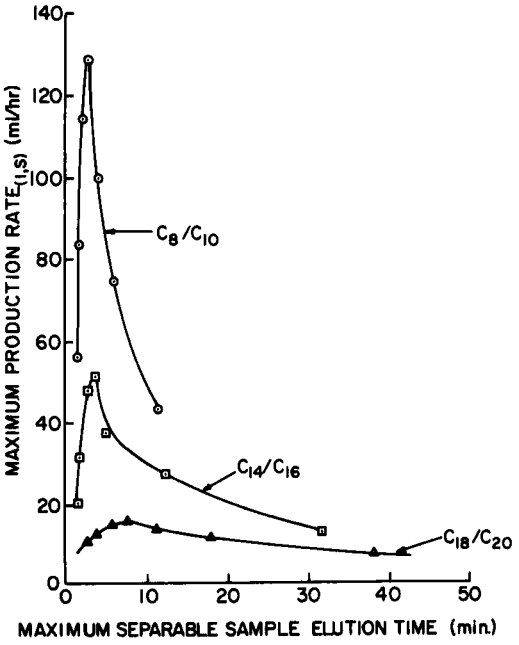

FIG. 8. Maximum production rate for varying sample cycle times for SE30 column; carrier gas flow rate 2.86 liters/min; 1-in. I.D. × 3-ft column.

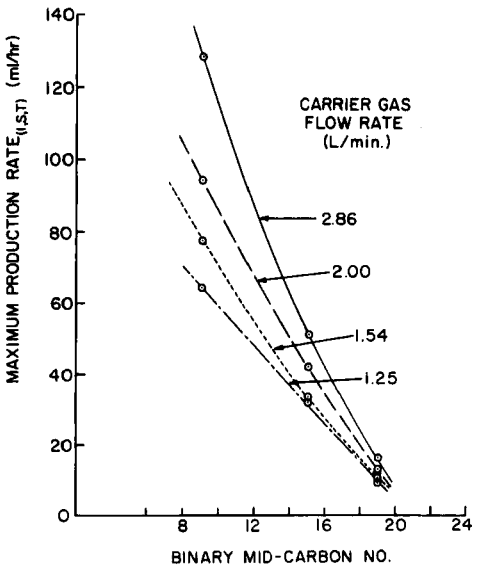

FIG. 9. Maximum production rate (*I*, *S*, *T*) variation with carbon number SE30 column, 1-in. I.D. × 3-ft column.

relate the maximum production rate (I, S, T) to the binary mid-carbon numbers and gas flow rates as shown in Fig. 9. Figure 9 therefore indicates the highest production rate possible for each binary mixture for the stated operating conditions and experimental design used in this study.

Methyl Ester Injections on egs Column

Analogous experiments to the methyl ester injections in the SE30 column were performed with the same equal-weight binary mixtures in an egs column. Figures 10 and 11 illustrate that the effects of the column temperature and carrier gas flow rate on the maximum production rate (I, S) of an equal-weight mixture of methyl caprylate and methyl caprate in the egs column were quite comparable to that noted for the SE30 column in Figs. 1 and 2. Maximum-production-rate (I, S) values for comparable operating conditions were, however, lower than obtained in the SE30 column. Although comparable sample resolution occurs in both egs and SE30 columns, the elution rate of the preparative scale methyl ester samples is much more rapid with SE30 columns than in egs columns. Sample injections of methyl myristate and methyl palmitate and of methyl stearate and methyl arachidate in the egs column

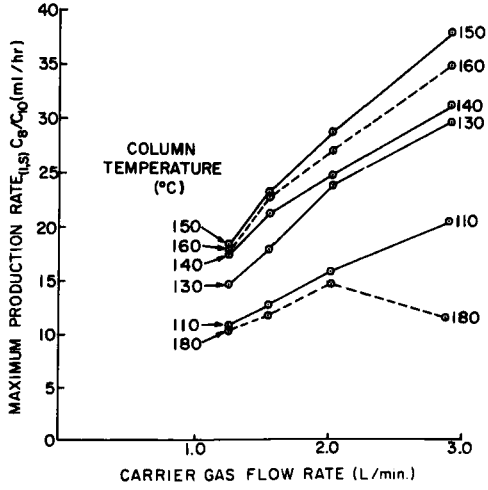

FIG. 10. Maximum production rate studies, C_8/C_{10} injection, egs column, 1-in. I.D. × 3-ft column.

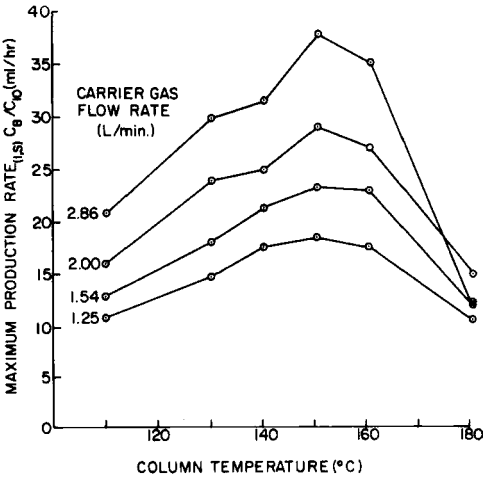

FIG. 11. Maximum production rate studies, C_8/C_{10} injection, egs column, 1-in. I.D. × 3-ft column.

(Figs. 12 and 13) showed comparable results with the same sample injections in the SE30 column in Figs. 3 and 4, respectively. Again the maximum-production-rate (I, S) values obtained in the egs column were lower than for the SE30 column. An experimental discrepancy apparently has appeared in Fig. 12 for carrier gas flow

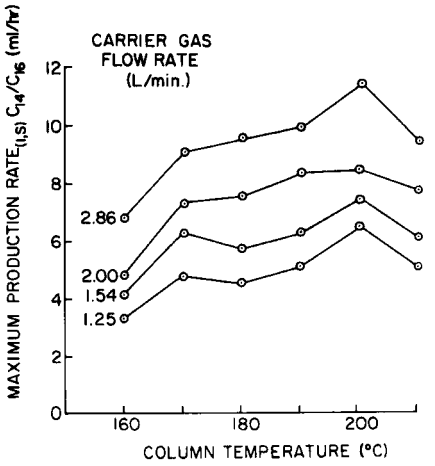

FIG. 12. Maximum production rate studies, C_{14}/C_{16} injection, egs column, 1-in. I.D. × 3-ft column.

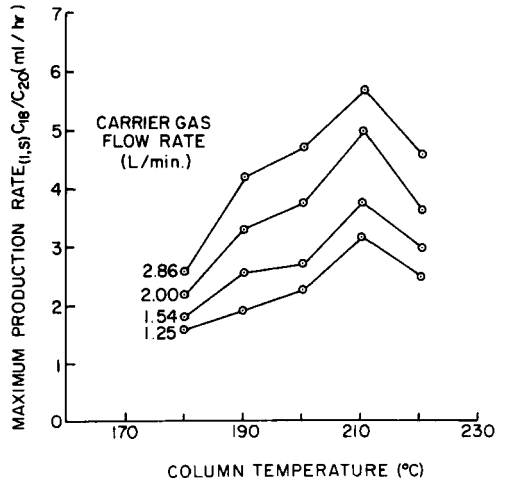

FIG. 13. Maximum production rate studies, C_{18}/C_{20} injection, egs column, 1-in. I.D. × 3-ft column.

rates of 1.25 and 1.54 liters/min at a column temperature of 170°C, in which a higher than expected maximum production rate (*I, S*) of the methyl ester sample occurred. The reason for this discrepancy is unknown.

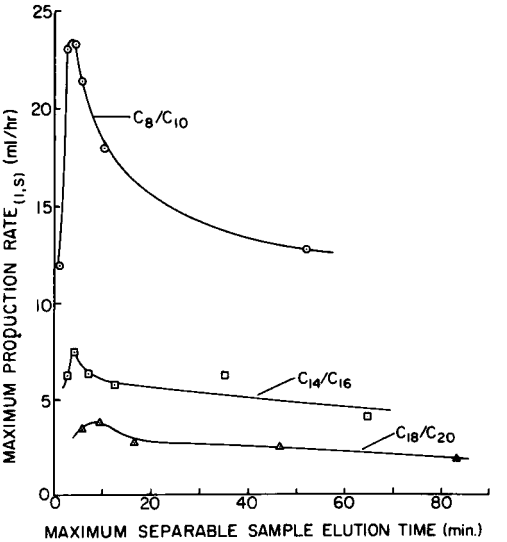

FIG. 14. Maximum production rate for varying sample cycle times for egs column, 1-in. I.D. × 3-ft column, carrier gas flow rate 1.54 liters/min.

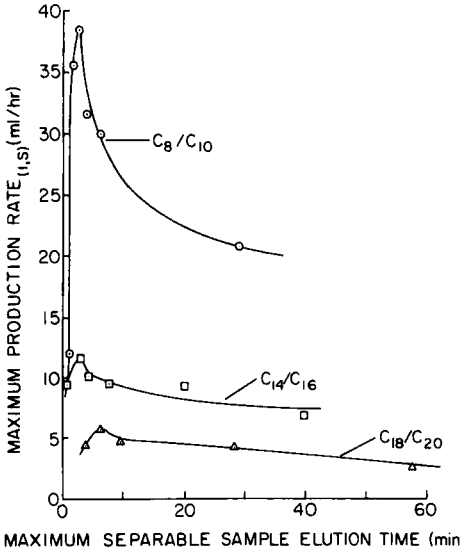

FIG. 15. Maximum production rate for varying sample cycle times for egs column, 1-in. I.D. × 3-ft column, carrier gas flow rate 2.86 liters/min.

It is evident from Figs. 11 through 13 that relatively high column temperatures result in increasing maximum production rates (*I*, *S*) for each methyl ester injection in egs columns as well as in SE30 columns. Figures 14 and 15 illustrate that a proper choice of oper-

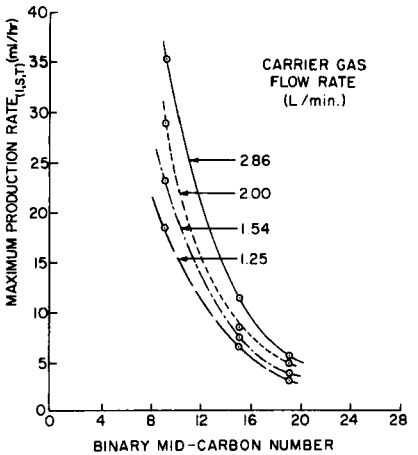

FIG. 16. Maximum production rate (*I*, *S*, *T*) variation with carbon number, egs column, 1-in. I.D. × 3-ft column.

ating conditions is necessary to achieve maximum sample production rates for the egs column. A summary of the methyl ester data obtained with the egs column is shown in Fig. 16.

DISCUSSION

The significance of this work is to point out the considerable effect that carrier gas flow rate and column temperature can have on the production rate of preparative scale samples. It has been found that small sample injections which elute rapidly give the best sample production rates.

An increase in the carrier gas flow rates hastens the elution rate and normally increases the production rate. The sample production rate in this work was found to increase approximately linearly with carrier gas flow rate at a given column temperature. Exceptions to the preceding statement were noted only for sample injections made at high column temperatures (significantly above the optimum column temperature) and at the highest carrier gas flow rate. At the operating conditions just mentioned, the sample elution rate was quite rapid. It was noted for the carrier gas flow rate of 2.86 liters/min that the maximum separable sample size was usually noticeably lower than expected at the highest column temperatures investigated for each sample. This resulted in the sample production rate being lower for a carrier gas flow rate of 2.86 liters/min than for the carrier gas flow rate of 2.00 liters/min, as shown in some of the data presented above.

The carrier gas flow rate cannot be increased indefinitely because, at some point, column damage will occur in the form of flow channeling or a removal of the stationary liquid phase from the solid support. Column damage, which can be attributed only to an excessive carrier gas flow rate, has been observed in several experimental columns used in this laboratory. The flow rate at which damage occurred was influenced to a great extent by the column temperature. For example, SE30 columns which had been operated successfully at carrier gas flow rates of 4.0 liters/min at column temperatures up to 215°C for several weeks failed to give routine separations at lower flow rates after the column had been operated at a carrier gas flow rate of 4.0 liters/min at temperatures of 240 to 250°C for only a relatively short time. The carrier gas velocity at which column damage occurred was only about one-third to one-half the velocity suggested for high-speed analysis in

preparative scale columns (e.g., *10*) in which carrier gas velocities of 100 cm/sec were used for calculational purposes. The necessity of using relatively low carrier gas rates to prevent column damage as found in this work may prove to be a serious limitation in gas-liquid preparative chromatography.

Selection of the proper column operating temperature has been shown to be an especially important variable, because the sample production rate varies greatly with the column temperature. At a relatively low column temperature for a given sample the separation factor is high and sample loading may be quite high per unit area of column packing. However, the high sample loading results in overloading and wide sample bands. As a result, the elution time is lengthy and the sample production rate is quite low. A rise in the column temperature results in a shift of phase equilibrium toward the gas phase and shortens the retention time, thereby resulting in an increased production rate. However, the column temperature increase also decreases the separation factor, which in turn limits sample loading and production rate. Although sample elution is quite rapid, excessive column temperatures result in a drastic decrease in the permissible sample loading, with a resulting decrease in the production rate. It is quite apparent, then, that the column temperature regulates both the sample separation and elution rate and that a balance between these two factors must be effected to obtain the highest column productivity.

There are still other important variables that would have to be investigated before the absolute maximum rate of sample production for the methyl ester samples could be reported for this experimental system. Two important variables which merit further study would be the column length and the amount of stationary-phase support. Such studies would most certainly suggest further modifications in the operating conditions and/or system design.

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